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Measurement results from fires

Analysis of Environmental Incident Service measurement data from 2008–2021

RIVM report 2023-0367
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Synopsis

Measurement results from fires

Analysis of Environmental Incident Service measurement data from 2008–2021

Fires produce many substances that are harmful if people inhale them or come into contact with them. These substances can spread in the surrounding area. The type and amount of substances that are produced and how they spread depends on the materials that burn, the weather conditions and how the fire develops.

Some hazardous substances, such as soot and particulate matter, are produced by all fires. Other substances are only produced when certain materials burn. Examples include dioxins (from certain plastics) and metals (from sources like scrap fires).

Between 2008 and 2021, RIVM’s Environmental Incident Service (*Milieuongevallen Dienst*, MOD) measured whether hazardous substances were released into the air during 132 fires. These samples were mainly gathered within 300 m of a fire. RIVM has rarely detected substances at harmful concentrations more than a kilometre away from a fire. This is because substances dissipate as they spread through the air. The health risks in this case are very small. It is enough to advise residents to stay at home, close all windows and doors and keep out of the smoke. For these situations it is not always necessary that RIVM takes samples for additional measurements.

These conclusions, already drawn in 2007, have now been confirmed by a new extensive systematic analysis of the results of measurements during recent fires. In certain situations, RIVM recommended continue examining the hazardous substances. This concerns fires that last for a long time, take a long time to fully extinguish, produce a great deal of smoke, or produce smoke that lingers and does not rise much.

This is especially true for fires at industrial sites used for waste processing, demolition and recycling, and fires in warehouses and large buildings. Measurements can also be useful in the event of social unrest or if requested by emergency response teams or a relevant competent authority. Furthermore, the MOD will continue to develop their measuring strategy in case of a fire to be able to keep up with innovation and be prepared to measure new substances.

Keywords: MOD, hazardous substances, rule of thumb, measure, fire, dioxins, PAHs, VOCs, heavy metals, aldehydes

Publiekssamenvatting

Meetresultaten bij branden

Analyse van meetgegevens van de MOD in de periode 2008–2021

Bij branden ontstaan veel stoffen die schadelijk zijn als mensen ze inademen of ermee in contact komen. Deze stoffen kunnen zich verspreiden in de omgeving. Het hangt af van de materialen die verbranden, de weersomstandigheden en hoe de brand zich ontwikkelt welke stoffen ontstaan, hoeveel en hoe ze zich verspreiden.

Sommige schadelijke stoffen ontstaan bij elke brand, zoals roet en fijnstof. Andere stoffen ontstaan uit de verbranding van bepaalde materialen. Voorbeelden zijn dioxinen (uit bepaalde kunststoffen) en metalen (onder andere bij schrootbranden).

De Milieuongevallen Dienst (MOD) van het RIVM mat tussen 2008 en 2021 bij 132 branden of er schadelijke stoffen in de lucht zaten. Dat is vooral het geval op minder dan 300 meter van de brand. Op meer dan 1 kilometer van de brand meet het RIVM ze bijna nooit. Dat komt omdat de stoffen zich in de lucht verspreiden en verdunnen. De gezondheidsrisico’s zijn hierbij heel klein. Het is dan genoeg dat bewoners het advies krijgen om thuis te blijven, ramen en deuren dicht te doen en uit de rook te blijven. Extra metingen van het RIVM zijn niet altijd nodig.

Deze conclusies zijn in 2007 getrokken en worden nu bevestigd in een uitgebreide analyse van de metingen. Het RIVM wil in bepaalde situaties de schadelijke stoffen blijven onderzoeken. Het gaat om branden die lang duren, waarbij lang moet worden nageblust, met veel rookontwikkeling, of waarbij de rook blijft ‘hangen’ en weinig opstijgt.

Dit geldt vooral voor branden bij bedrijven in de afvalverwerking, sloop en recycling en in opslagloodsen en grote gebouwen. Meten kan ook nuttig zijn bij maatschappelijke onrust of als hulpdiensten of bevoegd gezag erom vragen. Verder is het wenselijk dat de MOD stoffen gaat meten in de rook die nu nog niet bij branden worden gemeten.

Kernwoorden: MOD, schadelijke stoffen, vuistregel, meten, brand, dioxinen, PAK, VOS, zware metalen, aldehyden

Contents

Summary

Introduction

Fires produce many substances that are hazardous for humans and the environment. These substances can be dispersed throughout the surrounding area and can be hazardous to health if people inhale them or come into contact with them. The type and quantity of hazardous substances produced and spread by a fire depends on factors including the materials involved in the fire and the combustion process. Virtually all fires form certain hazardous substances, including soot, particulate matter, CO, CO_2, various volatile organic compounds (VOCs) and polycyclic aromatic hydrocarbons (PAHs). Other substances may be released specifically as a result of the combustion of certain materials, such as dioxins (from PVC) and metals (including heavy metals) from sources including scrap metal, construction materials and waste. In 2007, RIVM published a report on the nature and quantities of substances that may be emitted during fires based on i) data from the literature; ii) fire tests conducted in a laboratory and full-scale tests with controlled fires; and iii) measurements taken by the MOD at fires in the 1997–2007 period. This report concluded that, while substances may be released in high concentrations, this is not necessarily harmful to health, depending on the rise, dispersion and diffusion of the smoke plume. Particularly at locations more than 1 km from the origin of the fire, the health risks are extremely small. In practice, this is known as the ‘one-kilometre rule of thumb’.

Purpose of the study

The MOD has taken measurements of hazardous substances in the living environment in connection with more than 130 fires after 2007. This measurement data has been systematically analysed as a subsequent study of the report from 2007. This update of the ‘emission from fires’ report from 2007 has the purpose of determining whether it is necessary to adjust and/or supplement the insights and conclusions from the 2007 report, based on an analysis of the MOD’s measurement data from fires after 2007. In addition, this new study could potentially provide answers to questions the MOD has received from the network of Fire department advisor hazmat (AGS) and or the Public Health Advisor Hazmat (GAGS) of the GHOR and/or GGD(s), for instance: is the one-kilometre rule of thumb still valid? Are there criteria that make taking measurements at fires a matter of necessity? Through this study, it is tried to determine whether the measurement strategy of the MOD requires adjustment.

Method of the measurement results study

RIVM has obtained data from the MOD’s reports on fire incidents and systematically arranged it in an overview. This data includes information such as the date, time and location of incidents, the materials burned, the samples which were taken and the main points of the analyses. Based on this overview, in-depth analyses were conducted on the various substance groups measured. This was done by systematically compiling and comparing the quantitative and semi-quantitative measurement results for each substance group.

Results

For the analyses, we made use of a data set consisting of measurement data collected by the MOD at 132 fire incidents in the 2008–2021 period. The MOD conducted most of the measurements at building fires and fires in which materials such as plastic, waste, rubber, chemicals, scrap metal, electronic equipment and wrecked/demolished cars were involved in the combustion process.

Results for gas-phase compounds (VOCs, aldehydes, ketones)
In case of a fire, the MOD often detected concentrations of VOCs that were elevated compared to the background levels in both the source and effect areas. Aromatic compounds (benzene, toluene, styrene etc.) and aliphatic compounds (alkanes, alkenes and alkynes) in particular are formed in nearly every fire. Benzene is nearly always detected in the highest concentration, followed by styrene, toluene and naphthalene. In only five incidents was the Dutch intervention value instruction guidance value (VRW)exceeded and only one incident involved an exceedance of the Alarm boundary value (AGW). These incidents involved substances such as acrolein and methyl methacrylate that were sampled directly from the smoke plume. At distances greater than 300 m the MOD detected levels of VOCs that were barely elevated than normal. The same was true for aldehydes and ketones.

Results for dust-bound compounds (PAHs, elements, dioxins)
Of the 132 fire incidents, 58 incidents involved testing for elements, 52 were tested for PAHs and 46 for dioxins. In some of the incidents, these substances were identified in total suspended particulate (TSP) samples. The deposition was also frequently determined, by testing deposited dust (dustfall) wipe samples and/or analysing grass and crop samples. This study showed that high concentrations of PAHs, dioxins and some elements (mostly metals such as lead, zinc, copper and antimony, but sometimes other elements) were often present in the source area (<300 m from the origin of the fire), especially in TSP samples – but not always. The MOD measured elevated concentrations in the effect area (medium distance: 300 m to around 1 km from the origin of the fire) as well, although not as high and not as often as in the source area. In rare cases, concentrations higher than the background level were measured further away from the fire than 1 km. This usually pertained to dioxins. In dustfall wipe samples and grass and crop samples, the concentrations of PAHs, dioxins and elements were less elevated than in the TSP samples.

Despite the fact that elevated concentrations of PAHs and metals may occur in the effect area, exposure to these concentrations generally does not lead to intake higher than the health-based guidance value, whether through inhalation, hand-to-mouth contact or the ingestion of crops. The MOD detected (slightly) elevated concentrations of metals and dioxins in grass samples taken at distances of up to 1 km and – in the case of a handful of fires – even at distances greater than 1 km. These concentrations sometimes exceeded the limits for dioxins in livestock feed. While exceedances tend to be small, there is a risk that contaminated grass will find its way into livestock feed. This could lead to an exceedance of the maximum permitted levels of dioxin in milk and meat.

Conclusion and recommendations

Based on the results of this study, it is possible to conclude that the research findings based on measurement results from the 2008–2021 period are largely in agreement with those of the 2007 study. This study confirms the ‘rule of thumb’ that risky concentrations of substances are almost never present at distances greater than 1 km from the origin of the fire, neither in the air nor through deposition (dustfall). With regard to VOCs, aldehydes and ketones, measurements taken at distances of less than 1 km also detected no concentrations that would pose a health risk. For this reason, we recommend either to stop these types of measurements or conducting them only in exceptional circumstances or at the request of emergency response teams or a relevant competent authority.

We recommend that measurements of PAHs, elements (metals) and dioxins in TSP samples, dustfall wipe samples and grass and crop samples should be performed especially in fires with the following characteristics:

- very large and long-lasting fires (duration guidance value of 4 hours or more;
- long-lasting late stage fire-suppression process until smouldering fires are fully extinguished;
- a limited plume rise, in any case during a portion of the fire;
- heavy smoke development.

Measurements are particularly advisable for fires at industrial sites involved in waste processing, demolition and recycling, and in warehouses and large buildings, when the burning materials are scrap metal, plastics (such as PVC), bitumen, car tyres, rubber materials, chemicals, wood waste (especially impregnated wooden garden products) and electronics. In these types of fires, there is a risk that hazardous substances (particularly dioxins and metals) will be produced and spread. Specifically with regard to dioxins, measurements are worthwhile only if grazing land for livestock, crops for human consumption and/or grass or crops that are being grown for livestock feed are present in the downwind area less than 3 km from the fire. The MOD can also supplement this by taking samples of TSP in the smoke plume, for which it uses a rapid XRF screening to determine the chlorine content. This provides an indication of whether it is necessary to sample and analyse dioxin levels. The MOD will use these recommendations to revise its measurement strategy for fire incidents.

Another important conclusion is that the information from the 2007 study, which identified the types of substances that were emitted during fires involving specific types of material, is still up to date and relevant. This information has now been incorporated into the ‘Incident App’. It remains desirable that further research be conducted into types of substances that have – as of yet – not been measured by the MOD, but which may be present in the smoke from fires. A few examples of such substances are isocyanates, amines, nitriles, nitro-PAHs, flame retardants, brominated dioxins, hydrogen bromide and hydrogen fluoride. It is also possible that new developments, such as the energy transition, will give rise to new kinds of fires that might release other potentially hazardous substances or where the concentrations of the hazardous substances released will be different.

1 Introduction

Fires produce and disperse many substances in the surrounding area. These substances may be hazardous to people and the environment. People may come into contact with these substances by breathing them in or through physical contact with dust particles that have fallen to the ground. The spread of hazardous substances can also result in contamination of grass and crops and therefore pose a risk to food safety, either when people consume food crops directly or when they consume products made from animals that have eaten contaminated grass or soil.
Insight into the nature and quantities of substances that are released during fires is valuable to the emergency response teams and government services involved. This insight helps them determine which measurement strategy to use for the purpose of estimating risk and identifying potential response measures. The MOD can measure these substances. Appendix 1 contains an overview of the various methods the MOD uses to collect and analyse samples.

In 2007, RIVM published a report on the nature and quantities of substances that can be released during fires [1].
This report used i) data from the literature; ii) fire experiments conducted on a laboratory scale and full-scale experiments with controlled fires; and iii) measurements taken by the MOD at fires in the 1997–2007 period as a basis for determining which substances are released by the combustion of certain kinds of materials [1]. During this period, the MOD measured the concentrations of substances in the air and the deposition of those substances in the surrounding area in connection with more than 50 fires. The MOD measured the deposited dust (dustfall) wipe samples collected from smooth surfaces and/or samples of grass or crops. The report from 2007 contains:

1. an overview of the emissions volume of the major combustion products for different types of materials (e.g. plastics, wood, paper and cardboard, waste and petroleum products);
2. an overview of the nature and quantity of substances that may be present in the living environment (air, deposition) downwind of a fire.

While substances may be released in high concentrations, this is not necessarily harmful to health, depending on the rise, dispersion and diffusion of the smoke plume. The report concludes that health risks are negligible at locations greater than one kilometre from the origin of the fire, with the exception of extremely large fires or fires with unusual characteristics such as a PVC fire. In current practice, this is known as the ‘one-kilometre rule of thumb’.

At the time of publication, the results of the study were shared with emergency response teams and other government services for use in responding to fires. RIVM also made the information available in the Incident App [2]. This information pertains to the kind of combustion products that are released by different types of materials, the dispersion of these combustion materials and the associated health risks.

1.1 Follow-up study: ‘update to the emission from fires report’

The MOD has taken measurements of hazardous substances in the living environment in connection with more than 130 fires after 2007. These measurement data has been systematically analysed and the results are considered to be an update to the ‘emission from fires report’ published in 2007. The goal of this project is to enrich the insights from the 2007 report or to adjust them if necessary. Is the current measurement strategy of the MOD still up-to-date, or have there been developments – such as new materials or the increasing use of solar panels and batteries – that make it necessary to update the measurement strategy? Those solar panels and batteries have been investigated in separate studies as well [3, 4].

In November 2019, the Public Health Advisor Hazmat (GAGS) submitted several questions to RIVM about the dispersion and measurement of dioxins during fires. Other partners, including the fire department advisor hazmat (AGS), have also asked questions about the insights and conclusions from the 2007 report. These questions have been summarised as follows:

1. Does the ‘one-kilometre rule of thumb’ still apply, i.e. ‘in most fires, no concentrations of substances that are hazardous for people and the environment are present more than 1 km from the origin of the fire’? These conclusions were drawn with the caveat that harmful concentrations of these substances can potentially spread further than 1 km in case of extremely large fires or fires with certain characteristics.
2. Does the rule of thumb which says virtually no deposition exceeding the background value will occur at distances greater than 1 km from the origin of the fire still apply? Which characteristics of a fire should result in an exception to this rule of thumb?
3. Is it possible to develop a set of criteria which the AGS and GAGS can use as a basis for determining whether it is useful and/or necessary to conduct certain measurements during or after a fire (such as those measuring dioxins and/or metals)?
4. When might a fire pose a potential threat to health? Does this take direct exposure to the smoke or exposure from deposition on crops or exposure through livestock into account?
5. What is the greatest distance at which the MOD has measured depositions that entailed a risk to food safety and therefore to public safety?

The ‘update to the emission from fires report’ project endeavoured to provide answers to these questions.

1.2 Purpose of the study

The purpose of this study is to determine whether it is necessary for us to adjust and/or supplement the insights and conclusions from the 2007 report, based on an analysis of the MOD’s measurement data from fires after 2007, and to answer the questions above. The result of this study gives input to determine whether the measurement strategy the MOD requires adjustment.

1.3 Reading guide

The structure of this report is as follows. In section 2, we explain which fire incidents were reviewed and what method was applied in the study. We also provide an overview of the number and type of fires in the period between 2008 and 2021. The results of the measurements taken by the MOD are provided in section 3. We also explain the results of the analysis for each substance group and address the dispersion of substances (distance), the potential effects on health and the substances emitted by different kinds of materials during combustion. In section 4, we discuss the findings and address the limitations of the study. Finally, in section 5 we set out the conclusions of this study, provide answers to the questions from the GAGS and AGS and offer several recommendations regarding the measurement strategy of the MOD.

2 Overview of MOD fire incidents 2008–2021

2.1 Selection of fire incidents

This study involved the systematic compilation and analysis of all fire incidents at which the MOD conducted measurements in the period from January 2008 until December 2021. There were 132 fire incidents at which the MOD was asked to conduct measurements in or near the smoke plume and/or in the corresponding downwind area for the purpose of assessing the risks to human health and the environment.

Not included in the 132 fire incidents is the 2011 Moerdijk fire [5], as this incident is categorised as exceptional. Because it is addressed separately in a few of the substance group sub-sections in section 3, this incident has not been addressed in the analysis set out below[1]. At the Moerdijk fire, the dispersion of potentially hazardous substances was also tested at a range of 10–60 km from the site of the incident [6]. This is extremely unusual: generally speaking, the MOD's dispersion studies are limited to a distance of a few kilometres.

