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Modelling accidental releases of phosphorus in air

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Diplomarbeit an der Universität Trier im Studiengang
Angewandte Umweltwissenschaften

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This investigation has been performed by order and for the account of the Centrum Veiligheid, within the framework of a diploma thesis in cooperation with the University of Trier under the supervision of Paul Uijt de Haag, Ph.D., and Prof. Dr.-Ing. Markus Casper.

Abstract

In the Netherlands, the computer model SAFETI-NL has to be applied by companies handling dangerous chemicals to calculate the individual risk (risk at specific location) and societal risk (risk to overall population) of accidental releases of toxic or flammable substances to the atmosphere. One of these dangerous substances is elemental phosphorus (P_4). Some characteristics of P_4 combustion are not covered by the current model and essential information has to be added in order to improve the modelling of accidental releases of P_4 .

In case of an accidental release from a pipeline or a ruptured railroad tank wagon, P_4 mostly forms a liquid pool (P_4 melts upon combustion). The main feature of the pool is the exothermic reaction with ambient oxygen leading to spontaneous ignition of P_4 . The reactions occurring in the combustion plume are complex and diverse and depend on the amount of oxygen and water available in the atmosphere. First, the combustion reaction forms several oxides (or their charged ions) with phosphorus pentoxide (P_4O_{10}) being the most important oxide. The oxides react to polymers maintaining acid properties, which are subject to hydrolysis in the dispersing plume and form phosphoric acid (H_3PO_4) ultimately.

The purpose of this study is to give recommendations how the modelling of the formation of P_4 combustion products in the atmosphere can be improved, referring to literature findings, accident reports and a sensitivity/uncertainty analysis using the present POLF/UDM (Pool Fire/Unified Dispersion Model) spreadsheets from the model developer DNV.

The reactions within the combustion plume are strongly affected by the amount of water available in air. Growth of particle size with increasing humidity and downwind distance was reported as well as subsequent rainout of H_3PO_4 particles. Although the present UDM fails to account for the impact of the humidity parameter, it indicates that area-specific burn rate, pool diameter, wind speed and Pasquill stability class also have a strong effect on the results.

Finally, future improvements of the UDM should include the polymerisation of combustion oxides, increase of particle size with downwind distance due to coalescence as well as the growing effect of humidity on smoke formation. A general approach is suggested in this report.

Keywords:

Accidental releases, risk modelling, white phosphorus, combustion products, area-specific burn rate, atmospheric dispersion modelling

Rapport in het kort

In Nederland moeten bedrijven die werken met gevaarlijke stoffen de veiligheidsrisico's voor de omgeving berekenen met behulp van het rekenprogramma Safeti-NL. Het gaat dan om het bepalen van het plaatsgebonden risico en het groepsrisico. Deze risicomaten geven de ruimtelijke consequenties weer van het werken met gevaarlijke stoffen. Eén van deze gevaarlijke stoffen is elementair fosfor (P_4), dat veel gebruikt wordt in de chemische industrie. In Safeti-NL ontbreken echter essentiële gegevens die voor een goede modellering van de verspreiding van P_4 bij ongevallen nodig zijn. Zo moet bijvoorbeeld het rekenpakket nog worden verbeterd met de specifieke verbrandingskenmerken van P_4 .

Bij het accidenteel vrijkomen van vloeibaar P_4 door het falen van een transportleiding of een spoorwag, wordt meestal een vloeistof plas gevormd, die spontaan aan de lucht kan ontbranden. Dit is een belangrijke eigenschap van P_4 . De verbrandingsreacties zijn complex en afhankelijk van de concentratie zuurstof en water in de atmosfeer ontstaan er verschillende verbrandingsproducten. Primair worden bij de verbranding van P_4 , fosforoxiden gevormd, waarvan fosforpentoxide (P_4O_{10}) de belangrijkste is. De oxiden kunnen polymere verbindingen vormen met zuurvormende eigenschappen. Door hydrolyse in de dispergerende pluim vormt zich uiteindelijk fosforzuur (H_3PO_4) en andere fosforige zuren.