2.2 Method for analysing fire incidents

For this study, data was gathered from the various incident reports and systematically arranged in an overview. This data includes information such as the date, time and location of incidents; what was burning (the materials); the height and dispersion pattern of the smoke plume (if available in the report); which samples were taken and the results of the main points of the analyses (which substance groups were measured, was the concentration elevated or not, including distance from the source); and certain other particulars of the fire in question. Next, in-depth analyses were carried out for each of the various substance groups measured on the basis of this overview. This was done by systematically compiling and comparing the quantitative and semi-quantitative measurement results for each substance group.

The MOD's measurement strategy is intended to yield a specific estimate of the health risks (see Appendix 1). For each individual incident, the MOD determines what will be sampled and analysed. Sometimes, for instance, it tests only a few Tedlar bags or canisters collected by the fire brigade for volatile organic compounds (VOCs) (this would be an example of minimal involvement of the MOD). In other cases, however, an MOD field team with an extensive measurement kit is deployed to collect air, dustfall wipe and grass samples and test them for a wide range of substances: VOCs, elements, polycyclic aromatic hydrocarbons (PAHs), dioxins, aldehydes and so on. Appendix 1 also contains an overview of information on the different sampling and analysis techniques used by the MOD. The choice of which samples to take and which analysis techniques to use depends on the location of the incident in relation to vulnerable objects and/or areas, the type of incident (what

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[1] In the sub-sections discussing compounds bound to dust particles (sub-sections 3.4, 3.5 and 3.6), measured values from the area 10–60 km from the fire are included directly in the distance category 'greater than 1 km', because no significant differences were found between any of the measured values from more than 1 km away from the origin of the fire.

was burning and how the fire developed), what stage the incident was in at that moment and the corresponding expected health and/or environmental risks. For each individual incident, the MOD determines its measurement strategy through consultation between various officials from the MOD and the requesting party like (G)AGS.

2.3 Number and type of fire incidents investigated by the MOD

For the analyses, we made use of a data set consisting of 132 fire incidents on which the MOD collected measurement data. During the period on which the study focuses, the MOD was involved in an average of 9 fire incidents per year. Table 1 contains a further breakdown of the number of fire incidents per year.

Table 1 Number of fire incidents investigated by the MOD per year and percentage compared to total number of fires.

Year	**Number**	**Percentage**
2008	12	9.1
2009	12	9.1
2010	9	6.8
2011	7	5.3
2012	5	3.8
2013	7	5.3
2014	11	8.3
2015	6	4.5
2016	12	9.1
2017	10	7.6
2018	16	12.1
2019	15	11.4
2020	6	4.5
2021	4	3.0
Total	**132**	**100.0**

In some incidents, the MOD carried out follow-up measurements, which are recorded in the statistics as a separate incident. One example of this is the fire that took place at a waste processing plant in Hengelo. This fire lasted from the evening of Saturday 30 June until the morning of Monday 2 July 2018. In the initial investigation, dioxin concentrations that exceed the limit for livestock feed [7] were detected in grass. With regard to this specific incident, a follow-up investigation was recommended in order to gain a better insight into the spread of dioxins and the potential risk to food safety. The MOD conducted these follow-up measurements as well and they are included in the analyses.

A number of waste processing plants suffered more than one fire, each of which was counted as a separate incident for statistical purposes. Examples are the fires at a waste processing plant in Leiderdorp in 2013 and 2016, at a waste processing plant in Varsseveld in 2017 and 2018 and at a waste processing plant in Wilp in 2013, 2014 and 2019. At a waste processing plant in Wijster, there were five separate fire incidents in 2019, followed by another fire in 2020.

2.3.1 *Types of fires*

Table 2 contains a breakdown of the types of materials involved in the combustion process.

Table 2 Number of fire incidents and materials involved.

Materials, potential fuel	**Number**	**Percentage**
Building fire with multiple fuels	37	28.0
Plastic (not otherwise specified)	32	24.2
Waste (not otherwise specified)	18	13.6
Chemicals (not otherwise specified)	9	6.8
Scrap metal and/or demolished cars	7	5.3
Paper/wood	5	3.8
Rubber/car tyres	5	3.8
Electronics	4	3.0
Organic material	4	3.0
Fires involving heavy metals, such as lead, mercury et cetera	3	2.3
Oil/petrol and so forth	3	2.3
PMD waste	2	1.5
Compost/garden waste	2	1.5
Clothing shop selling fireworks	1	0.8
Total	**132**	**100.0**

Accounting for 28.0 per cent of the total (n=37), building fires were the most common type of fire incident. These fire incidents involved multiple kinds of materials, which are not further specified in the reports. While most of the remaining fires were building fires as well, these fires did have specific materials listed as a source/fuel for the combustion process in the reports. However, in the latter group of fires, there were also other materials present in the combustion process in addition to the materials specified. It is also possible for the composition of materials to change in the development of the fire .

Plastic fires (usually involving plastic waste) are often occurring incidents, accounting for 24.2 per cent (n=32). These virtually always require extensive deployment of the MOD. This is largely due to the possible presence of PVCs in the plastics. PVC is a known chlorine donor contributing to the formation of dioxins and dioxin-like substances, especially in uncontrolled combustion reactions [8]. With this type of incident, the question is often whether dioxins have been released and what risks that may entail. Depending on the composition, a range of hazardous materials may be released during plastic fires, including CO, CO_2, various VOCs such as styrene and benzene, aldehydes, ketones, esters, carboxylic acids, PAHs, phthalates and certain metals that are utilised as pigments, stabilising agents or fillers [1]. Waste fires accounted for 13.6 per cent (n=18) of incidents and are a type of fire incident that frequently involves activation of the MOD. Waste fires often occur in other countries as well and causes may include heat produced by unintended fermentation, thermal runaway[2] in batteries, friction,

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[2] A chain reaction within a battery in which an extremely rapid rise in temperature takes place as a result of physical damage or another cause.

technical or electric malfunction, undesirable combinations of stored materials, and human action [9]. Waste fires are often limited by the available oxygen and result in numerous odour-related complaints. In many cases, the exact composition of the materials is unknown. As a result, the potential emissions of hazardous substances can be difficult to estimate in advance. In such cases, the MOD can perform measurements to determine the emissions. There are also fires involving other types of materials to which the MOD is less often dispatched, yet where there is a significant risk (due to the nature of the materials) that hazardous substances will be released: scrap/demolished cars (mostly metal), rubber/car tyres (mainly aromatics and PAHs), chemicals, and electronics (metals, combustion products of plastics and flame retardants).

3 Results of the MOD measurements

3.1 Introduction

From the data set, a number of fire incidents were selected for further quantitative analysis. In this section, this data is elaborated in several sub-sections and categorised by the specific chemical substance group and/or the analysis technique that was used. The substance groups that the MOD regularly measures at fire incidents are VOCs in the air; aldehydes and ketones in the air; elements in TSP samples and deposition (dustfall wipe samples, grass/crop samples or both); PAHs in TSP samples and/or deposition; and dioxins and dioxin-like substances in TSP samples and/or deposition. In the past, the MOD investigated and reported the total concentration and/or concentration of fine particulate matter in the air as well. For practical reasons, these measurements have not been carried out since 2017. They are therefore not taken into consideration in this report. The MOD determines what type of samples to take based on the incident in question. This depends in part on any 'vulnerable' receptors that are present downwind and primarily concerns the potential exposure and absorption routes. If vegetable gardens and farmland are present, the MOD will take samples of the crops and/or grass. The MOD will also take dustfall wipe samples when the chance of hand-to-mouth contact is present, for example when there are children's playgrounds in the effect area. The MOD will take samples of air and TSP only if an active fire with active smoke plume is present and there is a possibility that people may inhale the substances, or for the purpose of identifying substances in the smoke plume in order to conduct more targeted analyses of dustfall wipe and or grass samples.

In the following sub-sections, we will discuss the results of the MOD's measurements for each substance group. In doing so, we will address the dispersion of substances (range); the potential effects on health and/or the environment; and the emissions of substances when various materials are involved in the fires. We will also compare samples taken upwind to the background values. With regard to the dispersion of substances, we will make a distinction between source area (short distance) and effect area (medium and large distance) in the various sub-sections. We will use metres to describe these distances for the various substance groups, with slight variations between groups. These are primarily due to:

a) the differences in the size of the source and effect areas of different fires, a distinction we make based on the size, rise and distribution of the smoke plume and how it is influenced by weather conditions;
b) the availability of measurement data, which may have been collected in the source and/or effect areas at different distances from the fire; and
c) the fact that samples to test for different substances are collected at different distances, depending on the situation and the underlying questions.

3.2 VOCs in air samples

VOCs are hydrocarbons with a high vapour pressure and low boiling point that are present in gaseous form. During pyrolysis and combustion reactions, various VOCs are formed and dispersed along with the smoke.

If the VOC concentrations at incidents are found to exceed the limit of detection on the basis of a gas chromatograph–mass spectrometer (GC-MS) analysis, the MOD will include these concentrations in its report. The MOD's standard analysis tests for 63 individual VOCs (see the list in Appendix 2). This list is based on the US EPA TO-15 method [10]. The MOD can also use the Automated Mass Spectral Deconvolution and Identification System (AMDIS) method [11] to identify and quantify other VOCs not listed in Appendix 2 when these are present in the air sample.

3.2.1 VOC measurement results

In the 2008–2021 period, a VOC analysis was conducted at 81 of the 132 fire incidents. This involved samples taken near the source area and/or in the effect area. In Table 3, the fire incidents are categorised based on exceedance of the Dutch intervention or background values. We compared the measured values with the instruction guidance value (VRW) and the alarm boundary value (AGW) after 1 hour.

Table 3 Overview of VOC measurements and values.

VOC results	**Number**	**Percentage**
Not measured	51	38.6
VOCs elevated compared to background value, but still under VRW	66	50.0
VOCs elevated (exceeding VRW)	5	3.8
VOCs elevated and exceeding AGW	1	0.8
VOCs not elevated compared to background value	9	6.8
Total	**132**	**100.0**

At 51 of the fire incidents, no VOC analysis was conducted. Most of these cases involved fires where there was no longer an active smoke plume. Here, then, the MOD's presence was aimed primarily at investigating potential deposition.

Of the 81 fire incidents where VOC measurements were conducted, 75 were subjected to further analysis. This entailed looking at the materials involved in the fire and the dispersion of specific VOCs. At 6 incidents, no information was available on the sampling locations or the materials involved in the fire. Fire is a dynamic process and the materials involved in the fire can change over time. For a number of incidents, we have data indicating the nature of the materials in the fire (such as wood or car tyres), but even in these cases, there will have been other substances involved in the combustion process as well. Not all fires fit neatly into a specific category. Examples are the multiple building fires with no further specification and incidents where the only samples were taken by the fire brigade and do not include an exact description.

General

When fires occur, we frequently find that measured values are elevated in comparison to the background values in the source and effect areas. Aromatic compounds (benzene, toluene, styrene etc.) and aliphatic compounds (alkanes, alkenes and alkynes) in particular are formed in nearly every fire. Benzene is nearly always detected in the highest concentration, followed by styrene, toluene and naphthalene. A considerably elevated value for propene is generally detected as well. The type of fire seems to make almost no difference in this regard. Acetone, acrolein and chloromethane are virtually always detected in the measurements as well.

Waste

At 6 of the 12 waste fires, clearly elevated values were measured in the source and effect area. At all 12 fires, aromatic compounds were present in relatively high concentrations compared to the background level. Naphthalene, 1,3-butadiene and chloromethane were also present in the majority of samples. Propene was detected in samples from 9 of the 12 fires. Acetone and ethanol were also present at levels well in excess of the background concentrations.

Plastics

In 24 cases, synthetic substances (generally plastics) were involved in the combustion process. The type of plastic is often unknown. These fires, too, almost always produce aromatic compounds. These compounds were not detected at 2 fires, with the question being whether the fires were still ‘plastics fires’ at the time the samples were taken since no other typical decomposition or combustion products were detected, either. In addition to the aromatics (primarily styrene and benzene), propene, acetone and ethanol were also detected in elevated concentrations in one-third of the cases. Chlorinated compounds were detected at only 3 fires, 2 of which were PVC fires, while the other involved plastic crates (among other materials). High levels of dioxins were detected at these fires as well (see sub-section 3.6). At 2 fires, naphthalene was found to greatly exceed the background level.

Scrap metal

We expect scrap waste to contain iron or other metals. In practice, scrap metal usually consists of a mixture of metals, plastics, greases and oils. Most of these greases and oils are contamination from other processes (such as cutting oil, lubricant or protective grease). The plastics derive primarily from cables, coverings, tyres and so on. In the recycling sector, scrap is permitted to include up to 10 per cent plastics (by mass) to still be eligible for handling as scrap metal. As a result, scrap fires are often not only metal fires, but plastic fires as well. The substances measured for these fires will therefore be similar to those measured for a plastic fire. When there is a scrap metal fire, the MOD also measures various types of metals/heavy metals; see sub-section 3.4 on elements in TSP and deposition.

Rubber

Five fires were categorised as rubber fires. Such fires typically also involve other materials you would expect to find in an auto garage or scrapyard. Besides aromatics (primarily benzene and toluene), high concentrations of 1,3-butadiene are also released. Methyl ethyl ketone is relatively often measured for these fires as well. Chloromethane is measured only at short distances from the fire.

Foam
Two different types of foam fire at which the MOD conducted measurements were, on the one hand, fires with PU (polyurethane) foam, and on the other, fires involving foam mattresses (polyether). At the foam mattress fires (five incidents), it was notable that the measured concentrations of VOCs were quite low and the MOD detected only a few substances at levels above the limit of detection. These were, without exception, aromatics. In two instances, the measurements also revealed the presence of chloromethane, which could also have originated from packaging material. A broader range of substances were present for 3 polyurethane fires, where the MOD detected not only aromatics, but naphthalene, propene and acetone as well. The MOD also measured chloromethane at one of these incidents.

Vegetable matter/wood
Fires with vegetable matter including wood, bamboo, livestock feed, hay and compost are a kind of fire that occurs relatively frequently, but which seldom involves deployment of the MOD. The MOD responds to such fires when the fire lasts a long time and/or the smoke plume does not rise. Like the fires discussed above, these fires tend to produce relatively large quantities of aromatics and propene. Ethanol and acetone were detected at 6 of the 8 fires as well. At 4 of the 8 fires, the MOD also detected chloromethane. Naphthalene and 1,3-butadiene were present in elevated concentrations at 3 of the 8 fires.

Following an initial scan of the identified substances and measured concentrations, we looked at the distances at which these substances were detected. In order to compare the fires and the corresponding distances, a comparison value was established: this was 0.5 per cent of the VRW of the individual BTEXS substances[3] (benzene, toluene, ethylbenzene, xylene and styrene). These substances were consistently found to have the highest measured concentrations. By applying these comparison values (substantially lower than the one-hour VRW), we can compare incidents with each other based on the number of exceedances at different distances (see Table 4). Three distance categories (ranges) were defined:

- Short distance: <300 m (also defined as the source area).
- Medium distance: 300–1,300 m, potential effect area.
- Large distance: >1,300 m. According to the rule of thumb, there should be virtually no health risk beyond this distance.

No values detected in areas at either medium or large distances exceeded this comparison value. In areas within a short distance, the comparison value was exceeded in 14 of the 75 cases.

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[3] The 0.5% comparison value of the one-hour VRW was pragmatically selected from the data set, as multiple exceedances at or above this value were evident.

Table 4 Number of fires investigated by the MOD where the BTEXS comparison value was exceeded.

Category	**>0.5% BTEXS <300 m**	**<0.5% BTEXS <300 m**	**Percentage compared to the total in the category**
Waste (12)	4	2	50%
Tyres/rubber (5)	3	1	80%
Building (6)	1	-	17%
Vegetable matter (8)	-	1	13%
Plastic (24)	4	-	17%
Scrap metal (2)	1	-	50%
Foam (9)	1	-	11%
Other (15)	-	1	7%

3.2.2 *Assessment of health risks*

To determine whether a health risk in connection with VOCs is present at a fire, the MOD compares the measured concentrations to the thresholds associated with acute risks, also known as intervention values. RIVM has determined Dutch intervention values for a select group of VOCs. These values are intended to facilitate incident management and are divided into 3 categories [12]:

- Instruction guidance value (VRW) comparable with AEGL-1
- Alarm boundary value (AGW) comparable with AEGL-2
- Life-threatening value (LBW) comparable with AEGL-3

The MOD reports compare the analysis results with the one-hour reporting limit. If no Dutch intervention value has been established, these reports refer to the American Acute Exposure Guideline Levels (AEGLs) for guidance values. Like the Dutch intervention values, the AEGLs are intended for the purposes of incident management. The United States Environmental Protection Agency (US EPA) is responsible for overseeing and coordinating the AEGLs. Until 2007, RIVM expressed all intervention values in terms of the one-hour value. After 2007, a large portion of the intervention values were revised and 6 different time periods were introduced. Emergency response teams tend to base their actions on the one-hour value. Aside from the fact that a different time period is not available for all substances (though these can be determined using a serial method), emergency response teams consider the one-hour intervention value to be the most relevant value for assessing the exposure duration of persons in the effect area without any form of protection. Where this report compares a measured concentration with the VRW, we are referring to the one-hour VRW (unless otherwise indicated). In the event no intervention values are available, we can also compare the measured values to the minimal risk level (MRL), provided this is known. The MRL is an estimate of the daily exposure to a substance for a human being that is unlikely to pose an appreciable risk of adverse, non-cancer-related health effects during a specific exposure duration [13]. Although long-term or labour-related standards may also be available, the MOD generally does not compare these to the incidents it investigates.