Het doel van deze studie is om aanbevelingen te geven op welke wijze het modelleren van de verspreiding van P_4 verbrandingsproducten in de atmosfeer kan worden verbeterd, met verwijzing naar literatuur bevindingen, rapporten over ongevallen en een gevoeligheid / onzekerheidsanalyse met behulp van de huidige POLF / UDM (Poolfire / Unified Dispersion Model) spreadsheets.

De chemische reacties in de verbrandingspluim worden sterk beïnvloed door de hoeveelheid water in de lucht. De deeltjesgrootte van de fosforhoudende verbrandingsproducten neemt toe met toenemende vochtigheid met een toenemende depositie van pluim deeltjes tot gevolg.

Bij de verspreidingsberekening met het huidige UDM wordt rekening gehouden met aspecten als verbrandingssnelheid, plasvorming en windsterkte- en richting, maar nog niet met de luchtvochtigheid, terwijl laatstgenoemd aspect ook een grote invloed heeft op het resultaat.

Het is aan te bevelen om het UDM aan te vullen met de factoren die voor de verspreiding van (verbrandingsproducten) van P_4 van belang zijn. Dat zijn: de polymerisatie van verbrandingsoxiden, verhoging van deeltjesgrootte met wind afstand door coalescentie en het toenemende effect van vochtigheid op rookontwikkeling.

Trefwoorden:

Accidentele uitstoot, risicomodellen, witte fosfor, verbrandingsproducten, vuurrate, atmosferische dispersiemodellen

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1 Introduction

Background of white phosphorus

Nowadays white phosphorus (P_4) is produced at large quantities from phosphate rock in industrial settings. The world production of P_4 equalled 1,600 kilotons per year in recent years (Wang et al. 2011) reflecting a sharp increase in the world production by a factor of 2 since the late 1980s.

Accidental releases in the chemical industry can occur. A loss of containment (LOC) exposes the P_4 inventory to ambient oxygen causing the substance to ignite. The harsh combustion reaction forms an acid smoke plume putting third parties at risk due to exposure to irritant gasses and particles.

P_4 ignites spontaneously at 30 °C in moist air (ATSDR 1997, Pande & Pandey 2004). Acute exposure to burning P_4 causes serious direct irritation and severe burns to skin, eyes and mucosal surfaces (Robles 2005). Exposure to the combustion fumes of P_4 causes irritation of the eyes, respiratory tract, and other mucous membranes. Respiratory failure and airway dysfunction is likely in extreme cases (Gad & Babare 2005).

For example, a major accident of a goods train occurred in the area of Lviv (Ukraine) 16 July 2007. The train was heading from Kazakhstan to Poland. Fifteen wagons were filled with a total load of 700 tons P_4 . All fifteen wagons overturned and six tank wagons were punctured. A leakage of P_4 followed and the ambient oxygen supply favoured the self-ignition of the spill to form a huge fire (ARIA 2012). The combustion products formed a plume covering an area of 80-90 km². 184 persons were sent to the hospital due to inhalation of acid fumes. 800 persons were evacuated (Badyugin 2009). Air measurements indicated a phosphorus pentoxide (P_4O_{10}) concentration of 3.5 mg·m⁻³. See Figure 1 to Figure 3 for accident footage.

Given the possibly dangerous outcomes of accidental releases involving P_4 , an analysis of the atmospheric fate of P_4 combustion products is of importance and therefore subject of the present study.



*Figure 1: Accident scene of the Railroad accident in the Ukraine 2007
(see references for source)*



Figure 2: Accident scene of the railroad accident in the Ukraine 2007 (see references for source)



Figure 3: Smoke plume of the accident in the Ukraine 2007 (see references for source)

According to the available information, large P_4 capacity producers are USA, Canada, Kazakhstan and China. Three 210 MW furnaces recently stopped the production of P_4 in the Netherlands due to revenue constraints (Diskowski & Hofmann 2000, Maas & Durka 2012) caused by other P_4 producers on the world market. Tonnage quantities of P_4 are mostly transported via rail in special tank wagons or drums or via road in special road containers operating at slight overpressure. P_4 is usually stored as a liquid in heated vessels. It is constantly kept covered with warm water, and the free space above is ventilated with nitrogen (N_2), so that no air is present in any part of the vessel. (Diskowski & Hofmann 2000).

Quantitative Risk Assessment

Having this impact in mind, the evaluation of the behaviour of P₄ combustion products in the air after a chemical accident is of relevance to determine the risk an accident might entail. This is of particular interest because people, living in the vicinity of industrial facilities or transport routes might be exposed to threats imposed by industrial activities. In order to assess the risk of a possible accident a full quantitative risk assessment (QRA) is generally performed. A QRA consists of the following steps:

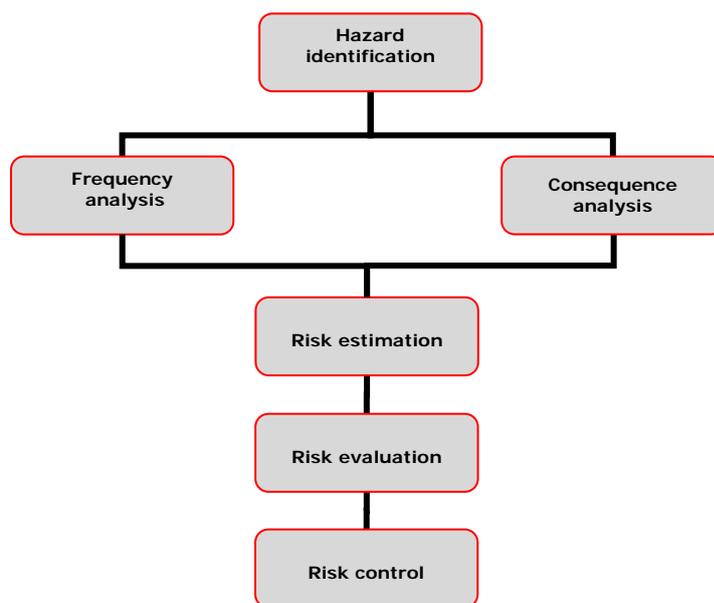


Figure 4: Step by step approach of a QRA

First, hazard identification indicates potentially hazardous events posed by industrial facility. The recognition of the fact that humans can be injured or killed as a result of an accident, constitutes the relevance of the hazard identification step.

Second, consequence analysis involves modelling the behaviour of releases of dangerous substances and the impact of hazardous substances on vulnerable objects using dose-response relationships.

Third, the frequency analysis uses historical data for industrial facilities of interest, to determine which types of accidents should be included in the risk analysis. Using probability approaches, fault- and event-trees are incorporated in this step as well as installation characteristics.

Fourth, risk estimation combines the output of the frequency analysis with the severity of an accidental event to calculate the value of risk for the occurrence of an accident (CSChE 2004).

Fifth, the risk evaluation step deals with public acceptability of the estimated risk posed by an industrial facility. Moreover, it is judged whether policy intervention by national agencies is necessary to deal with the risk. Especially important is the involuntary risk to people living in the vicinity of a hazardous facility. People neighbouring such facilities are often designated as 'third parties' (RIVM 2009).

Finally, the last step of the QRA is defined by controlling the risk that is calculated in the risk estimation step. If the risk is considered to be non-acceptable, intervention measures in the risk control step include (adapted from CSChE 2004):

- Improved safety management of the hazardous facilities, such as process safety management practices, technological measures, risk elimination, and management measures like training, maintenance etc.
- Accident management, emergency preparedness plans and exercises
- Land use restrictions

Although a full risk assessment is of relevance, it is important to fit the scope of this study to the time required to complete it. Consequently, the focus of this study will lie on the consequence analysis step to account for the various chemical and physical processes in the dispersion cloud of P_4 combustion products. Further information on how to perform QRAs for hazardous facilities can be found elsewhere (RIVM 2009).