In fires where VOCs were measured, the vast majority were shown to have a concentration of VOCs (present in both the source and effect area) that remained under the VRW (81.5 per cent (n=66)). In 11.1 per cent (n=9) of cases, this value was not even elevated as compared to the background value. In 6 incidents, the measured VOC values were higher than the VRW, with concentrations exceeding the AGW value in only one incident. We will discuss this briefly below.

At the waste fire in Wilp in 2013, the fire brigade used Tedlar bags to take its own samples at a distance of 30 m from the fire. The MOD tested these samples for VOCs. The concentration of acrolein in the air was found to be 675 µg/m^3 (one-hour AGW = 230 µg/m^3). At these values, symptoms including irritation of eyes and airways, shortness of breath and pulmonary oedema may occur. At the same fire, the methyl methacrylate concentration was 1,476 µg/m^3 – higher than the VRW threshold of 1,000 µg/m^3. However, the current VRW threshold limit for methyl methacrylate, established in 2021, is higher (odour was eliminated as a parameter): it is now 69,000 µg/m^3. When samples were collected further from the origin of the fire and on the boundary of the plant's premises, the values for all VOCs were well below the VRW. In 2014, another fire occurred at this same waste processing plant in Wilp, where (again) the MOD measured a high concentration of methyl methacrylate (2,180 µg/m^3), which is under the VRW limit according to the current intervention values.

Of the 5 other incidents where the VOC concentrations exceeded the VRW, the substance acrolein was also released at 3 of the fires. At a fire in Kilder in 2012 (silos of livestock feed), the concentration of acrolein was 55 µg/m^3, which is under the current VRW of 70 µg/m^3, but 4 days passed between the time the sample was taken (in the full smoke plume) and when the Tedlar bags were analysed. The MOD assumes that the actual concentration was higher in this case. At a 2013 fire at an industrial park in IJsselstein, the respective acrolein concentrations were 21 and 14 µg/m^3, measured at 350 and 650 m from the fire. The then-applicable 8-hour VRW of 10 µg/m^3 was used in this case. Today, the VRW is 70 µg/m^3 for all time intervals. At a fire at a household waste processing plant in Weurt (2014), the acrolein concentration was 88 µg/m^3 at a distance of 50 m from the fire. Acrolein is frequently present in the smoke from fires [14], but also in other combustion products such as cigarette smoke [15]. Exposure to this substance often results in irritation to the eyes, nose and airways [16]. In sub-section 3.3, we also analyse the results of aldehyde and ketone measurements using the method of high-performance (or high-pressure) liquid chromatography (HPLC).

At a fire in the crawl space of a home (Haarlem, 2009) where PU foam had recently been installed, high concentrations of various VOCs were detected. 1,2-dichloropropane and benzene were at that time above the acute MRL for inhalation, with respective concentrations of 4,138 and 1,066 µg/m^3. According to the current intervention values, this is under the VRW. For this fire, however, the measurements were conducted indoors. That makes them unsuitable for comparison to the other fires where the measurements were conducted outdoors.

When fires occur, the population may experience nuisance from the smoke and there are certain measures that can be taken (individually and otherwise). These include closing windows and doors and evacuating the area. In an emergency, the safety region/fire brigade will generally make the standard announcement urging people to ‘stay away from the smoke’ [17], sometimes by means of an ‘NL Alert’. Health problems due to exposure to various VOCs are to be expected only when the exposure to smoke takes place near the origin of the fire. At greater distances, the MOD detected no VOC concentrations that exceeded the VRW.

3.3 Aldehydes and ketones in air samples

Aldehydes is a collective term for a group of chemicals that contain a carbonyl group and a hydrogen atom. When the carbonyl group is located between 2 carbon atoms, the substance is what is known as a ketone. The simplest aldehyde is formaldehyde ($H_2C{=}O$); the simplest ketone is acetone (CH_3-CO-CH_3). To test for aldehydes and ketones, the MOD took samples using a 2,4-dinitrophenylhydrazine (DNPH) cartridge and analysed these samples using the HPLC method. The MOD tests for various aldehydes and ketones at fire incidents. In addition to fires, it can be useful to measure aldehydes and ketones at incidents in an indoor environment as well.

3.3.1 Measurement results for aldehydes and ketones

Among the 132 fire incidents at which the MOD took measurements, there were 18 incidents where analyses for aldehydes and ketones were conducted. We will address the measurements from the 2011 Chemiepack fire separately. Table 5 shows the average concentrations at the 18 incidents, with the aldehydes being further divided into 3 distance categories. These were taken directly at the origin of the fire (source): <100 m, at medium distance: 100–1,000 m and at a distance >1,000 m. There may be more than one measurement result for each incident.

Table 5 Measurement results for aldehydes and ketones in relation to distance with background concentration and VRW.

'unknown' means impossible to calculate (multiple values < limit of detection (LOD)) or not detected. *The following aldehydes have not been included in table 5 because the majority of the measured values were below the LOD: iso-valeraldehyde, n-valeraldehyde, o-tolualdeyde, m-tolualdehyde, p-tolualdehyde, hexanal and 2,5-dimethylbenzaldehyde.

	Average concentration in µg/m^3 (max. value in µg/m^3; number of analyses)			Average value measured upwind (µg/m^3)	VRW after one hour (µg/m^3)	Known background concentration in air (µg/m^3)
Substance*	0–100 m	100 –1,000 m	>1,000 m			
formaldehyde	49.5 (max. 135; N = 11)	9.9 (max. 27; N = 22)	2.12 (max. 5.1; N = 5)	2.3	1,300	2.5
acetaldehyde	33.5 (max. 67; N = 8)	11.1 (max. 38; N = 19)	11.6 (max. 29; N = 5)	2.6	82,000	3
acrolein	5.7 (max. 17; N = 7)	0.7 (max. 2; N = 18)	unknown (max. <0.1; N = 4)	unknown	70	0.5
acetone	35.8 (max. 67; N = 6)	26.9 (max. 280; N = 18)	32.7 (max. 87; N = 4)	5.6	480,000	2.5
propionaldehyde	9.3 (max. 21; N = 6)	2.1 (max. 5; N = 15)	0.9 (max. 2; N = 3)	0.3	110,000	0.3
crotonaldehyde	2.6 (max. 4.4; N = 6)	unknown (max. 5; N = 15)	unknown (max. 2; N = 3)	3.3	560	unknown
n-butyraldehyde	5.9 (max. 13; N = 5)	1.7 (max. 9.5; N = 16)	0.7 (max. 1; N = 3)	0.6	unknown	unknown
benzaldehyde	21.0 (max. 40; N = 6)	2.2 (max. 11; N = 18)	unknown (max. 0.9; N = 2)	0.8	unknown	unknown

Table 5 also contains an overview of the average measured values for aldehydes at the various upwind sampling points. These correspond to the known background concentrations [1].
Of the 18 incidents at which the MOD measured aldehydes, elevated values (as compared to the background levels) were detected at 4 fires, though all of these values were detected at distances no more than 100 m from the origin of the fire. The fires in question were the following:

- A 2021 fire at a scrap processing facility in Den Bosch, where values included a formaldehyde concentration of 44 µg/m^3 at a distance of 100 m from the fire.
- A 2016 fire at a recycling facility in Someren, where values included a formaldehyde concentration of 98 µg/m^3 at a distance of 20 m from the fire.
- A 2014 fire at a waste processing plant in Weurt, where values included a formaldehyde concentration of 135 µg/m^3 at a distance of 50 m from the fire.
- A 2009 fire at a scrapyard in Emmen, where values included a formaldehyde concentration of 72 µg/m^3 at a distance of 20 m from the fire.

All of these fires lasted between 12 hours and 5 days, with control measures lasting a long time after the fire was extinguished and with very little plume rise.

The 2007 report [1] on emissions at fires also states that the MOD detected greatly elevated concentrations of aldehydes at several fires. Most of these samples were taken directly in the smoke plume.

Chemiepack fire

The MOD conducted various measurements during and after the Chemiepack fire on 5 January 2011. Here, too, samples were taken at various distances to determine the levels of aldehydes and ketones. Table 6 sets out the measured values in the immediate vicinity of the origin of the fire (0–300 m). Here we see that a formaldehyde concentration higher than the background value was measured at a single location, but that this was well below the VRW. The other measured values were at the background levels. This fire was characterised by a tall plume rise, which carried hazardous substances high into the atmosphere and diffused them. When aldehydes were measured at a large distance (>5 km), no aldehydes or ketones were detected [18].

Table 6 Aldehyde values measured in the immediate vicinity of Chemiepack Moerdijk.

	Location 06	**Location 07**	**Location 08**	**Location 16**
	µg/m³	**µg/m³**	**µg/m³**	**µg/m³**
formaldehyde	0.5	82	6.8	0.4
acetaldehyde	1.3	3.9	1.8	1.4
acrolein	-	0.1	0.2	0.1
acetone	0.9	2.5	1.0	0.9
propionaldehyde	0.2	1.2	0.4	0.2
n-butyraldehyde	0.3	3.4	0.7	0.3

3.3.2 Assessment of health risks

The reason that the MOD measures aldehydes and ketones at fire incidents is that smoke inhalation poses an increased health risk when it contains these irritants, such as in the form of formaldehyde and acrolein [19]. Table 5 shows that all measured values are well under the VRW. The highest measured value for formaldehyde was 135 µg/m^3, which is about 10 times lower than the VRW. Close to the origin of the fire, the MOD typically does detect concentrations that are elevated compared to the background values. Concentrations tend to be lower further away from the origin of the fire. Only in a few incidents did the MOD also detect concentrations of aldehydes and ketones at medium and large distances that were higher than the background level. These concentrations were still far below the VRW. This is in keeping with the international literature, which indicates that the formaldehyde concentration at any significant distance from the origin of the fire will be negligible. However, it is possible that occupational exposure limits may be exceeded close to the origin of the fire (particularly in the case of forest fires) [20]. Similarly, at oil fires, the MOD detected virtually no aldehyde concentrations that are potentially harmful to health at any significant distance from the fire [21]. Health problems due to exposure to various aldehydes or ketones are to be expected only when the exposure to smoke takes place near the origin of the fire. At greater distances (>100 m), virtually no concentrations in excess of the VRW were detected.

3.4 Elements in TSP and deposition

One substance group the MOD often tests for at fires is metals, heavy metals and other elements. These can occur in many different compounds, some of which are extremely toxic. While a number of these elements and specific compounds are categorised as substances of very high concern (SVHC), other elements can be harmful to health and the environment as well.

Some of these compounds may be released during fires because they are present in the materials involved in the fire, including the structure, or because they are formed during the combustion processes. Which compounds and how much of them can be produced and spread in the living environment depends on the circumstances: the size and characteristics of the fire (combustion temperature, oxygen supply, duration of the fire, degree of plume rise and so on), the materials and the weather conditions. The MOD does not conduct measurements of individual compounds, but only of the metals and elements that occur in these compounds. This is because the measurement and analysis methods used by the MOD are not suitable for identifying individual metal compounds. For example: while the MOD does not measure concentrations of iron oxide, iron sulphate or iron chloride, it does measure iron – i.e. the total amount of the element iron that is present in various compounds.

First, all fire incidents where the concentrations of metals and elements were measured in TSP, dustfall wipe and/or grass samples were selected from the data set. Element analyses in TSP and dustfall wipe samples were sometimes carried out using X-ray fluorescence spectrometry (XRF) (usually at the incident site, as this method yields indicative values – especially when used on wipe samples) and sometimes with inductively coupled plasma mass spectrometry (ICP-MS) (in the laboratory, after processing). After extraction, grass samples are always analysed using ICP-MS.
This selection process yielded 58 fire incidents. Excluded from consideration were:

- incidents at which only combustion residue or debris was analysed (typically using XRF);
- indoor fires at which samples were collected inside a building. There were two such cases: a distribution centre and a penitentiary;
- the fire in an oil refinery on Bonaire, because the situation there could not be effectively compared to the situation in the Netherlands and only soil samples were tested for metals. Those tests detected no concentrations higher than the Dutch background levels.

We analysed the measurement data for metals in the reports from the 58 incidents selected. The data was categorised by type (TSP, deposition = dustfall and grass samples) and by distance from the fire, with one of 4 categories being assigned:

- Close to the origin of the fire (source location): by ‘close’, we mean at a distance of between 30 and 200 m and in the smoke plume (this does not include samples taken at a relatively short distance outside the smoke when a rising smoke plume was present; see the explanation at the end of sub-section 3.1).
- At a medium distance from the origin of the fire: by ‘medium’, we mean distances of between 200 and around 1,000 m. It is not always known whether these measurements were taken in or under a smoke plume (at the majority of incidents, it was the latter).
- At a large distance from the origin of the fire: by ‘large’, we mean distances greater than 1,000 m. At such distances, the smoke plume generally diffuses to such a degree that it is imperceptible (or nearly so). In some cases, however, the smoke

- plume at these distances can settle to ground level and remain somewhat perceptible, often through odour.
- Upwind from the origin of the fire (reference samples).

Due to the semi-quantitative nature (in the event measurements were perform using XRF) and the remaining uncertainties concerning the measured concentrations of metals[4], we chose not to use the measured values themselves, but rather the degree of elevation in comparison to the background level. We expressed this degree of elevation qualitatively:
0 (no or only negligible increase observed)
+ (increased by a factor of 3–20)
++ (increased by a factor of 20–100)
+++ (increased by a factor of more than 100)

We note here that the background value for each of the metals detected in air, deposition or grass is not a single fixed value, but rather a range of values. The calculated degree of increase is therefore indicative. For each category, the measured values of the incident were added up and averaged. The number of measured values is also given, as well as the distances (ranges) at which they were found.
The results for each type of sample are listed below (TSP, dustfall wipe and grass samples).

3.4.1 *TSP*

In 33 of the 58 incidents selected, various elements were measured in the TSP. The results for each distance category are as follows:

- Upwind reference samples: this group included 29 measurements, 12 of which were conducted with ICP-MS and 17 with XRF. In the majority of incidents, the MOD detected concentrations that were within the range of background values in the Netherlands; this is as we would expect. In 6 cases, however, a handful of metals were detected at levels exceeding the background values (5 times using ICP-MS and once using XRF). These cases involved nickel (4 instances), chromium and zinc (2 instances) and vanadium (1 instance). This could have been caused by a local source or contamination or an inaccurate measurement.
- Large distance: at 10 fires, metals were measured at one to three locations more than 1 km from the origin of the fire, 4 times using ICP-MS and 6 times with XRF. With the exception of one fire, the MOD detected no metals at concentrations exceeding the background level. The exception was a fire at a scrap processing facility in Den Bosch, where the MOD used ICP-MS to test samples taken at 1.3 km from the origin of the fire and detected elevated concentrations of aluminium, arsenic, barium, copper and antimony, along with strongly elevated concentrations of cadmium, lead and zinc. This fire burned in a large pile of iron, metal and rubber waste, was accompanied by heavy smoke development and lasted longer than a day. For the

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[4] This pertains not only to uncertainties related to the analysis techniques (these are greater with XRF than with ICP-MS), but especially to uncertainties that emerged due to the extraction of metals and other elements from the samples.

metals detected, it has been shown that they can be released due to the combustion of shredder waste from wrecked/demolished cars, large domestic appliance and audiovisual equipment [1].

- Medium distance: at 16 fires, metals were measured at one to four locations between 200 and 1,000 m from the origin of the fire, 6 times using ICP-MS and 10 times with XRF. In 9 cases (4 of which were measured using XRF), the MOD detected only one to a handful of metals present at levels exceeding the background level. In virtually all cases, the metals in question were zinc and lead. At 4 of the 9 fires, copper and antimony were present as well. In one or two instances, barium, cadmium, chromium, bromine, nickel, titanium and cobalt were also detected. Several of these fires occurred at waste processing and recycling facilities (the materials varied from plastics, bitumen and car tyres to assorted rubbish). One fire took place in a warehouse with computer equipment and several occurred in large buildings where furniture and packaging materials were being stored, among other items.
- Near the origin of the fire: at 23 fires, metals were detected in the smoke plume at a distance of a few dozen metres to 200 m from the origin of the fire, 8 times using ICP-MS and 15 times using XRF. In most of these cases (20, of which 12 were measured using XRF), the MOD detected multiple metals at levels exceeding the background level. As in the medium-distance samples, the MOD detected zinc and lead the most frequently: at 15 and 13 fires respectively. Other frequently detected metals were copper, aluminium, iron, bromine, calcium and antimony. Barium, chromium, nickel, lithium, titanium, cadmium, cobalt, manganese and arsenic were detected in one to a handful of cases as well. The most frequent and highest concentrations measured by the MOD were detected at fires at waste processing and recycling businesses (scrap metal, car tyres, plastics, wall coverings and assorted rubbish), a scrapyard, the aforementioned warehouse containing computer equipment and a packaging facility. The MOD also detected various metals at fires in warehouses and buildings (livestock feed, poultry, mattresses). The extent to which the MOD detected elevated concentrations of metals was usually limited to a degree of magnitude (+). Exceptions to this were the following:
    - The fire at a scrap processing facility in Den Bosch, where elevated concentrations of metals were also detected at a distance of 1.3 km. In the smoke plume, concentrations of cadmium, lead and zinc were extremely high (+++), arsenic, copper and antimony levels were strongly elevated (++) and aluminium, barium, iron, lithium and manganese were elevated as well (+).
    - A fire at a recycling facility that mostly involved old car tyres. In the smoke plume, the concentrations of lead zinc and antimony were extremely high (+++), while levels of arsenic, cadmium, cobalt, chrome and copper were elevated (+).
    - A fire in an industrial hall where electric bicycles were being stored. In the smoke at this fire, the MOD detected strongly elevated concentrations of lithium, cobalt and nickel (++) and

also detected chrome, copper, lead and zinc (+). In the case of this fire, the Li-ion battery metals were readily detectable in the smoke.