Current situation

For establishments with hazardous substances, risk assessments for land-use planning are carried out using the requirements of the Reference Manual for Bevi Risk Assessments (RIVM 2009) and the software tool SAFETI-NL. For the default installation of SAFETI-NL, the substance database includes about 60 substances. This default database does not include P_4 (CAS No. 7723-14-0), P_4O_{10} (CAS No. 1314-56-3) and H_3PO_4 (CAS No. 7664-38-2). RIVM has administration rights for the software tool and has access to a larger substance database. This database does include the substances mentioned above. However, essential data for these substances are missing. For example, for each listed substance it is not yet specified if the substance must be modelled as flammable, toxic or both, and required data for flammable and toxic properties are currently left blank. The reactivity with ambient air is not specified either.

Users of SAFETI-NL who desire to carry out a risk analysis must consult the SAFETI-NL Helpdesk, because P_4 , P_4O_{10} and H_3PO_4 are not available in the default substance database. In recent years, questions were posed relating to the QRA (risk assessment) for Thermphos International B.V., Vlissingen, on a few occasions. No calls for assistance have been received for other sites. For Thermphos, tailor-made solutions were proposed by consultants. P_4O_{10} was used as the substance to disperse. A source term for the dispersion of P_4O_{10} was derived using assumptions additional to the Reference Manual. The QRA was assessed by the competent authority (Province of Zeeland) with input from RIVM.

For transportation of hazardous substances, solid substances are by default excluded from the risk analysis. Exceptions can be made following specific requests. There is no indication that transportation of white phosphorous (P_4) by rail, road or water has been included in any recent risk assessment.

Legal framework in the Netherlands

Due to different national requirements, QRAs for hazardous facilities have to fit within the legal framework of a country. As an EU member state, the Netherlands have to implement Directives by the European Commission into national law.

In response to an accident at a chemical plant in Seveso (Italy) in 1976, the European Commission adopted the EU Directive 82/501/EEC, the so-called Seveso Directive, in 1982 (European Commission 2012), which applies to all industrial establishments handling amounts of dangerous substances exceeding the thresholds set in the Directive. The Directive sets regulations to prevent major accidents of chemicals. Since then, the subsequent revision, Council Directive 96/82/EC, or Seveso II Directive, replaced the Seveso Directive in 1996, which was further amended on July 4 2012 to account for technical updates and executive changes in the frame work of the Seveso

III directive (European Commission 2012). This amendment has to be implemented by June 1 2015.

In the Netherlands, the "Besluit risico's zware ongevallen 1999" (BRZO 1999 in short) is the Dutch implementation of the Seveso II Directive into national law (Dutch Government, 1999). The Dutch decree, "Besluit externe veiligheid inrichtingen", Bevi (Dutch Government, 2004), sets the maximum tolerable risk for individuals and societies to be exposed to chemical hazards, including industrial establishments that are covered by the BRZO 1999 law. The consequent Dutch legal provision "Regeling externe veiligheid inrichtingen" (Revi) sets standards on how to implement the rules of the Bevi. The Revi defines the calculation methods to perform QRAs for establishments that handle and/or store hazardous substances (Dutch Government 2004). The actual methodology on how to perform QRAs in the Netherlands is described in the "Reference Manual Bevi Risk Assessments", which can be used by local authorities, companies and consultants (RIVM 2009).

The Dutch government selected the software package SAFETI-NL by software developer Det Norske Veritas (DNV, London, UK) to offer a uniform platform, which can be used by numerous stakeholders to achieve QRA calculations for the purpose of fulfilling the requirements in the Bevi (Witlox & Worthington 2007). The "Reference Manual Bevi Risk Assessments" (RIVM 2009) and the documentation of the model package SAFETI-NL, give all information necessary to perform a QRA calculation within the Dutch legal framework.

Two relevant risk estimates are prescribed and are calculated by SAFETI-NL, the individual risk and the societal risk. The individual risk is the risk that someone at a specific location may die as a result of an accident with hazardous substances in a given period. (DNV MPACT Theory 2007). It is usually calculated for a per year base. As such, risk contours that show the distribution of individual risk for a site handling hazardous substances can be presented on map. The number of fatalities following a possible accident strongly depends on the concentration of the compound in question. The societal risk combines the expected number of fatalities (N) for possible accidents with the corresponding frequencies (f). It is often presented as a F-N curve in which the frequencies (f) are cumulated (F). This graph then shows the frequency that an incident with N or more fatalities may occur.