3.4.2 *Deposition (dustfall wipe samples)*

In 41 of the 58 incidents selected, metals were measured in dustfall wipe samples. The results for each distance category are as follows:

- Upwind reference samples: this group included 25 measurements, 14 of which were conducted with ICP-MS and 11 with XRF. At virtually all fires, the MOD detected concentrations that were within the range of background values in the Netherlands; this is as we would expect. In two cases, the MOD detected slightly elevated values (+) for nickel and zinc (using ICP-MS). This could have been caused by a local source or contamination or an inaccurate measurement.
- Large distance: at 19 fires, metals were measured at one to eight locations more than 1 km from the origin of the fire, 13 times using ICP-MS and 6 times with XRF. At 4 of these fires, a higher deposition value of certain metals was detected (each time using ICP-MS) at a distance of more than 1 km from the fire. At the fire at a scrap processing facility in Den Bosch, the MOD detected more or less the same metals at elevated levels (+) in the dustfall wipe sample at a distance of 1.3 km from the fire as in the TSP sample. The MOD detected depositions with elevated levels of barium, iron, antimony and zinc (+) at distances between 1.4 and 1.8 km from a fire at a recycling facility that processed artificial grass mats. The MOD also detected barium and zinc in dustfall wipe sample downwind of a fire in a warehouse containing various plastic materials, including insulating foam. And finally, the MOD detected elevated levels of calcium, vanadium and zinc at distances of between 1 and 1.4 km from a fire at a business that makes beeswax-based products.
- Medium distance: at 31 fires, metals were measured at one to seven locations between 200 and 1,000 m from the origin of the fire, 17 times using ICP-MS and 14 times with XRF. In 8 cases, the MOD detected levels of only one or a handful of metals that were higher than the background level (using ICP-MS). Two of these incidents were the fires in the warehouse containing various plastic materials and artificial grass mats at the recycling facility, where elevated depositions of metals were also detected at a distance greater than 1 km from the fire. At several other fires, barium (5 times) and zinc (4 times), as well as aluminium, chromium, copper, lead, antimony, iron, nickel, manganese and vanadium (1 or 2 times each) were detected at elevated levels (+ in all cases). These fires occurred in industrial buildings were car tyres, rubber, plastics and various kinds of waste were present. At the fire in an industrial hall where electric bicycles were being stored, both the smoke (TSP) and deposition were found to contain elevated concentrations of lithium (++), cobalt, nickel and copper (all +).
- Near the origin of the fire: at 22 fires, metals were measured in deposited dust particles collected at a distance of between a few dozen metres and 200 m from the origin of the fire, 9 times

using ICP-MS and 13 times using XRF. In 9 cases, the MOD detected concentrations above the background levels of one or more of these metals (mostly using ICP-MS, but with XRF in one or two cases) – the same ones that were identified at medium and large distances. At 6 of these fires, the MOD also detected elevated depositions at a medium and or/large distance, generally of the same metals. In most cases, the deposition values were highest closer to the fire (usually +, sometimes ++), but not in all cases. This might have to do with the fact that the vast majority of the dust particles in the smoke plume settled to the ground at some distance from the origin of the fire, following their initial rise. At the fires in a scrapyard, a recycling facility for plastics and a former restaurant, elevated depositions of bromine (++), chromium, lead and zinc (all +) were only detected near to the origin of the fire.

3.4.3 *Deposition on grass and/or crops*

In 21 of the 58 incidents selected, metals were measured in grass samples. The results for each distance category are as follows:

- Upwind reference samples: this included 16 measurements taken by the MOD, in which it detected a single instance where elevated levels of lead and antimony were present upwind of the fire. This was presumably a contamination due to a local source (the location was in an urban area). At all other fires, the MOD detected concentrations that were within the range of background values in the Netherlands; this is as we would expect.
- Large distance: at 15 fires, metals were measured at one to 10 locations more than 1 km from the origin of the fire. With two exceptions, the concentrations of these metals were within the range of background values in the Netherlands. One of these exceptions was an elevated concentration of aluminium detected 5 km from the origin of the fire (+), which was probably caused by a local source. The other exception was the fire at Chemiepack in Moerdijk in 2011. At this fire, the MOD measured elevated levels of aluminium and sometimes iron (both +) in the downwind area up to 20 km from the origin of the fire. We cannot discount the possibility that the background values for these elements in grass were higher in this entire area than in other parts of the Netherlands.
- Medium distance: at 16 fires, metals were measured at one to three locations between 200 and 1,000 m from the origin of the fire. In 4 cases, the MOD detected levels of only one or a handful of metals that were higher than the background level (+): titanium (at a fire in a large pileof rubbish containing plastic, construction and demolition waste), chromium (fire in a warehouse containing old tyres), lead, antimony and zinc (fire in a lot of big bags containing semi-manufactured lead products) and aluminium, chromium, iron and titanium (fire in a batch of rubber and plastics). In the latter case, an elevated concentration was not observed at every sampling point in the downwind area.
- Near the origin of the fire: at 7 fires, metals were measured in grass samples collected at a distance of between a few dozen metres and 200 m from the origin of the fire. At the

aforementioned fire in the lot of big bags containing semi-manufactured lead products, the MOD detected an elevated concentration of lead (+). The MOD also detected strongly elevated concentrations of antimony, titanium and zinc (++) in the grass near a large, long-lasting fire in a waste warehouse. Finally, at two fires involving rubber materials and old car tyres, the MOD detected elevated levels of cobalt, chromium, iron, manganese, lead, antimony, titanium, vanadium and zinc (all +).

Based on all measurement results, elevated concentrations of various metals were detected in TSP, dustfall and (less often) grass samples taken at distances up to 1 km from the origin of the fire at approximately 10 of the 58 fires where the MOD measured metals. At the 48 other fires, the MOD detected no (or virtually no) elevated values. In a single case, strongly elevated concentrations were detected in TSP samples. At 4 of these fires, elevated values were also detected in deposition and (in one case) TSP sample at a distance greater than 1 km from the fire. The majority of these incidents were characterised by a long duration, heavy smoke development and a limited plume rise. While, for the most part, no detailed information is available on what kind of materials burned, it is possible to draw a number of conclusions from the measurement results. Lead and zinc were the most frequently detected metals, which is in keeping with the findings of the 2007 report [1]. Copper and antimony were frequently detected in concentrations exceeding the background level as well, particularly in TSP samples. Metals that were detected in elevated values in TSP, dustfall and grass samples in a few instances were aluminium, barium, bromine, calcium, iron, manganese, chromium, nickel, titanium and vanadium. This is largely in keeping with the findings of the 2007 report. At the time, the explanation given for these findings was that lead, zinc, copper, iron and aluminium are extremely common in buildings due to their use in construction materials, roofing, water pipes and electrical wire. To a lesser extent, the same is true of chromium, nickel and vanadium. Compounds containing barium, lead, zinc, cadmium and titanium are found in plastics, paints, lacquers and textiles. Bromine and antimony compounds are used as flame retardants. Bromine and zinc are also found in car tyres.

In terms of the types of businesses and materials associated with incidents where elevated levels of the aforementioned metals were detected, there is a similarity with the results that were analysed and reported in the 2007 report as well. Many of the fires occurred at waste processing, demolition and recycling businesses (including scrapyards) and in warehouses and large buildings. These fires often involved materials such as scrap metal; plastics (including insulating foam and artificial grass mats); bitumen; new and used car tyres and rubber materials; plastic, construction and demolition waste; computer components and electronics, packaging materials and various types of rubbish. When fires occur in buildings, the materials present inside the building – such as furniture, wall coverings, construction materials and computers – burn as well.

A few specific cases deserve individual attention:

- At the fire in a scrap processing facility in Den Bosch, extremely high concentrations of cadmium, lead and zinc (+++), high concentrations of arsenic, copper and antimony (++) and aluminium, barium, iron, lithium and manganese were detected in the smoke plume and in dustfall wipe samples. Concentrations of a number of these metals were still elevated in TSP and dustfall wipe samples at a distance of 1.3 km downwind. The characteristics that set this fire apart were the heavy smoke development, long duration (more than a day), a low plume rise during a significant portion of the fire and the involvement of a large quantity of scrap metal that contained various metals.
- The MOD detected strongly elevated concentrations of lithium, cobalt and nickel (+++) near a fire in an industrial hall where electric bicycles were being stored. These metals are 'unusual' in the sense that they were not detected in such high concentrations at any of the other fires. Lithium, cobalt and nickel are present in the Li-ion batteries found in electric bicycles. Though in relatively less-elevated concentrations, the MOD also detected chromium, copper, lead and zinc (+). The MOD detected slightly elevated levels of a few of these metals (including lithium) in dustfall wipe samples taken 450 m from the fire. No grass samples were collected.
- The concentrations of lead, zinc and antimony were notably high (++) as were – though to a lesser extent – those of arsenic and copper (+) in the smoke plume and in deposited dust and grass samples collected close to a fire in a lot of old tyres at a recycling facility in Someren. In the downwind area, the MOD detected slightly elevated values for these metals at distances up to 1 km. At several other fires involving car tyres, the MOD also detected elevated concentrations of lead, zinc and copper (+), although these values were not as high as those at the fire in Someren. Fires involving car tyres are often difficult to extinguish. They tend to produce thick smoke and hefty emissions of PAHs and aromatic hydrocarbons. Metals such as zinc, lead and bromine may be released as well [1].
- It is therefore not surprising that, at a fire in a lot of 'big bags' containing semi-manufactured lead products, the MOD detected a large amount of lead (++) in grass samples near and up to 750 m downwind of the fire. Antimony and zinc were elevated here as well (+). At a greater distance (>1,000 m), the measured values were in keeping with background levels. The MOD did not collect any air or dustfall wipe samples at this fire.

3.4.4 *Assessment of health risks*

In order to determine when it is necessary to measure for metals at a fire, it is important to have an idea of the health risks associated with exposure to metals at certain types of fires. Exposure can occur when a person inhales particulate matter containing metals, when they inadvertently ingest metals in dust on their hands (known as hand-to-mouth contact) and when they ingest crops that have been contaminated by metals. Consumption of animal products contaminated by metals can pose an indirect risk as well.

The incident reports of the MOD identify the potential health risks associated with the incident in question. In all reports compiled based on the fires where the MOD has taken measurements for metals since 2008, the conclusion has consistently been that virtually no health risks are expected due to exposure to metals as a result of a fire. This applies to both exposure via air and exposure via hand-to-mouth contact and ingestion. This conclusion is based on the measured concentrations in TSP, dustfall wipe and grass samples in the downwind area (effect area) and not the values measured in or near the smoke plume, as (in principle) no people were present in the latter area to be exposed to the substances there. Despite the fact that we expect no specific health risks in connection with the elements measured in the effect area, we nevertheless (without exception) recommend avoiding exposure to smoke or deposited dust particles whenever possible, as the smoke and soot particles emitted by fires always contain hazardous substances and exposure to them is undesirable [17]. It is also advisable to clean objects such as playground equipment and outdoor furniture as thoroughly as possible.

At a few fires, the risk threshold (limit value) based on lifelong exposure for one or more metals was exceeded in the effect area, although the concentrations remained well below the threshold for occupational exposure (exposure duration of 8 hours per day, 5 days per week for 40 years). An example of this is the fire at a scrap processing facility in Den Bosch, where the concentrations of arsenic, cadmium and lead were above the limit value based on lifelong exposure, yet well under the threshold for occupational exposure. On top of that, exposure to substances during fires is mostly short-term.

3.4.5 *Risks via the food chain*

Another route by which people can be exposed to metals via the food they consume is by eating contaminated animal products such as meat, milk, dairy products and eggs.
To gain insight into this risk, we can compare the concentrations of metals in grass to the EU limit for livestock feed [7] given to cattle. At the fire in Someren, the MOD detected concentrations of arsenic and lead close to the origin of the fire that exceeded the limit for livestock feed (measured values: 3.45 mg/kg arsenic and 78.5 mg/kg lead; limits: 2 mg/kg arsenic and 30 mg/kg lead). With regard to other metals and samples taken at other locations, the concentrations in grass at this fire were under the respective limits for livestock feed. At a fire in a lot of ‘big bags’ containing semi-manufactured lead products, the MOD detected concentrations of lead that exceeded the limit for livestock feed not only in the effect area, but also at the upwind reference sampling point. Other than that incident, none of the fires investigated involved an exceedance of the livestock feed limits for metals. A local, limited exceedance of the limit for a metal in grass is unlikely to lead to an exceedance of the maximum permitted levels of metals in milk or other animal products.

Eggs can become contaminated with metals when chickens that spend time outdoors pick up and ingest bits of contaminated soil. When a fire occurs, the amounts of metals that are deposited on soil in the downwind area are so small (besides which the deposition is a one-time event) that they result in no (or virtually no) perceptible additional contamination of the underlying soil. We therefore consider the health risk that could emerge via this route to be negligible.

3.5 PAHs in TSP and deposition

PAHs are a group of hundreds of organic substances that consist of two or more benzene rings, have mutagenic and carcinogenic qualities, and are formed by the complete or incomplete combustion of organic substances [22]. PAHs can be released during fires and enter the environment, but they can also be emitted by other sources, including cigarette smoke, wood burning, barbecues, industrial activity and traffic. Exposure to high levels of PAHs can pose a health risk. The primary exposure routes are inhalation and food.

3.5.1 Analysis of quantitative measurement data on PAHs

From the MOD's data set of incidents, we selected all fire incidents where PAHs were measured in TSP, dustfall wipe and/or grass samples. From among the 132 fire incidents, 52 incidents were selected. Excluded from consideration were:

- Incidents at which PAHs may have been measured (according to the information in the data set or report), but for which no quantitative data is available. This applied to 5 incidents.
- The fire in an oil refinery on Bonaire was excluded because the situation there cannot be effectively compared to the situation in the Netherlands.

At the 52 incidents, 26 TSP samples, 33 dustfall wipe samples and 37 grass/crop samples were collected and analysed, including in some cases more than one sample per incident and matrix.
The data was categorised by type (TSP, deposition = dustfall wipe and grass/crops samples) and by distance from the source, with one of four categories being assigned:

- Near the origin of the fire: from 0 up to a maximum of 300 m
- At a medium distance from the origin of the fire: 300–1,300 m.
- At a large distance from the origin of the fire: more than 1,300 m.
- Upwind from the origin of the fire (reference samples).

For each category, the measured values of the incident were added up and averaged. The number of measured values is also given, as well as the ranges of the samples.

3.5.2 TSP

With regard to measuring PAHs in TSP samples, the MOD measures and reports only the benzo[a]pyrene concentration. Table 7 provides an overview of the average benzo[a]pyrene concentration for each distance category, expressed in ng/m^3. The background value for benzo[a]pyrene is 0.2 (0.02–1.0) ng/m^3. Table 7 shows that the benzo[a]pyrene concentration was usually elevated at fires. The MOD detected the highest concentrations close to the origin of the fire. Further away, the concentration was generally lower – although the MOD sometimes detected elevated levels there as well.

Table 7 Benzo[a]pyrene results in TSP samples per distance category.

Substance		Upwind	0–300 m	300–1,300 m	>1,300 m
Benzo[a] pyrene	Average (ng/m^3)	1.0	445.2	79.0	6.3
	Max. (ng/m^3)	6.2	775	434	13.7
	Number of sampling points	19	31	21	6

Of the 26 fire incidents for which TSP sampes were measured for PAHs, there was only one fire incident (plastic factory in Nijkerk, May 2012) where the PAH concentrations were not found to be significantly elevated compared to the background values and/or upwind measurements.
This was probably due to the strong rise of the smoke plume and the sampling locations chosen. In the other 25 fire incidents, PAH concentrations were found to be elevated or strongly elevated. Incidents with extremely high benzo[a]pyrene values in the TSP samples included:

- Recycling facility in Someren, November 2016, many old car tyres. The benzo[a]pyrene concentration here was 2,062 ng/m^3.
- Scrapyard in Emmen, July 2009, with a benzo[a]pyrene concentration of 2,302 ng/m^3.
- Recycling facility in Kampen, May 2008, large amounts of plastics, PVC, wood waste and carpet, with a benzo[a]pyrene concentration of 2,775 ng/m^3.
- Computer warehouse in Blerick, January 2008: the benzo[a]pyrene concentration here was 1,209 ng/m^3.

At all these fires where extremely high concentrations of benzo[a]pyrene were detected, the samples were collected near the origin of the fire (0–300 m). However, elevated PAH values are frequently detected at greater distances as well:

- Warehouse in Amsterdam, February 2011: the benzo[a]pyrene concentration here was 13.7 ng/m^3 at 5,000 m. This incident involved a fire with rubber and latex raw materials.
- Scrap processing facility in Den Bosch, March 2021: here, a benzo[a]pyrene concentration of 13 ng/m^3 was measured at 1,300 m.
- At the aforementioned computer warehouse, where the benzo[a]pyrene concentration at 2,600 m was 7 ng/m^3.