Model structure of SAFETI-NL

In short, the model SAFETI-NL covers a number of models to calculate the individual risk (risk at specific location) and societal risk (risk to overall population) of accidental releases of flammable and/or toxic chemicals to the atmosphere. The SAFETI-NL software package includes several sub-models which calculate distinct steps (Figure 5). An extensive introduction to SAFETI-NL and its sub-models can be found in Appendix A.

First, upon loss of containment (LOC), the chemical is discharged, which is calculated by the discharge model (DNV DISC Theory Document 2005). Second, if the chemical is flammable and if an ignition source is available, the fire model calculates fire characteristics (e.g. flame geometry) as well as its heat radiation (DNV POLF Theory Document 2005) as input for the subsequent death probability calculations by the Risk Model. Third, the discharge itself will give gases and aerosols which disperse in the atmosphere. This is modelled by the Dispersion Model, which also accounts for different atmospheric conditions (DNV UDM Theory Document 2005). Fourth, if it comes to toxic effects on humans downwind of the accident site, the Toxic Effects Model will calculate the probability of death at a specific location (DNV TXCS Theory 2005). Fifth, if it comes to exposure to the heat radiated by a fire, the heat radiation model will account for the relative position of the observer to the flame and thus for the lethality of the heat radiation (DNV EXPS Theory Document 2005). The Risk Model finally calculates individual and societal risk values and

requires, among other input data, an estimation of the probability of an event as well as weather data indicating directional probabilities for several wind speed and atmospheric stability combinations (DNV MPACT Theory 1997). The output of the risk model constitutes the risk estimates to fulfil the requirements of the Dutch law (Bevi). All these models rely on mathematical equations with certain assumptions to describe the actual physicochemical processes and to calculate relevant estimates. These models have been developed from limited sets of experimental data. The application scope is usually wider than the validation scope of the models. For example, the consequences of a release of P_4 can be calculated in SAFETI-NL, but the outcomes may not be very reliable because no phosphorous data were used for the development of the model.

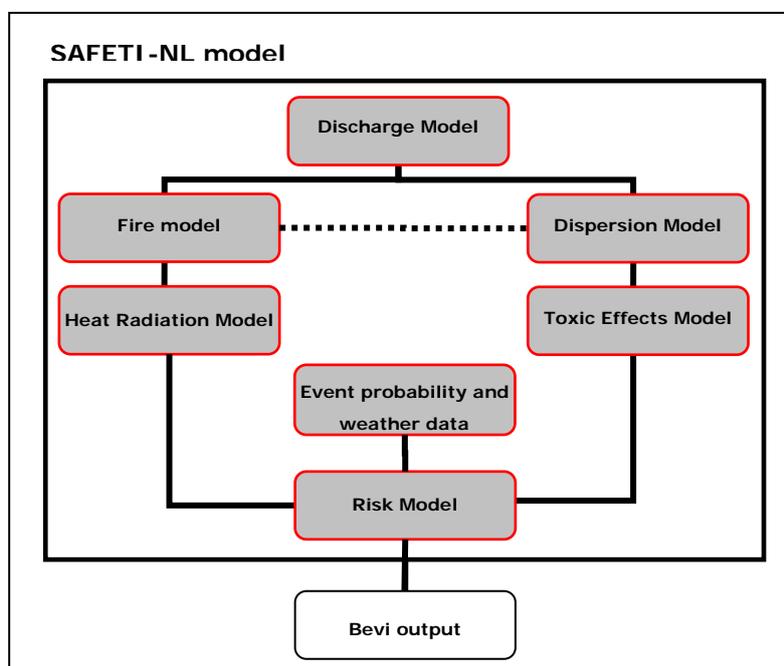


Figure 5: SAFETI-NL model structure (simplified for the present study)

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Witlox & Woodward model

A specific model to calculate consequences and risk resulting from a release of phosphorus (P_4) was developed by DNV (Witlox and Woodward, 1997). This model presumes that the released phosphorous forms a pool. The P_4 in the pool oxidises to P_4O_{10} which is released to the atmosphere. The P_4O_{10} disperses and further reacts with moisture in the air to H_3PO_4 . The source term for the release of P_4O_{10} (mass flux and temperature) depends primarily on the pool size and the 'burn rate' of the phosphorous. The transition of P_4O_{10} to H_3PO_4 depends on the reaction rate and the humidity of the ambient air. The reaction rate is available as a user input. Other properties of the 'pool fire' and gas dispersion are taken from generic DNV models (POLF for pool fire and UDM for dispersion).