All of these fires lasted between 12 hours and 5 days, with control measures lasting a long time after the fire was extinguished and with very little plume rise. The fire in Blerick was an exception to this, as it involved a large plume rise.

Table 7 shows that while the average benzo[a]pyrene concentration of the upwind samples falls within the range of existing background values, it is slightly higher than the average of those background values. When high concentrations are detected at upwind locations, there is usually a perceptible affect from traffic, industrial activity or potential wood burning.

3.5.3 *Deposition (dustfall wipe samples)*

Table 8 provides an overview of the measurement data for benzo[a]pyrene and sum PAH4 at 33 fire incidents whether the MOD collected and analysed dustfall wipe samples. In general, the MOD's reports list concentrations for benzo[a]pyrene and sum PAH4. Over the years, however, the concentrations for sum 16 EPA PAH, sum 16 EU PAH and benzo[a]pyrene equivalents have occasionally been reported as well (see Appendix 3 for an explanation of the different PAH sum values). These PAH results have not been taken into consideration this report. The unit in which PAHs are measured in dustfall wipe samples reports is always µg/m^2. The PAH background value for benzo[a]pyrene is 0.1 (0.025–0.25) µg/m^2 and for sum PAH4, the value is 0.35 (0.04–1.0) µg/m^2.

Table 8 PAH results in dustfall wipe samples per distance category

Substance		Upwind	0–300 m	300–1,300 m	>1,300 m
Benzo[a] pyrene	Average (µg/m^2)	0.1	2.7	0.2	1.5
	Max. (µg/m^2)	0.22	45.8	1.3	18.0
	Number of sampling points	15	32	32	22
Sum PAH4[1]	Average (µg/m^2)	0.3	5.6	0.8	0.6
	Max. (µg/m^2)	0.6	19.5	3.8	3.8
	Number of sampling points	12	13	21	10

[1] PAH4: sum of benzo[a]pyrene, benzo[a]anthracene, benzo[b]fluorantene and chrysene.

Of the 33 fire incidents where dustfall wipe samples was collected and tested for PAHs, there were a few incidents where the PAH deposition was 10x higher than the background value or the range of background values. This was the case at the following incidents:

- Den Bosch 2021 (scrap processing facility), with a benzo[a]pyrene deposition in the source area of 2.9 µg/m^2.
- Kampen 2008 (scrap metal recycling facility), with a benzo[a]pyrene deposition in the source area of 4.8 µg/m^2.
- Ede 2008 (tyre company), with a benzo[a]pyrene deposition in the source area of 45.8 µg/m^2.

At greater distances, almost no concentrations exceeding the background values were detected. The only exception to this was a 2018 fire at a recycling facility with artificial grass mats in Dongen, where a benzo[a]pyrene deposition of 18 µg/m^2 was measured at a distance of 1,700 m. This measurement is responsible for the relatively high average of 1.5 µg/m^2 in the >1,300 m category.

3.5.4 *Deposition on grass and/or crops*

Table 9 sets out the benzo[a]pyrene and sum PAH4 measurement data for 37 fire incidents. As with dustfall wipe samples, the MOD reports generally include the detected concentrations of benzo[a]pyrene and sum PAH4 and Table 9 does not take into consideration the results for 16 EPA PAH, sum 16 EU PAH and benzo[a]pyrene equivalents. The background value for benzo[a]pyrene is 2–5 µg/kg at 88 per cent dry matter and for sum PAH4, it is 50 (4–800) µg/kg at 88 per cent dry matter.

Table 9 PAH results in grass and crop samples per distance category.

		Upwind	*0–300 m*	*300–1,300 m*	*>1,300 m*
Benzo[a] pyrene	Average (µg/kg) 88% d.m.	4.2	20.6	10.8	5.0
	Max. (µg/kg) 88% d.m.	25	102	82	39
	Number of sampling points	18	19	28	25
Sum PAH4[1]	Average (µg/kg) 88% d.m.	18.7	90.4	51.5	30.0
	Max. (µg/kg) 88% d.m.	54	524	151	175
	Number of sampling points	11	9	18	17

[1] PAH4: sum of benzo[a]pyrene, benzo[a]anthracene, benzo[b]fluorantene and chrysene.

Table 9 shows that the average PAH concentration was higher than the background value, especially close to the source. At a greater distance from the origin of the fire, the concentrations decreased and fell within the range of applicable background values. There are a few exceptions to this, including the fire in a refinery in the Botlek (Rotterdam) in August 2018, where benzo[a]pyrene concentrations of 14 and 15 µg/kg were detected at the respective distances of 5,000 and 6,000 m (the value at an upwind location was 0.3 µg/kg). Other examples of fires where elevated values were detected are those at waste processing facilities, such as the fire at a waste processing facility in Zaltbommel in January 2014, where a sum PAH4 concentration of 524 µg/kg was detected at 50 m from the origin of the fire and 116 µg/kg at a distance of 750 m. At a fire at an slaughterhouse waste processing facility that occurred in Wijster in February 2019, the benzo[a]pyrene concentration at a distance of 3,100 m was 39 µg/kg (Sum PAH4 175 µg/kg).

Table 9 shows that the average value for benzo[a]pyrene and the sum of PAH4 concentrations of the grass and/or crop samples taken upwind fell within the range of background values. A single value was found to be higher, possibly due to local circumstances.

3.5.5 *Assessment of health risks*

Exposure to PAHs from fires can occur through inhalation, through oral exposure via hand-to-mouth contact or by ingesting contaminated crops. For exposure to PAHs, we estimate the additional risk of cancer by comparison against the maximum tolerable risk level corresponding to 1 additional case of cancer per 1 million people with lifetime exposure (10^{-6}) or the negligible risk level (10^{-8}).

In order to assess the risk associated with exposure via inhalation, we have used benzo(a)pyrene as a stand-in indicator for the sum total of PAHs. With regard to exposure to PAHs in dustfall wipe samples, we use

a scenario in which a child comes into contact with PAHs through hand-to-mouth contact to estimate the additional risk of cancer. In doing so, we assume benzo(a)pyrene equivalents for the various PAHs. The MOD carries out these calculations at incidents where PAHs have been measured. They are based on US EPA [23], European [24] and RIVM [25] guidelines, methods and/or reports.
The toxicological assessments that the MOD conducted at incidents show that no elevated risk was present at any of the incidents. In other words: the calculated exposure was always well below the maximum tolerable risk and, at the majority of incidents, was even below the negligible risk level. This is primarily due to the relatively brief duration of the potential exposure. Nevertheless, any exposure to PAHs will increase an individual's risk of developing cancer. Other major sources are smoking [26], food (such as burnt foods) [27] and air pollution [28]. Compared to these sources, the exposure to PAHs associated with smoke from a fire is negligible.

Unlike for dioxins, no limits for levels in livestock feed have been established for PAHs. Although in the past, grass samples were often tested for PAHs, this was primarily in order to gain an indication of the deposition. Livestock that eats grass contaminated with PAHs poses virtually no risk to food safety because the toxic substances are not passed on in their milk. Another reason to analyse grass samples is to find evidence pointing to potential PAH contamination in nearby vegetable gardens, which would pose a risk to food safety.

3.6 Dioxins and dioxin-like substances in TSP and deposition

Dioxins are a group of chemical compounds, some of which are extremely toxic. Because dioxins are extremely persistent in the environment, non-biodegradable in humans and animals and readily soluble in fats, they tend to accumulate in the food chain. Dioxins may be released by combustion processes involving materials that contain hydrocarbons and chlorine, such as certain plastics (especially PVC). The quantity of dioxins produced and dispersed in the living environment will depend on the circumstances: the size and characteristics of the fire (combustion temperature, oxygen supply, duration of the fire, extent of the plume rise and so on), the materials which are burning and the weather conditions.

In the living environment, people may come into contact with the emitted dioxins by inhaling the dust particles or by touching dust that has settled (with which dioxins have bonded). The spread of dioxins can also lead to contamination of grass and crops and therefore pose a risk to food safety via the consumption of animal products such as milk from livestock or eggs from chickens that have eaten contaminated grass or soil, or via the consumption of contaminated vegetables.

3.6.1 Analysis of quantitative measurement data on dioxins

From the MOD's data set of incidents, we selected all fire incidents where dioxins were measured in air, dustfall wipe and/or grass samples. In some cases, only the data from XRF measurements (screening) for chlorine (Cl) was reported, with the conclusion that the data did not give

cause for performing dioxin analyses. These incidents were naturally not selected for further analysis.
The selection process yielded 46 incidents. Excluded from consideration were:

- incidents in which dioxins were potentially detected (according to the information in the data set or report) but for which no quantitative data was available. This applied to 3 incidents;
- The fire in an oil refinery on Bonaire was excluded because the situation there cannot be effectively compared to the situation in the Netherlands. The dioxin concentrations measured there (in vegetation samples) were also extremely low).

We then analysed the measurement data for dioxins in the reports from the 46 incidents selected. The data was categorised by type (TSP, deposition = dustfall wipe, and grass) and by distance from the source, with one of four categories being assigned:

- Near the origin of the fire: 30–200 m.
- At a medium distance from the origin of the fire: 200–approx. 1,000 m.
- At a large distance from the origin of the fire: more than 1,000 m.
- Upwind from the origin of the fire (reference samples).

For each category, the measured values of the incident were added up and averaged. The number of measured values is also given, as well as the distances (ranges) at which they were found.

3.6.2 *TSP samples*

In 16 of the 46 incidents selected, dioxins were measured in the TSP samples. The results are shown in Table 10.

Table 10 Dioxin concentrations (in ng TEQ/m^3) measured in TSP samples for each distance category.

	Upwind	0–200 m*)	200–1,000 m	>1,000 m
Average	0.2	170	12	3
Max.	1.8	953	35.5	10
Number of sampling points	12	12	8	6

*) A single measurement was taken approximately 350 m from the fire. The measured value (953 ng TEQ/m^3) was measured in the heart of the smoke plume in the source area and has therefore been placed in the 'near the origin of the fire (0–200 m)' category.

Table 10 shows that the MOD detected the highest values near the source and that the average value decreased as the distance from the source increased. Measurements in the large-distance category (>1,000 m) were taken at six incidents. In three cases, the dioxin concentration was significantly higher than the background value. These incidents were: a fire in a waste pile (heat produced by unintended fermentation), a processed meat factory (where a large quantity of plastic packaging material was present) and the previously mentioned warehouse with computer equipment. At these fires, the MOD detected elevated to highly elevated values near the origin of the fire and (often) at a medium distance.

The results of the upwind reference samples are in keeping with the range of background values in the Netherlands: 0.015–0.15 pg TEQ/m^3. There was one exception with a value of 1.8 pg TEQ/m^3. A possible explanation for this exception is that the volume of the air sample was quite small, resulting in a large degree of uncertainty in the measured dioxin concentration.

3.6.3 *Deposition (dustfall wipe samples)*

In 22 of the 46 incidents selected, dioxins were measured in dustfall wipe samples. The results are shown in Table 11.

Table 11 Dioxin deposition (in ng TEQ/m^2) measured in dustfall wipe samples by distance category.

	Upwind	0–200 m	200–1,000 m	>1,000 m
Average	18	113	14	21
Max.	62	860	27	185
Number of sampling points	14	11	13	17

In the ‘large distance’ category (>1,000 m), measurements were conducted at one to seven locations more than 1 km from the origin of the fire at 17 incidents. With the exception of one sample, all the measured values were between <1 and 27 pg TEQ/m^2, placing them within the range of background values. The exception was a deposition with a concentration of 185 pg TEQ/m^2 detected at 1500 m from the origin of the fire (and 23.6 pg TEQ/m^2 at 2 to 4 km from that same incident, at which no deposition was tested at a distance of less than 1.5 km). This was a fire with a limited plume rise, which occurred in a large heap of plastic waste at a waste processing plant. The MOD detected slightly elevated dioxin concentrations in grass at this fire as well. No measurements of the dioxin level in the TSP samples were taken here.

The measured values in the ‘near the origin of the fire’ category (0–200 m) were between 2.8 and 54 pg TEQ/m^2. Although this is slightly higher than values measured at a larger distance, these values are still barely above the background level. Two measured values were significantly higher, namely 147 and 860 pg TEQ/m^2. These values were detected at, respectively, a fire at a plastic recycling facility (plume rise 100–150 m) and a fire at a waste processing plant (plume rise unknown). At the latter incident, the deposition at larger distances was analysed as well, but was not found to contain elevated concentrations. In grass samples from this incident – taken at between 500 and 650 m from the fire – the MOD did detect slightly elevated values. At the fire in the plastic recycling facility, an elevated value (34 pg TEQ/m^3) was also detected in the TSP samples near the fire, but the deposition at a distance of 700 m did not contain a higher concentration than that.

The measured values in the 14 upwind reference samples varied from 3 to 37 pg TEQ/m^2 (with one exception, a value of 62 pg TEQ/m^2). The range of background values detected in an earlier study in the Netherlands was 5 to 25 pg TEQ/m^2. Taking all uncertainties into account, we can conclude that the concentrations measured in depositions do not deviate from the background values in the Netherlands.

3.6.4 *Deposition on grass and/or crops*

In 44 of the 46 incidents selected, dioxins were measured in grass samples. Because the background concentration of dioxins in grass depends on the season, the incidents are roughly divided by the season in which they occurred: spring (March until May), summer (June until August), autumn (September until November) and winter (December until February).
The results for each distance category and season are given in Table 12.

Table 12 Dioxin concentrations in grass, expressed in ng TEQ/kg (88 per cent dry matter), measured at over 40 fires.

	Background value (indication)	Upwind	0–200 m	200–1,000 m	>1,000 m
Spring	1–2	Average: 0.32 Max.: 0.8 n = 10	Average: 47 Max.: 221 n = 5	Average: 1.8 Max.: 8.7 n = 7	Average: 0.8 Max.: 2.2 n = 8
Summer	0.5–1	Average: 0.19 Max.: 0.35 n = 15	Average: 5.4 Max.: 9.6 n = 4	Average: 1.7 Max.: 7.5 n = 8	Average: 0.5 Max.: 3.0 n = 14
Autumn	1–2	Average: 0.4 Max.: 0.7 n = 7	Average: 15 Max.: 44 n = 5	Average: 1.0 Max.: 1.3 n = 7	Average: 0.5 Max.: 1.1 n = 5
Winter	2–4	Average: 1.1 Max.: 2.0 n = 6	Average: 9 Max.: 25 n = 3	Average: 4.4 Max.: 6.9 n = 6	Average: 2.2 Max.: 6.7 n = 9

From this data, it is possible to conclude the following:

- The concentrations at the reference sampling sites were generally well below the background level for each season. Concentrations were lowest in the summer and somewhat higher in the winter. This is also in agreement with the WFSR report from Hoogenboom and colleagues [29], for which grass samples from various forelands were analysed. Generally speaking, the concentrations at the vast majority of the upwind reference sampling sites are under the limit for livestock feed (0.75 ng TEQ/kg (88 per cent dry matter) [7] and exceedances of this limit at upwind reference sampling sites usually occur in the winter. Concentrations are somewhat higher in winter because the grass is not growing: dioxin concentrations become diluted as grass grows. Based on these results and the WFSR report, it seems that the background values of dioxins have decreased, potentially as a result of the measures taken to reduce dioxin emissions. While the background values could be adjusted to lower values, it is possible that this would require additional research.

- At large distances (>1,000 m), the average and maximum values are slightly higher than the at the reference sampling sites, although virtually all these values are around or under the background level for the relevant season. In a number of cases, the concentrations at a larger distance were slightly elevated compared to the background level. This pertained to fires involving waste (4 incidents, including one with scrap metal and cable waste. No information is available on the composition of the waste at the other 3 fires), a fire in a warehouse containing plastic pellets and gas cylinders and the fire at Chemiepack in Moerdijk, where a wide range of chemicals were being stored (6.7 ng TEQ/kg (88 per cent dry matter) at 3,500 m, no increase in value from 5,000 m). At this fire, it is worth noting, the grass sample with an elevated dioxin level was found to have a deviating dioxin pattern, meaning those dioxins very likely did not originate from the fire.
- At a medium distance (200–1,000 m), the average values were slightly higher than at the reference sampling locations and the background level. This average, however, was influenced by a few elevated levels which were generally among the highest concentrations measured. At most fires, the concentrations were not higher, or at most slightly higher, than the background level. The fires where elevated values were present were the same fires where an exceedance was detected at a large distance from the origin of the fire (as summarised above): at several fires at waste processing facilities (sometimes with PVC), at fires in an slaughterhouse waste processing facility, at a processed meat factory (both were cases where large quantities of plastic packaging were present) and at a mixed-use industrial building, where items including LED screens and insulation materials were being stored.
- Near the origin of the fire (<200 m), the dioxin concentrations in grass were nearly always elevated, in 17 of the 44 fires measurements were caried out at less than 150 m from the origin of the fire. This is mostly consistent with the findings from the air and deposition samples that were taken. The highest values were detected at a waste processing facility (with scrap metal and cable waste) and a fire at an industrial site where PVC components and numerous PVC storage tanks were present. At the latter incident (the fire), the dioxin concentrations at 300 m and further from the origin of the fire were found to be barely elevated – probably due to heavy rainfall during and after the fire.