The model from Witlox and Woodward was developed in Excel and has not been implemented in PHAST or SAFETI-NL. Therefore, it can only be used to develop scenarios and to test the reliability of outcomes of tailor-made solutions in SAFETI-NL.

Research question

Large accidental releases of P_4 often lead to fires forming a thick cloud of irritant combustion products, which possess toxic properties. Moreover, several chemical and physical processes were reported to occur within the moving cloud of P_4 combustion products (Berkowitz et al. 1981, Spanggard et al. 1983, 1985, Yon et al. 1983, ATSDR 1997).

The use of the prescribed SAFETI-NL model to calculate risk outcomes regarding P_4 accidents has limitations. Most importantly, the area-specific burn rate for P_4 is unknown. This determinant can be regarded as a flux parameter of burned material into the air, which is crucial as this parameter partly determines the concentration in the air. Therefore the area-specific burn rate is also relevant for lethality. Moreover, the variety of combustion products that are formed during P_4 combustion is only partly known and needs to be characterised. The calculation of the combustion mixture dispersion is additionally hampered by the variety of chemical and physical processes occurring in the smoke plume. This might lead to different plume behaviour than predicted by the model.

The goal of the present study hence culminates in the means by which the modelling of the formation of P_4 combustion products and the atmospheric dispersion can be improved. Relevant processes within a combustion cloud will be identified and it will be assessed which processes are already covered by the SAFETI-NL model package and which not. It will be further judged how relevant the processes are that are not covered by the model and how large the uncertainty is.

This report will first present the used methods in chapter 2. This is followed by an investigation of accident reports from several accident databases to point out important accident scenarios in chapter 3. Chapter 4 subsequently includes the results from chapter 3 to align the outcome with the standard scenarios stated in the Dutch regulations. Chapter 5 presents the results of the literature survey on P_4 and its

combustion products. The outcome of chapter 5 is partly included into the modelling step in chapter 6, which will present a sensitivity and uncertainty analysis of important parameters determining plume behaviour. Chapter 7 will present the discussion of the findings, which is followed in Chapter 8 by recommendations how the modelling of accidental releases of P₄ can be improved.

2 Methods

Accident investigation

In order to find relevant accident case reports involving the production, storage, transport and use of P_4 , a search in several chemical accident databases was performed. These databases included:

- ARIA (Analysis, Research and Information on Accidents, F)
- MARS (Major Accident Reporting System, EU)
- ZEMA (Zentrale Melde- und Auswertestelle für Störfälle und Störungen in verfahrenstechnischen Anlagen, GER)
- FACTS (Failure and Accidents Technical Information System, NL)
- Disasters Database of the United Nations Environmental Program, UNEP (United Nations, UN)
- Accident reports database of the Pipeline and Hazardous Materials Safety Administration (PHMSA, USA).

Literature review

In order to reveal the state of research in the field of P_4 accidents, P_4 -related modelling and, the physicochemical processes in the plume of P_4 combustion, a full search was performed in the MEDLINE and SCOPUS databases using Boolean logic.

A search strategy for both databases was designed in cooperation with the RIVM library and can be found in Appendix B. The output of this search was 160 publications of which 24 publications were chosen by individual judgment for further reading.

A subsequent simple Google search using Boolean search input revealed additional publications, which were incorporated in this study.

Site visit

In addition, a site visit at P_4 manufacturer Thermphos International B.V. Vlissingen in collaboration with the company's Health, Safety and Environment (HSE) experts was undertaken in order to improve the understanding of the thermal production process of P_4 and the downstream onsite transport, storage and filling operations. For this purpose, a questionnaire was prepared in order to characterise possible influencing factors of P_4 ignition, typical process conditions, production capacities of phosphorus compounds, loss of containment scenarios, typical amounts of possible LOC releases of P_4 onsite and, questions regarding the behaviour of a pool of released P_4 .

Expert interviews and personal correspondence

To improve the understanding of the atmospheric fate of P_4 and its combustion products as well as the intrinsic behaviour of P_4 , several expert interviews were undertaken. Namely these interviews were conducted with

- Chemists of the RIVM 'Laboratory for Ecological Risk Assessment' (LER) unit, Dik van de Meent and Dick de Zwart and
- Tomasz Durka, chemist, and Franklin Maas, HSE coordinator of P_4 manufacturer Thermphos International B.V. Vlissingen

Moreover, a workshop with DNV senior researcher Henk Witlox was undertaken to give an insight into the SAFETI-NL-associated POLF (Pool Fire Model) and UDM (Unified Dispersion Model) spreadsheets.

Sensitivity and uncertainty analysis

To determine the relevant parameters of P_4 smoke dispersion and the associated uncertainty, an analysis was done with the POLF and UDM spreadsheets, which use the same underlying assumptions and equations as SAFETI-NL but allow parameter variation by the user (Witlox & Worthington 2007).

3 Chemical accidents with P₄

The following chapter emphasises the investigation of the accident report databases to present major P₄ accident scenarios.

The French ARIA database operated by BARPI (Bureau for Analysis of Industrial Risks and Pollutions) lists accidental events which represent a threat for human health, public safety, agricultural activities or the environment. These events are mainly caused by industrial or agricultural facilities that handle hazardous substances. The database also includes transportation accidents with hazardous materials as well as other events in this context. The list covers accidents in France and abroad since 1992. Taking together all events, the database lists over 37,000 accidents, of which about 30,000 took place in France. Foreign accidents are listed mainly due to the severeness of their consequences or their valuable information on accident aetiologies and courses.

The European MARS database is held by the MAHB (EU Major Accident Hazards Bureau) and contains 759 major accidents that fit the criteria as defined by the EU Directive 96/82/EC (Seveso II directive). Based on the requirements of the Seveso II directive, MARS is dedicated to collect data on only major industrial accidents involving dangerous substances from the Member States of the European Union since 1996. The database records accidents and near misses. The sectors covered by MARS are chemical processing, aviation and nuclear industry activities.

The inclusion criteria are:

The German ZEMA database was established 1993. The legal base is the Störfall-Verordnung (12. BImSchV), which determines that reportable events are recorded, analysed and published in annual reports. Reportable events are classified either as accidents or disturbances of normal operations. The purpose of the systematic collection and analysis of the recorded events is to provide findings that serve as an important basis for further improvement of the technology currently available. The ZEMA database covers ca. 600 accidents.

The Dutch FACTS accident database contains information on more than 24,500 industrial accidents involving hazardous materials. The data cover worldwide information from the past 90 years. The main objective of the FACTS chemical accident database is to provide knowledge on accidents or accidents. Besides major large-scale accidents also near-misses are included in the database.

The Disasters Database of the United Nations Environmental Program (UNEP) covers data from within the years 1970-1997. Extensive contribution to this database was carried out by numerous European bodies such as MHIDAS (Major Hazard Accident Data Service, UK), TNO (Netherlands Organisation for Applied Scientific Research, NL), SEI (Stockholm Environmental Institute, SWE), UBA (Umweltbundesamt, GER) and BARPI (Bureau for Analysis of Industrial risks and Pollution, F). The inclusion criteria to this database are:

- 25 people or more death; or
- 125 people or more injured;
- 10,000 or more people evacuated; or
- 10,000 people or more deprived of water

Oil spills at sea from ships, mining accidents, voluntary destruction of ships or aeroplanes and damage caused by defective products are not included in the database. The Accident reports database of the Pipeline and Hazardous Materials Safety Administration (PHMSA) covers data from 1970 to present. It offers exclusively information about transportation accidents involving hazardous materials upon loading,

transport and unloading procedures. Particularly, the database includes railway, air, highway and water transport.