3.6.5 *Assessment of health risks*

In order to determine when it is necessary to measure for dioxins at a fire, it is important to have an idea of the health risks associated with exposure to dioxins at certain types of fires. Exposure can occur when a person inhales particulate matter containing dioxins, when they inadvertently ingest dioxins in deposited dust on their hands (known as hand-to-mouth contact) and when they ingest crops or animal products that have been contaminated by dioxins. The methods used by the MOD to estimate exposure to dioxins is based on EFSA limit values and methodology [30].

See Appendix 4 for more detailed information on the toxicological risk assessment for dioxins at fires. We can safely summarise that at most fires, the exposure to dioxins via inhalation and hand-to-mouth contact will not lead to an exceedance of the Tolerable Weekly Intake (TWI) of 2 pg TEQ/kg of body weight per week. When there is a high concentration of dioxin in the TSP samples (close to the origin of the fire), the exposure will usually be brief and we can advise people to stay away from the smoke. If the MOD detects a high deposition (approx. 150 pg TEQ/m^2 or more), they can advise that the surfaces of playground equipment, outdoor furniture and so on be thoroughly cleaned.

At most fires, the exposure via ingestion of crops is below the TWI. Additionally, these fires are one-time events and the exposure through eating vegetables from a specific area will be a one-time occurrence as well. We can summarise that, at the majority of fires, the exposure to dioxins via ingestion of crops does not result in a health risk. At fires where elevated concentrations of dioxins were detected in grass (or crops) in the effect area, it is wise to recommend that people avoid eating crops grown in that area near the fire.

With regard to milk consumption, we can compare the dioxin levels in grass to the EU limit for livestock feed for cattle. This limit is 0.75 ng TEQ/kg (88 per cent dry matter) and stems from Directive 2002/32/EG of the European Parliament and the Council of 7 May 2002 concerning undesirable substances in animal feed. The dioxin concentrations measured at reference locations at the fires and at large distances from them were, for the most part, well below this limit. We are excluding the winter season from consideration here, because no grass is harvested for livestock feed in that period and because the dioxin concentration will decrease once more when the grass grows in the spring. It is also the case that dairy cows are generally housed indoors during the winter period. At medium distances, exceedance of the limit is slightly more common outside of the winter season.
At a large distance (1 to 3 km) from 4 fires, a dioxin concentration above the limit for livestock feed was detected: 1.6 to 3 ng TEQ/kg (88 per cent dry matter). Three of these cases involved a fire with assorted types of waste. The remaining case was a fire in a warehouse containing (among other things) plastic pellets and gas cylinders. Concentrations exceeding the limit for livestock feed were detected more often at medium distances. These exceedances were usually slight, with a concentration of less than 1.5 ng TEQ/kg (88 per cent dry matter), although a higher concentration was detected in 4 instances, ranging from 1.8 to 8.7 ng TEQ/kg (88 per cent dry matter). This pertained to fires of the same type as when the MOD detected dioxin concentrations exceeding the limit for livestock feed at a large distance from the fire. These fires burned for a long time (6 to 40 hours, excluding control measures after the fire was put out), had heavy smoke development and took a long time to fully extinguish. In a few of these fires, the plume rise was large in the early stage of the fire. This might explain why the MOD detected elevated dioxin concentrations in grass at a greater distance from the fire.

While exceedances tend to be small, there is a risk that contaminated grass will find its way into livestock feed. This could lead to an exceedance of the maximum permitted levels of dioxin in milk [31] and meat [29]. It is therefore advisable to analyse any grass samples for dioxins. The risk to consumers is generally small, as the milk from cows that have eaten grass contaminated with dioxins is generally mixed with milk from cows in 'clean' areas. This dilutes the dioxin concentration in the milk being sold for consumption. For the farmers in question, there could be a business risk if they make their own cheese. That cheese could contain elevated concentrations that exceed the TWI limits. In such cases, the farmers could – as a precaution – avoid using the contaminated grass and it is advisable to prevent cows from grazing in the contaminated pastures until the dioxin level has sufficiently decreased.

Another potential route by which dioxin contamination can enter the food chain is through the eggs of chickens. Eggs can become contaminated with dioxins because chickens who spend time outdoors can pick up bits of soil that are contaminated with dioxins [32]. To date, however, little information is available on the extent to which fire incidents contribute to this contamination route.

3.6.6 Relationship to PAHs

At over half of the fires where dioxins were measured in TSP, deposited dust and/or grass samples, measurements of PAHs were conducted as well. The dispersion pattern of dioxins is generally similar to that of PAHs, which is to say that where elevated values for dioxins were measured, PAH concentrations were found to be elevated to a similar degree. The reverse, however, was not always the case. While both groups of substances are formed from carbonaceous materials under conditions where poor or incomplete combustion occurs, the formation of dioxins requires materials containing chlorine as well [8].

Occasionally, there are exceptions where a relatively high PAH value has been measured locally in the effect area (with no high PAH values detected at other locations in that effect area), while the dioxin value at the same location was either not elevated or elevated to a lesser extent. In such cases, the local elevated PAH value could stem from local sources or be the result of historical contamination.

4 Discussion

4.1 Considerations

As stated in section 1, a wide range of substances may be released during fires and these substances may – to a greater or lesser degree – be harmful to humans and the environment. The formation and dispersion of substances during a fire is both complex in nature and strongly dependent on the situation, the weather conditions, the circumstances and the progression of the fire, as well as on the materials present at the origin of the fire.

As a result, identifying the concentrations and deposition of hazardous substances in the living environment downwind of a fire calls for a case-by-case approach. Insights learned from the results of measurements conducted at previous fires can also be valuable in determining the optimum measurement strategy in a given situation. In 2007, therefore, RIVM compiled and analysed the results of measurements it took at approximately 50 fires during the 1997–2007 period [1]. This study also involved collecting data from the literature on fire experiments conducted on a laboratory scale and full-scale experiments with controlled fires. Based on this data, overviews were compiled of:

1. the emissions volume of the major combustion products for different types of materials (e.g. plastics, wood, paper and cardboard, electronics, construction materials, waste and petroleum products); and
2. the nature and quantity of substances that may be present in the living environment (air, deposition) downwind of a fire.

It was also concluded that, while high concentrations of hazardous substances may be released into the smoke plume during a fire, the health risks associated with exposure to these substances are negligible at downwind locations more than 1 km from the origin of the fire, with the exception of extremely large fires or fires with unusual characteristics. In practice, this is known as the ‘one-kilometre rule of thumb’.

This research combines the insights from the 2007 study with values measured by the MOD at over 130 fires in the period from 2008 to 2021. The analyses of these measured values and the resulting conclusions for each substance group are discussed in section 3. The key points of the results give no indication that it is necessary to revise the insights/conclusions from the 2007 study. The current study, for instance, confirms that VOCs and PAHs are often formed during fires, and that particulate matter released often contains lead and zinc (and sometimes other elements as well). The relationship between high concentrations and deposition of dioxins and certain types of materials involved in a fire (such as PVC, plastic waste, electronics and packaging materials) has also been confirmed. In a general sense, we can say that the information regarding which substances are released by certain types of materials, summarised in the tables on pp. 100 and 101 of the 2007 report [1], are still useful for determining which measurement strategy to deploy at a fire. The results of this study also show that the 'one-kilometre rule of thumb' can continue to be deployed and even be made more specific. These two important findings are summarised once more in the conclusions set out in sub-section 5.1.3.

The report from the 2007 study contains several recommendations. Some recommendations are due to a number of limitations of the study and the MOD's measurements. Because the MOD is not present in the initial phase of a fire, for example, there is virtually no measurement data regarding substances 'in the first hour' of a fire. One of the recommendations in the report was to equip the fire brigades with the means to collect samples of the air in the smoke plume and in the source and/or effect area 'in the first hour', which the MOD can then analyse when it arrives at the fire. All safety regions now have access to canisters. They can use these canisters to collect air samples 'in the first hour' of the fire, which the MOD can later analyse for substances such as VOCs. These are discussed in sub-section 3.2.

Another recommendation concerned limiting the types of substances measured by the MOD. Prior to the 2007 study, the MOD conducted a 'more or less standardised' range of measurements at fires: for VOCs, particulate matter, PAHs, elements, dioxins and a number of inorganic gases. Since then, a method has been developed for identifying levels of aldehydes and ketones in the air as well, and this method has been deployed at a number of fires. The results of these measurements are addressed in sub-section 3.3.1.
Other substances for which the 2007 study recommended further investigation are isocyanates, amines, nitriles, nitro-PAH, sulfur-containing PAH, flame retardants containing bromine, brominated dioxins and hydrogen bromide. Because no such follow-up research has been conducted, this recommendation remains in effect. At this time, it is unknown whether these substances pose an additional risk or whether, once quantified, they could potentially call for different actions.

Finally, it would be advisable to explore the extent to which the energy transition and other developments lead to new risks in connection with the formation and dispersion of potentially hazardous substances during fires. The first steps in this area have already been taken. In 2022, RIVM conducted a study of the dispersion and deposition of substances and debris (shards) produced by fires involving solar panels [3] and in 2019, it investigated which substances are released by fires involving Li-ion batteries [4].

4.2 Limitations of the study

A large number of fires (n=132) were analysed for the purposes of this report. The results of these analyses provide a supplement to those from some 50 fires examined in the 2007 study by Van Mennen and Van Belle [1], on which this research is a follow-up. The research described in this report does have a number of limitations.

Number of fires
Although the MOD has been involved in 132 fire incidents in the past 15 years, this represents only a small fraction of the large fires that actually

take place in the Netherlands. More than 100,000 fire incidents [33] occur in the Netherlands each year. In 2022, this included 483 large fires and 233 extremely large fires [34]. The MOD only conducts measurements at fires when asked to do so by the safety region fire department. No measurement data (of the type collected by the MOD) is available for the vast majority of large and extremely large fires in the Netherlands. This group undoubtedly includes fires at which various hazardous substances were released. Yet the measurement results examined in this research paint a consistent picture and, presumably, the fires for which no MOD measurement data is available would unlikely be different.

Measurements and measurement strategy
While the incidents have been compared to one another based on the relevant hazardous substance groups, no two incidents are the same. Various external causes may result in variations in the measurement data, including the weather, location, what is burning, the plume rise and so on. Variations in sample collection are possible as well. For example: has the sample been taken at the thickest point of the smoke plume, or more toward the edge? And in what phase of the fire was the sample collected? For each incident, the MOD determines which specific samples and substance groups it will or will not analyse. The number of measurements (samples) the MOD can take is limited because the period of time available to do so is relatively short (most fires last only a few hours) and the capacity of the field team is limited. The MOD must therefore make decisions about where it will collect samples, which instruments it will deploy and the analyses it will conduct (at the scene). Generally speaking, the MOD tries to take samples from both the source and effect areas. The MOD also looks for possible sensitive receptors in the downwind area (such as pastures where cattle graze and/or children’s playgrounds).

Plume rise
The extent of plume rise will impact the measurement results. The MOD arranges its instruments at ground level and, if a strong plume rise is present, the concentrations in air and TSP will be lower than in cases where the plume moves at ground level. The results of the deposition measurements depend on the plume rise as well. If the plume stays low, elevated values will be detected mainly in the immediate vicinity of the source. If there is a stronger plume rise, the deposition will be spread over a greater distance but at lower concentrations due to ‘diffusion’.

Information on fuels/materials
Another limitation is that often, there is no clear picture of what is burning. At incidents where the MOD was involved, the MOD was provided with this information by the safety region and/or the press. In this study, that exchange sometimes took place after the fact and the information was not always readily available. In addition, fires (such as building fires) usually involve a variety of materials. At a fire in a warehouse holding PVC items, for instance, the fuel will be reported as ‘PVC’, whereas in reality multiple substances will be burning, depending on the construction and what is being stored, and this composition will also change as the fire progresses.

5 Conclusions and recommendations

In order to support the response to large fires and fires involving hazardous substances, we have explored – by reviewing measurement data from 132 fires from the period between 2008 and 2021 – whether it is possible or necessary to enrich or adjust the insights and conclusions from the 2007 report on 50 fires. The results of the analyses of the measurement data in this report are in line with those of the 2007 study [1]. Like the previous study, this research shows that (with a very few exceptions) concentrations that pose a health risk are almost never present at a distance of more than 1 km from the origin of the fire. For a number of substance groups, the MOD could even lower the 'one-kilometre rule of thumb' (i.e. adjust it to a smaller distance) or conclude that taking measurements of these substance groups add virtually no value for first responders and the relevant competent authority in terms of choosing a course of action. The results of this study also confirm the findings of the 2007 report [1] with regard to which substances are formed during fires involving specific materials.

We have set out the (potentially revised) conclusions for each substance group below. In doing so, we have made a distinction between gaseous compounds (VOCs, aldehydes and ketones) and dust-bound compounds (elements, PAHs and dioxins). In sub-section 5.2, we answer the questions from the GAGS and AGS and in sub-section 5.3, we offer recommendations in connection with the MOD's measurement strategy at fires.

5.1 Conclusions

5.1.1 Partial conclusion for gaseous compounds (VOCs, aldehydes, ketones)

Various VOCs, aldehydes and ketones are produced during fires. The MOD detected elevated concentrations of aromatic compounds (benzene, toluene, styrene), but also aliphatic compounds (alkanes, alkenes and alkynes), aldehydes, ketones and sometimes other substances such as chlorinated VOCs in various smoke plumes. At distances of 1 km or more from the fire, the concentrations were no longer elevated (with the exception of a few incidents). Elevated concentrations of VOCs and aldehydes were detected mainly at fires involving waste (scrap metal, plastic) and recycling facilities that process cars, tyres and rubber. These results are in keeping with those of the 2007 study.

The measurement results show that in only a handful of cases did the MOD detect a concentration of one or more VOCs that was higher than the VRW or AGW. In all cases, this pertained to a sample collected directly from within the smoke plume and near the origin of the fire. Taking into account all incidents where the MOD conducted measurements, there was not a single instance in which the VRW for aldehydes was exceeded. Outside the source area, the MOD sometimes detected values that were elevated compared to the background level, but never in concentrations that could potentially pose a health risk. This confirms the rule of thumb that there is no health risk as a result of exposure to VOCs, aldehydes and ketones at distances of 1 km or more from a fire. In fact, it may be possible to refine the rule of thumb for this substance group by adjusting it to a smaller distance (<300 m).

5.1.2 *Partial conclusions for dust-bound compounds (PAHs, elements, dioxins)*

Fires emit not only gaseous compounds, but dust particles as well, especially particulate matter. These dust particles contain hazardous substances including PAHs, metals (and other elements) and dioxins. Besides being distributed by air, the dust particles are also deposited (dustfall) in the area downwind of the fire. The MOD therefore collects TSP, dustfall wipe and grass or crops samples.

Like VOCs, PAHs are formed and spread during virtually all fires. The highest PAH concentrations (in TSP and deposition samples) were detected in fires at waste processing, demolition and recycling businesses, scrapyards and warehouses where the fires involved materials such as car tyres, bitumen and rubber products, plastics, PVC, wood waste, carpets and computer components. At such fires and when such materials are involved, the dust particles released will often also contain certain metals and other elements, along with (provided large quantities of materials containing chlorine are present, such as PVC) dioxins as well. Other materials involved in fires where metals were detected in dust particles were scrap metal, batteries, electronics and impregnated garden wood. Generally speaking, PAHs, metals and dioxins can be released by materials commonly found inside buildings, such as furniture, wall coverings, construction materials and computers.

This study showed that the MOD often – but not always – detected high concentrations of PAHs, dioxins and other elements (mostly metals such as lead, zinc, copper and antimony, but sometimes other elements) in the source area, especially in TSP samples. The MOD also detected elevated concentrations in the effect area (medium distance: 300 m to 1 km), although not as high and not as often as in the source area. In rare cases, concentrations higher than the background level were measured further away from the fire than 1 km. This usually pertained to dioxins. In dustfall wipe, grass and crop samples, the concentrations of PAHs, dioxins and elements were less elevated than in the TSP, which is in keeping with the findings of the 2007 study [1]. Elevated values occurred in the source area (<300 m) and sometimes in the effect area, usually only at a medium distance of 300 m to 1 km. However, there were exceptions in which the depositions of PAHs, dioxins and certain metals were found to exceed background values at a distance greater than 1 kilometre. These exceptions were extremely large fires and fires that lasted a long time (6 to 40 hours, excluding control measures after the fire was put out), had heavy smoke development and a lengthy period of control measures like wetting down after the fire was extinguished. In addition, the plume rise was usually limited, at least during a portion of the fire.

In short, the ‘rule of thumb’ – which states that the MOD will detect no (or virtually no) elevated values for PAHs, dioxins and metals or other elements in dustfall wipe samples collected more than 1 km from the fire – can continue to be applied, with the exception of fires that have the characteristics we just described.

In grass samples taken at distances of up to 1 km, the MOD sometimes detected (slightly) elevated concentrations of metals and dioxins and, in the case of a handful of fires, even at distances greater than 1,000 m. In nearly all of these cases, the concentration of metals was within the limit for livestock feed, while the dioxin values were not within the limit for livestock feed. These findings are also in keeping with those of the 2007 report. An exceedance of the dioxin limit for livestock feed in grass samples or feed crops such as corn yields a potential risk of dioxins entering the food chain. It is advisable that grass samples be analysed for dioxins when the smoke plume has spread over pastures where cattle graze and other crops that are intended for use as livestock feed. If dioxin levels exceed the limit for livestock feed, it can be recommended that the grass in question not be used for livestock feed.

Despite the presence of elevated concentrations of PAHs and metals in the effect area, exposure to these concentrations generally does not lead to intake higher than the health-based guidance value, whether through inhalation, hand-to-mouth contact or ingestion of crops. This is because the exposure is always brief in duration and experience has shown that, at fires where the MOD has carried out measurements, the maximum tolerable risk was not exceeded in a single case, and in most cases the exposure was below the negligible risk level as well. With regard to dioxins, exposure via inhalation or ingestion does not generally result in a health risk, yet it can be recommended that people avoid eating crops from the effect area for a while if grass or crops are shown to be contaminated.

5.1.3 Conclusion

In summary we can conclude that the findings of this study of measurement results from the 2008–2021 period are largely in agreement with those of the 2007 study [1]. This study confirms the ‘rule of thumb’ that risky concentrations of substances are almost never present at distances greater than 1 km from the origin of the fire, neither in the air nor through deposition. With regard to VOCs, aldehydes and ketones, measurements taken at distances of less than 1 km also detected no concentrations that would pose a health risk. Exceptions to the rule of thumb are fires that last a long time (sometimes multiple days), heavy smoke development, limited plume rise (during at least for part of the fire) and, in many cases, a lengthy period of late stage fire-suppression process until the fire is fully extinguished. This usually pertains to fires at waste processing, demolition and recycling businesses, and fires in warehouses and large buildings. In terms of materials, the types involved are usually scrap metal, plastics, bitumen, new and used car tyres and rubber materials, computer components, packaging materials and various kinds of rubbish.

Another result of the study pertains to the relationship between the substances that are produced and spread during fires and the materials that burn in those fires. As part of the 2007 study, research into this relationship was conducted by i) collecting data from the literature on fire experiments conducted on a laboratory scale and full-scale experiments with controlled fires, and ii) analysing the measurements taken by the MOD at fires in the 1997–2007 period. In sub-section 4.1, we explain that the results of this research give no indication that it is necessary to revise the insights/conclusions from the 2007 study. In short, the insights regarding which substances are released by the combustion of certain types of materials, as summarised in the tables on pp. 100 and 101 of the 2007 report [1] can continue to be applied and are now part of the Incident App.

5.2 Answers to questions from the GAGS and AGS

We have answered the questions below. Each question (Q) is followed by the corresponding answer (A) beneath it:

Q1. Does the ‘one-kilometre rule of thumb’ still apply, i.e. ‘in most fires, no concentrations of substances that are hazardous for people and the environment are present more than 1 km from the origin of the fire’? These conclusions were drawn with the caveat that harmful concentrations of these substances can potentially spread further than 1 km in case of extremely large fires or fires with certain characteristics.

A1. Yes, the ‘one-kilometre rule of thumb’ still applies. This study has confirmed the rule. For some substance groups, it could even be adjusted to a lesser distance. However, this study also found a number of exceptions that indicate that it is possible for hazardous substances to spread further than 1 km in the case of very large fires with special characteristics.

Q2. Does the rule of thumb which says virtually no deposition exceeding the background value will occur at distances greater than 1 km from the origin of the fire still apply? Which characteristics of a fire should result in an exception to this rule of thumb (for measurement purposes)?

A2. Yes, this rule of thumb remains applicable as well. This study revealed that the highest deposition values in dustfall wipe samples measured by the MOD were detected in the source area (<300 m). While high deposition values were frequently detected in the effect area (>300 m) as well, the health risk associated with these was generally negligible. For exceptions, see the answer to question 3.

Q3. Is it possible to develop a set of criteria which the Public Health Advisor Hazmat (GAGS) and or fire department advisor hazmat (AGS) can use as a basis for determining whether it is useful and/or necessary to conduct certain measurements during or after a fire (such as those measuring dioxins and/or metals) and if so, where to take them?

A3. Fire characteristics that make it useful and/or necessary to take measurements include:

- very large and long-lasting fires (duration guidance value of 4 hours or more, excluding control measures after the fire is extinguished);
- long-lasting late stage fire-suppression process until smouldering fires are fully extinguished;
- a limited plume rise, in any case during a portion of the fire;
- heavy smoke development.

Typically at industrial sites with the following characteristics:

- Those involved in activities such as waste processing, demolition and recycling, and in warehouses and large buildings.
- Where the burning materials include scrap metal, plastics, bitumen, car tyres, rubber materials and/or electronic devices.

In these types of fires, there is a risk that hazardous substances (particularly dioxins and metals) will be dispersed in quantities that exceed safety standards. The locations at which the MOD should take measurements depends on the effect area for the incident in question. Locations where measurements are useful or even necessary include children's playgrounds and/or pastures where cattle graze.

Q4. When might a fire pose a potential threat to health? Considering direct exposure to smoke or exposure from deposition on crops or exposure through livestock.

A4. Direct exposure to smoke in a source area always entails a health risk. This is because smoke consists of a complex mixture of hazardous substances such as CO, CO_2, NO_x, HCN, soot, particulate matter and other dust particles, VOCs, PAHs and so on. The standard recommendation is 'stay away from the smoke, keep windows and doors shut and switch off mechanical ventilation'. As the distance from the origin of the fire increases, the health risk will decrease. The same applies to deposition, for which the standard recommendation is 'dispose of fire debris as regular or chemical waste and remove sooty residue with warm soapy water', usually with the additional recommendation that gloves be worn when doing so [17]. In terms of food safety, the producer is responsible for ensuring proper clean-up after a fire. For vegetable gardens, the standard recommendation to avoid eating vegetables or to clean them thoroughly before consumption can usually be applied. The risk is small, as the exposure to fire is a one-time and the ingestion of food from downwind of the fire incident is a one-time event as well.

Q5. What is the greatest distance at which depositions that posed a risk to food safety and therefore to public safety have been measured?

A5. Here, too, the one-kilometre rule of thumb applies – but see also A1–A4.

5.3 Recommendations for measurement strategy and further research

5.3.1 Gaseous compounds (VOCs, aldehydes, ketones)

Based on the incidents at which VOCs were measured, it has been concluded that no real health risk exists in connection with exposure in the effect area (>300 m from the source). With regard to aldehydes and ketones, in fact, no risk is present more than 100 m from the source. Measurements of VOCs, aldehydes and ketones at fires in the effect area provide no additional information for supplementing the existing standard recommendations such as 'stay away from the smoke'. These measurements in the effect area are not necessary. Likewise, these measurements provide little to no additional information when conducted in the source area. When preliminary screening with a photo ionisation detector shows there is cause to do so, the MOD can conduct a targeted measurement. If people are (going to be) present in the source area without protection (no breathing apparatus) for a long period of time, it could be useful to conduct measurements as well. That being said, anyone being present at the origin of a fire without protection for any length of time is highly unlikely, as this would violate the occupational safety principles of the fire brigade, which wears breathing apparatus inside the smoke .

5.3.2 *Dust-bound compounds (PAHs, elements, dioxins)*

PAHs are formed and spread during most fires, and during extremely large fires, this will lead to concern among the public when soot particles are deposited in residential neighbourhoods, playgrounds, vegetable gardens and farmland where crops intended for human consumption are being grown. In such cases, the MOD will usually detect PAH values that are higher than the background levels. However, taking into account all risk assessments that have been conducted to date, the maximum tolerable risk has never been exceeded. The recommended course of action for a downwind area contaminated with PAHs (on objects and/or in food) will, based on measured values, be no different than the standard recommendation: ‘dispose of fire debris as regular or chemical waste and remove sooty residue with warm soapy water’, usually with the additional recommendation that gloves be worn when doing so [17]. In terms of food safety, the producer is responsible for ensuring proper clean-up after a fire. For vegetable gardens, the standard recommendation to avoid eating vegetables or to clean them thoroughly before consumption can usually be applied. The risk is small, as the exposure to fire is a one-time and the ingestion of food from downwind of the fire incident is a one-time event as well. It is generally not necessary to conduct measurements for PAHs.

Collecting and analysing samples of PAHs can be useful for gaining insight into the extent of contamination and the associated health risk (although this risk is generally negligible). The MOD can limit the sampling sites to locations in the source and effect areas up to a distance of around 1 km. Only in instances involving very large and long-lasting fires fuelled by plastic, rubber and/or petrochemicals is it worth considering collecting samples more than 1 km from the source.

For fires where metals, heavy metals and/or dioxins are being released, it may be necessary to identify and quantify these substances if risky exposure is possible. Possibly elevated values typically occur at:

- very long-lasting fires (duration guidance value of 4 hours or more;
- long-lasting late stage fire-suppression process until smouldering fires are fully extinguished;
- a limited plume rise, in any case during a portion of the fire;
- most often at fires at industrial sites and involving materials related to waste processing, demolition and recycling, and in warehouses and large buildings. In terms of materials, the types involved are usually scrap metal; plastics (including insulating foam and artificial grass mats); bitumen; new and used car tyres and rubber materials; plastic, construction and demolition waste;

computer components; batteries and electronics; and packaging materials.

Generally speaking, the dispersion of metals will be limited to 1 km from the fire. Measurements of metals in TSP, dustfall wipe or grass samples provide no additional information when conducted more than 1 km from the fire. At distances further than 1 km, there is usually no exceedance of the limits that are associated with health risks. If no measurements are taken, a precautionary recommendation could be to clean all playground equipment within 1 km of the origin of the fire.

Dioxins are formed primarily at fires where one of the fuel sources is (presumably) a chlorine donor. This is mostly fires involving the following materials: waste (waste wood, impregnated garden wood, plastic waste, scrap metal), plastics (including PVC, plastic packaging and insulation materials), electronics (cable waste, electric bicycles, LED screens, computer equipment) and various unspecified kinds of chemicals. Testing for dioxins is primarily desirable if grazing land for livestock, crops for human consumption and/or grass or crops that farmers are growing for livestock feed are present in the downwind area less than 3 km from the fire. Collecting samples more than 3 km from the fire could be considered if a fire lasts an extremely long time, like the one in Moerdijk in 2011.

When deciding whether to conduct analyses for dioxins, the MOD can give an indication of potential dioxin release. This is done by collecting TSP samples near the origin of the fire and at some distance (taking 200 to 500 m as a guideline) downwind of the fire, in or under the smoke plume. The MOD can use XRF screening to determine the chlorine content in these TSP samples and, based on that information, determine whether it is possible that substantial quantities of dioxins have been formed during the fire. If so, it will be useful to collect a number of grass samples in the downwind area and analyse them for dioxins. Where the MOD will take those samples depends on how the smoke plume spreads. It is important that the MOD collects the samples *after* the fire has gone out and not during the fire, because dioxin formation remains possible as long as the fire is burning and not all dust particles containing dioxins will have been deposited.

5.3.3 *Summary of the MOD’s measurement strategy at fires*

This study provides sufficient evidence for revising the MOD’s measurement strategy at fires. With regard to most groups of hazardous substances, it has been shown that these have virtually no impact on the threat to health and the environment at distances greater than 1 km from the origin of the fire. Analyses of substance groups such as VOCs, aldehydes and ketones are not necessary at fires because they do not pose a direct health risk. For PAHs, too, the measurements generally do not yield useful information and the standard recommendations currently in place are sufficient. This study shows that it remains useful and necessary to conduct measurements of metals, heavy metals and dioxins, particularly in connection with specific fire characteristics and materials.

In exceptional cases (extremely large fires involving materials such as oil and chemicals), the MOD can consider taking measurements of VOCs, PAHs, aldehydes and ketones. Especially at fires where the smoke plume remains relatively low (moving at ground level), the MOD can also conduct these measurements in order to reassure the public.

5.3.4 Further research

One of the recommendations in the report from the 2007 study had to do with the types of substances that, up until that point, not been measured by the MOD, but which could potentially occur in the smoke from fires. These substances include isocyanates, amines, nitriles, nitro-PAH, sulphurous PAH, flame retardants containing bromine, brominated dioxins and hydrogen bromide. Because no such follow-up research has been conducted, this recommendation remains in effect.

The MOD could also explore the extent to which the energy transition and other developments lead to new risks in connection with the formation and dispersion of potentially hazardous substances during fires. RIVM has already begun efforts in this area, in the form of research into the spread and deposition of substances and shards released during fires involving solar panels.

Acknowledgements

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And of course we also wish to thank all MOD employees who, through their joint efforts, ensure that the MOD is standing by 24/7, 365 days per year, to provide expertise in various types of incidents.

List of terms and abbreviations

AEGL	Acute Exposure Guideline Levels
AGS	Fire department advisor hazmat
AGW	Alarm boundary value: the concentration in air above which irreparable or other serious health effects may occur, or at which exposure to the substance may impair people's ability to move to a safe location. Comparable with AEGL-2
AMDIS	Automated Mass Spectral Deconvolution and Identification System
CET-md	Crisis Expert Team for the environment & drinking water
CVE	Coordinator of an investigative unit
DCC I&W	Departmental Crisis Management Coordination Centre of the Ministry of Infrastructure and Water Management
DNPH	2,4-dinitrophenylhydrazine
d.m.	dry matter
EFSA	European Food Safety Authority
EPA	Environmental Protection Agency (United States)
EU	European Union
GAGS	Public Health Advisor for Hazardous Substances (GGD-GHOR)
GC-MS	Gas chromatograph–mass spectrometer
GGD	Municipal Public Health Services
GHOR	Medical Assistance in Accidents and Disasters Organisation
HPLC	High-performance (or high-pressure) liquid chromatography
ICP-MS	Inductively coupled plasma mass spectrometry
KMar	Royal Netherlands Marechaussee
LBW	Life-threatening value: the concentration in air above which fatal or life-threatening health effects may occur. Comparable with AEGL-3
LCMS	National crisis management system
LOD	Limit of detection
m	Metre
MOD	Environmental Incident Service
MRL	Minimal risk level
MVS	Medium Volume Sampler (device for collecting TSP samples with a filter
NVIC	National Poisons Information Centre
PAHs	Polycyclic Aromatic Hydrocarbons
PID	Photo ionisation detector
PMD	Plastic packaging, metal packaging and drink cartons
PVC	Polyvinyl chloride
PVO	Protocol on suspicious objects
SVHC	substances of very high concern
TEQ	Toxic equivalents: a standard to measure the toxicity of individual dioxin compounds as fractions of the toxicity of the most toxic dioxin (2,3,7,8-Tetrachlorodibenzo-p-dioxin, or TCDD)
TD tube	Thermal desorption tube
TWI	Tolerable weekly intake

UV	Ultraviolet
VOC	Volatile organic compounds
VRW	Instruction guidance value: the concentration in air that is extremely likely to pose a nuisance to the exposed population, or above which mild health effects are possible. Comparable with AEGL-1
WFSR	Wageningen Food Safety Research
XRF	X-ray fluorescence spectrometry

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Appendix 1 The MOD, measurement strategy, sampling and analysis techniques

The MOD is an RIVM response organisation which can offer 24/7 specialist support to emergency services in the region, as well as the relevant competent authority (and its advisors) in the event of an environmental incident. Examples of such incidents are large fires, loss of containment of harmful chemicals, odour nuisance or attacks or threats involving biological or chemical agents. The MOD collects information in order to assess the impacts of an incident on health and the environment. To that end, the MOD may conduct field measurements and take samples, carry out laboratory analyses and/or perform model calculations and collect and share information on substances which have been released. The MOD consists of around 90 RIVM experts and, when deployed, is led by the MOD coordinator, who is also the point of contact for the requesting party.

The MOD's presence is generally requested by the Fire department advisor hazmat (AGS) and or the Public Health Advisor Hazmat (GAGS) of the GHOR and/or GGD(s). The police or Royal Netherlands Marechaussee may also deploy the MOD as well. This typically occurs when the protocol on suspicious objects (PVO) has been activated. When responding to environmental incidents, the MOD cooperates with other bodies and laboratories, such as Wageningen Food Safety Research (WFSR) and the National Poisons Information Centre (NVIC). The MOD is part of the Crisis Expert Team for the environment and drinking water (CET-md) and is the central point of contact for the National Laboratory Network in connection with terrorist attacks (LLN-ta). The Departmental Crisis Management Coordination Centre of the Ministry of Infrastructure and Water Management (DCC I&W) is the commissioned the MOD for the maintenance and further development.

Emergency services, advisors of the relevant competent authority and the MOD have a shared interest in obtaining the most accurate and up-to-date insight into the types of substances that may be released by different kinds of fires in order to organise an effective response.

Measurement strategy of the MOD

The measurement strategy of the MOD is aimed at assessing potential health risk. Exposure may take place through inhalation of substances, via contact between substances and skin or by ingesting contaminated crops. Dust particles may also be ingested via hand-to-mouth contact. The MOD determines what type of samples to take based on the incident in question. This case-by-case consideration depends in part on what is burning, which substances could potentially be released and the 'vulnerable' receptors located downwind, and primarily concerns the potential exposure and absorption routes. If vegetable gardens and farmland are present, the MOD will take samples of the crops and/or grass. The MOD also takes dustfall wipe samples when the chance of hand-to-mouth contact is present, for example when there are children's playgrounds in the effect area. The MOD takes samples of air and TSP only when an active smoke plume is still present and there is a possibility that people may inhale the substances, or for the purpose of identifying substances in the smoke plume in order to conduct more targeted analyses of dustfall wipe and grass samples. Which analyses the MOD conducts depends on the circumstances as well: what is burning, which hazardous substances could potentially be released, what is the effect area and which sampling points are appropriate, given the situation at hand and the questions regarding health risks?

Sampling methods used by the MOD

In order to understand the measurement data and its context, we must have insight into the techniques used by the MOD to collect and analyse samples. The MOD uses multiple and diverse techniques to obtain samples, which it then further studies using a range of analysis techniques. The types of samples can be roughly divided into the categories:

- Air
- Total suspended particulate (TSP)
- Deposition (dustfall wipe, grass and crop samples)

Air

The MOD uses several different sampling techniques to collect air samples which can then be subjected to various types of analyses. Canisters, Tedlar bags and thermal desorption tubes (TD tubes) are used mainly to collect samples for VOC testing. These are analysed using a GC-MS.

Canisters

The MOD uses steel canisters (see photo 1) to collect samples consisting of a certain quantity of air. The size of the canister’s sphere and the pressure of the vacuum inside determine the volume of the sample the MOD is able to take. This sampling can be conducted immediately or weighted according to a time factor (usually 1 or 2 hours).

Photo 1 Canister for collecting air samples.

Tedlar bags
Air samples can also be taken using special plastic bags known as Tedlar bags. Tedlar bags are made of a polyvinyl fluoride (PVF) film. These bags are filled using a Vac-U-tube or a PID meter. The drawback to using Tedlar bags instead of steel canisters is that substances such as N,N-dimethylacetamide, phenol and acetonitrile can evaporate from the material used to make the bags and contaminate the air sample [35]. The air sample also has a limited shelf life. Because substances will break down, absorb or diffuse through the wall as time passes, speedy analysis is vital. Generally speaking, analyses carried out within 10 hours of sample collection are the most reliable in terms of sample accuracy [36].

Photo 2 Tedlar bag

For reasons including the drawbacks of using Tedlar bags, in 2019, RIVM loaned smaller canisters (with a volume of 1 litre and a one-hour restrictor for sample collection) to all the safety regions for their use. Each received a container with 3 canisters, filters and restrictors so that the safety regions can take reliable samples at an earlier stage of an incident, before the MOD arrives on the scene. The MOD can then analyse these samples.

Thermal desorption (TD) tubes
TD tubes (photo 3) works by means of an air pump that ‘sucks up’ various VOCs and traps them in the packaging material. Later, when the TD tube is heated, the substances in the packaging material are released. The MOD can then analyse these using the GC-MS. The ability to vary the quantity of air sucked through the tube is advantageous because it enables the MOD to identify and quantify low concentrations as well. This is particularly suitable for measurements in the indoor environment and less suitable for use at fire incidents.

Photo 3 GilAir plus air pump, equipped with a thermal desorption tube

DNPH cartridge

When the MOD is deployed, it takes samples to test for aldehydes and ketones using a 2,4-dinitrophenylhydrazine (DNPH) cartridge (see photo 4), through which a certain quantity of air is forced using the aforementioned air pump. Carbonyl groups react with DNPH to form a hydrozone compound and are then immobilised in the cartridge. The DPNH derivatives are eluted using an organic solvent and then analysed by means of high-performance (or high-pressure) liquid chromatography with an ultraviolet detector (HPLC-UV).

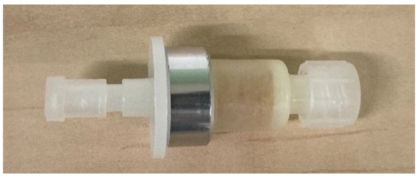

Photo 4 DNPH cartridge

Total suspended particulate (TSP) sample

The MOD collects TSP samples using a device called a Medium Volume Sampler (MVS, see photo 5). This air pump is run for 2 hours, sucking approximately 10 m^3 of air through a TSP filter head with a quartz filter (see photo 6). The MOD can then test the loaded quartz filter for elements such as chlorine, bromine, metals, heavy metals, PAHs (see also Appendix 3) and dioxins.

Photo 5 Medium Volume Sampler (MVS)

Photo 6 TSP filter head with quartz filter

Deposition
Deposition is made up of combustion particles that have settled or been emitted. These dust particles consist of various molecules, soot particles and debris. They usually contain hazardous substances such as metals, heavy metals, PAHs and dioxins. When taking samples of deposition, the MOD typically distinguishes between deposition of dustfall wipe samples on stationary objects and deposition on vegetation (grass and/or crops).

Deposited dust (dustfall) wipe samples
Dustfall wipe samples sampling is preferably conducted on stationary objects in the area downwind of the fire incident. Using a cotton wool pad moistened with demi water, the MOD wipes a predetermined surface

area (30 x 30 cm) of a non-porous and unpainted object (such as a utility shed). The MOD can test the cotton wool for the presence of metals (including heavy metals), PAHs and dioxins.

Photo 7 Cotton wool that has been used to collect a sample

Vegetation (grass and/or crop samples)
The vast majority of vegetation samples are grass samples that the MOD collects in accordance with NEN 5624:2009 [37]. This means the MOD collects (cuts) 200–300 g of grass from inside a surface area of 0.25 m^2 in an area downwind from the fire incident. The MOD can test grass samples for the presence of metals (including heavy metals), PAHs and dioxins. The MOD tests most grass samples for dioxins in order to assess whether there is a potential risk of dioxins entering the food chain via livestock. The MOD can also collect and analyse other crops for the presence of metals (including heavy metals), PAHs and dioxins in order to assess the health risk of possible consumption.

Photo 8 Grass sample

Analytical techniques used by the MOD

The MOD makes use of various analytical techniques, such as GC-MS, HPLC-UV, XRF and ICP-MS.

GC-MS
The GC-MS is an analytical device that combines gas chromatography with mass spectrometry in order to identify and quantify various substances. Samples are injected into the system, after which they are separated into components based on the chemical and physical qualities

of the molecules in the sample and the interaction with the column in the GC. Different molecules will emerge from the column at different intervals, known as the retention time. The molecules are then broken down into ionised fragments in the MS and identified based on their mass-to-charge ratio. The MOD uses the GC-MS to identify and quantify VOCs and PAHs.

The MOD’s standard analysis tests for 63 different VOCs (see the list in Appendix 2). This list is based on the US EPA TO-15 method for identifying VOCs that have been collected in canisters and analysed with GC-MS[10]. The current list of 63 VOCs is based on the availability of specific calibration gases for the GC-MS analysis. This is why certain substances have or have not been analysed over the years. In addition to the TO-15 method, the MOD can also use GC-MS to identify and quantify specific substances via the AMDIS method [11]. However, this method has a larger degree of quantitative measurement uncertainty, as it relies on derived calculations rather than direct calibration.

Photo 9 GC-MS system

A high-resolution mass spectrometer (HRMS) is commonly used to identify and quantify dioxins. This detector offers a more effective way to distinguish between similar substances. In most cases, GC is used as a separation method.

HPLC-UV
HPLC-UV is a method of liquid chromatography analysis that makes use of the different affinities of substances with both the mobile and stationary phase (column). Like in the GC method, substances with different retention times will exit the system at different intervals, after which they are detected and quantified using UV spectrometry. Identification generally takes place based on the retention time and the specific UV spectrum of the substance being measured. The MOD applies HPLC-UV to analyse aldehydes and ketones in air samples collected using a DNPH cartridge.

Photo 10 HPLC system

XRF
X-ray fluorescence spectrometry (XRF) is an analysis technique used to identify the chemical elements present in a sample. This technique relies on X-ray fluorescence and involves exposing the sample to X-ray radiation. The sample being measured then emits X-ray radiation with a longer wavelength that is (in most cases) unique to a specific element. At fires, the MOD applies this technique primarily to measure chlorine in TSP in order to gain insight into the potential formation of dioxins (see sub-section 4.4). The MOD also deploys XRF to screen for metals (including heavy metals) that may have been released, before using an ICP-MS technique to quantify those metals.

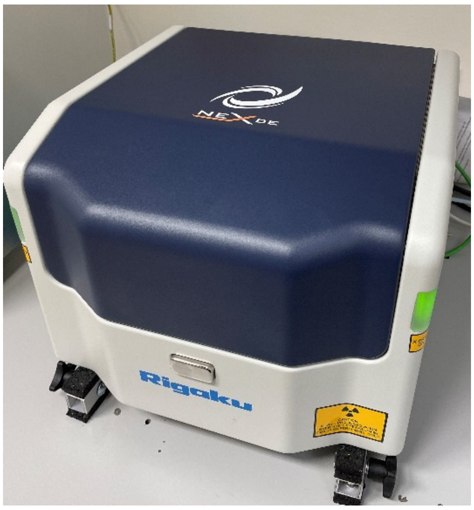

Photo 11 XRF

ICP-MS
Inductively coupled plasma mass spectrometry (ICP-MS) is an analytical technique that makes it possible to identify and quantify elements with great precision. This method involves using argon plasma to ionise the sample, which is then tested for elements using a mass spectrometer.

The MOD uses ICP-MS primarily to quantify metals (including heavy metals) in TSP and in deposition samples.

Photo 12 ICP-MS system

Appendix 2 List of VOCs included in the standard analysis in accordance with TO-15

Substance name	CAS no.
ethylbenzene	100-41-4
styrene	100-42-5
benzyl chloride	100-44-7
cis-1,3-dichloropropene	10061-01-5
trans-1,3-dichloropropene	10061-02-6
p,m-xylene	106-42-3
1,4-dichlorobenzene	106-46-7
1,2-dibromoethane	106-93-4
1,3-butadiene	106-99-0
1,2-dichloroethane	107-06-2
vinyl acetate	108-05-4
methyl isobutyl ketone (MIBK)	108-10-1
1,3,5-trimethylbenzene	108-67-8
toluene	108-88-3
chlorobenzene	108-90-7
tetrahydrofuran	109-99-9
n-hexane	110-54-3
cyclohexane	110-82-7
propene (propylene)	115-07-1
1,2,4-trichlorobenzene	120-82-1
1,4-dioxane	123-91-1
dibromochloromethane	124-48-1
tetrachloroethene	127-18-4
ethyl acetate	141-78-6
n-heptane	142-82-5
cis-1,2-dichloroethene	156-59-2
trans-1,2-dichloroethene	156-60-5
methyl tert-butyl ether	1634-04-4
1,3-dichlorobenzene	541-73-1
tetrachloromethane	56-23-5
2-hexanone	591-78-6
4-ethyltoluene	622-96-8
ethanol	64-17-5
2-propanol	67-63-0
acetone	67-64-1
trichloromethane	67-66-3

Substance name	CAS no.
benzene	71-43-2
1,1,1-trichloroethane	71-55-6
bromomethane	74-83-9
chloromethane	74-87-3
chloroethane	75-00-3
vinyl chloride	75-01-4
dichloromethane	75-09-2
carbon disulfide	75-15-0
tribromomethane	75-25-2
bromodichloromethane	75-27-4
1,1-dichloroethane	75-34-3
1,1-dichloroethene	75-35-4
trichlorofluoromethane	75-69-4
dichlorodifluoromethane (freon 12)	75-71-8
1,1,2-trichloro-1,2,2-trifluoroethane	76-13-1
1,2-dichloro-1,1,2,2-tetrafluoroethane (freon 114)	76-14-2
1,2-dichloropropane	78-87-5
2-butanone	78-93-3
1,1,2-trichloroethane	79-00-5
trichloroethene	79-01-6
1,1,2,2-tetrachloroethane	79-34-5
methyl methacrylate	80-62-6
1,1,2,3,4,4-hexachloro-1,3-butadiene	87-68-3
naphthalene	91-20-3
o-xylene	95-47-6
1,2-dichlorobenzene	95-50-1
1,2,4-trimethylbenzene	95-63-6

Appendix 3 Overview of various PAH compounds and groups

PAH compounds	PAH group
naphthalene	EPA
acenaphthylene	EPA
acenaphthene	EPA
fluorene	EPA
phenanthrene	EPA
anthracene	EPA
fluoranthene	EPA
pyrene	EPA
benzo[c]fluorene	EU
benzo[a]anthracene	EPA, EU, EFSA
cyclopenta[38]pyrene	EU
chrysene	EPA, EU, EFSA
5-methylchrysene	EU
benzo[b]fluoranthene	EPA, EU, EFSA
benzo[k]fluoranthene	EPA, EU, EFSA
benzo[j]fluoranthene	EU
benzo[a]pyrene	EPA, EU, EFSA
indeno[1,2,3-cd]pyrene	EPA, EU, EFSA
dibenzo[a,h]anthracene	EPA, EU, EFSA
benzo[g,h,i]perylene	EPA, EU, EFSA
dibenzo[a,l]pyrene	EU
dibenzo[a,e]pyrene	EU
dibenzo[a,i]pyrene	EU
dibenzo[a,h]pyrene	EU

For the purposes of drafting environmental policy and assessing the health risks, different groups of PAHs have been defined, for which the sum of the respective quantities must be determined. This sum is then compared to the limits and threshold values established for the environment or human health. The EPA PAH is a group of 16 PAHs established by the United States Environmental Protection Agency. The EU PAH is a group of 16 PAHs established by the European Union. Unlike the EPA PAH, this group is made up primarily of non-volatile PAHs. The EFSA PAH8 is a group of 8 PAHs established by the European Food Safety Authority. While other such groups exist, they are not (or no longer) significantly reflected in Dutch policy.

The filter used by the MOD to collect TSP samples cannot fully capture most of the volatile or semi-volatile PAHs, such as naphthalene, acenaphthene and acenaphthylene. As a result, any concentrations of these PAHs measured using this method will yield an underestimation of the actual value. The MOD can also measure the concentration of naphthalene – at the same time as other volatile organic compounds – by collecting samples in canisters, TD tubes and/or carbon tubes. While it is not known whether samples were collected of the naphthalene fraction bound to particulate matter, this does not pose a problem for estimating the concentration of naphthalene at incidents. In principle, the MOD can measure other semi-volatile PAHs using activated charcoal tubes as well, although for these compounds, the fraction bound to particulate matter (dust-bound fraction) will be relatively larger than that of naphthalene. Naphthalene is included in the VOC analysis, while other volatile/semi-volatile PAHs are not.

Appendix 4 Toxicological risk assessment for dioxins

This appendix contains a number of examples of risk calculations based on measured values of dioxins at fires described in this report. These have been broken down into 3 possible means of exposure: inhalation, inadvertent swallowing and ingestion.

Inhalation

For exposure via inhalation, the MOD multiplies the measured concentration of dioxins in the air by the duration of the exposure and the quantity of air that a person will inhale during the exposure duration. This is then divided by the person's body weight.
At the fires in the data set being studied, the highest concentration measured near the origin of a fire was 953 pg TEQ/m^3. Presumably, no residents of the surrounding area were exposed to this concentration during the fire, but for the purposes of a worst-case scenario, we will base our calculations on an exposure of no more than 10 minutes. In that case, the amount inhaled would be 2.6 pg TEQ/kg of body weight. While this is slightly above the EFSA 2 pg TEQ/kg of body weight per week tolerable weekly intake (TWI) [30], it pertains to a one-time increased exposure. The highest concentration measured at medium distance was 35.5 pg TEQ/m^3. At this concentration, an exposure duration of one hour would result in an inhaled quantity of 0.6 pg TEQ/kg of body weight. Even if the duration of the exposure were 3 hours, the total amount taken in would still be less than the TWI. Furthermore, the increased exposure in question is a one-time event.

Inadvertent swallowing after hand-to-mouth contact

In order to calculate exposure via this route, the MOD multiplies the quantity of dioxins in the dustfall wipe samples sample by a factor that takes into account the surface adhesion of the skin, the absorption of dioxins from dustfall wipe samples on the hands and the surface area of a 4.5-year-old child's hands. This is then divided by the average body weight of a 4.5-year-old child. Young children are especially prone to hand-to-mouth contact, on top of which their age makes them more vulnerable than adults.
For a deposition of 860 pg TEQ/m^2 – the highest value measured close to the origin of a fire, which happened to be a fire at a waste processing facility – the calculated exposure is 14.5 pg TEQ/kg of body weight per week. This is well above the TWI of 2 pg TEQ/kg of body weight [30]. For the highest deposition measured in the downwind areas of the fires studied (185 pg TEQ/m^2), the calculated exposure is 3.1 pg TEQ/kg of body weight per week, just above the TWI. The deposition of dioxins is usually at a level where the calculated exposure is less than 1 pg TEQ/kg of body weight per week.

Ingestion of contaminated food

There are two conceivable routes by which a person could be exposed to dioxins by ingesting contaminated food: by eating contaminated crops and by eating contaminated animal products such as milk, dairy products and eggs.

To calculate exposure via ingestion of crops, the MOD takes the concentration of dioxins measured in the grass (or vegetables, if these have been sampled; otherwise, grass is used as a stand-in for vegetables) and multiplies it by the quantity of vegetables a person consumes (assumption: the person will eat 100 g per day and eat vegetables from that area no more than once a week). This is then divided by the person’s body weight (assumption: 70 kg). For a dioxin concentration of 221 ng TEQ/kg (88 per cent d.m.), the highest value measured close to the origin of a fire, the calculated exposure through ingestion of vegetables is 0.3 ng = 300 pg TEQ/kg of body weight per week. This considerably exceeds the TWI of 2 pg TEQ/kg of body weight per week. For a dioxin concentration equal to the highest value measured at medium distance – 8.7 ng TEQ/kg (88 per cent d.m.) – the exposure is approximately 12 pg TEQ/kg of body weight per week, which is 6 times higher than the benchmark. In practice, a concentration greater than 1.4 ng TEQ/kg (88 per cent d.m.) will result in an exceedance of the benchmark of 2 pg TEQ/kg of body weight per week and, in such cases, it is advisable to tell people to avoid eating crops from the effect area of the fire.

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