The inclusion criteria are:

- 1 or more person killed or
- 1 or more person injured or
- fire, violent rupture, explosion or dangerous evolution of heat or
- 450 l of marine pollutant spilled or
- 1,000 gal (ca. 3,785 l) or greater cargo tank ruptured or
- loss of 25,000 USD (ca. 19,000 EUR) or more or 10% of prior total monetary value

Accidents from pipeline transport or storage operations are not incorporated in the PHMSA accident database.

The overall goal of the search in the accident databases was to collect as much as information as possible. Therefore, very broad Boolean logic search terms were chosen as described in Appendix C.

By far, the FACTS database revealed the most relevant results in terms of quantity of accident reports and profoundness of information. These results were combined with results from the PHMSA accident database in order to collect as much information as possible regarding accidents involving phosphorus compounds. The results from ARIA, MARS and ZEMA databases were already covered in the FACTS output and involve spillages of P_4 , phosphorus pentoxide, phosphorus wastes and other, not specified (N.O.S.) phosphorous compounds.

In total, 166 accidents or near misses were found between 1967 and 2012. Of the 166 accidents, 143 involve P_4 , accounting for 86% of all accidents in question. In the period 1967-2012 there were about 3 accidents worldwide per year involving P_4 . However, accidents maintain large differences in scale of the spilled substances (near miss vs. railroad tank car rupture).

Accidents consist of:

- 130 Rail transport accidents
- 9 Processing accidents
- 6 Transshipment accidents
- 6 Storage accidents
- 6 Use/Application accidents
- 4 Highway accidents
- 1 School accident
- 1 Waste treatment accident
- 1 Water accident
- 1 Cleaning Accident
- 1 Air accident

Figure 6 indicates the distribution of activities leading to accidents involving phosphorous compounds.

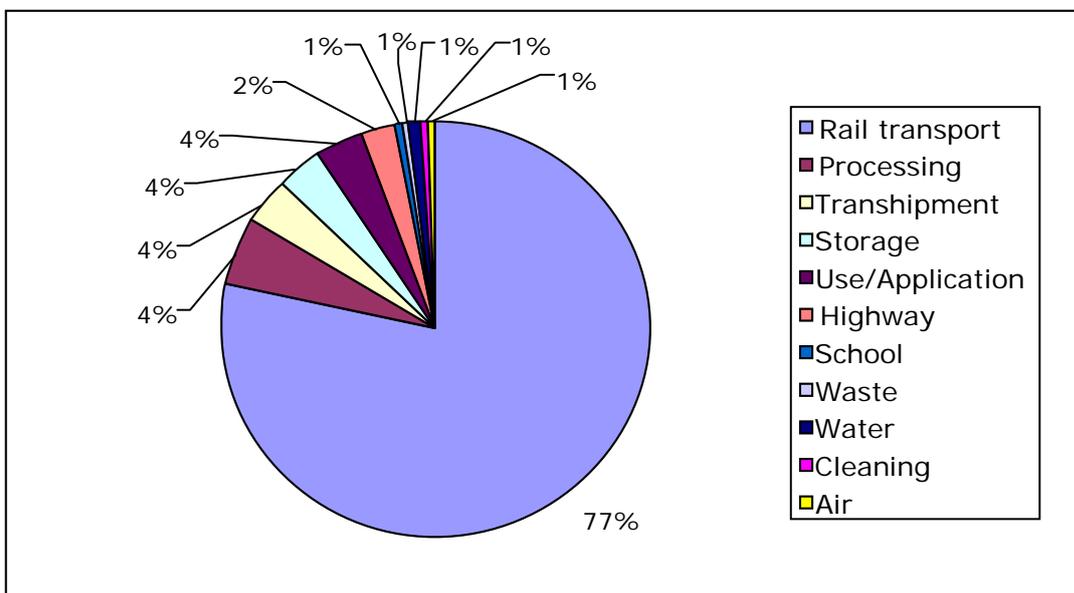


Figure 6: Distribution of activities leading to accidents involving phosphorous compounds

77% of all accidents occur upon rail transport activities. Often, derailment of tank wagons occurs due to weakened equipment components of the tracks/tank wagons. Processing accidents (4% in total) link to industrial activities that usually include pressurised transport of liquefied P_4 in closed systems. Here, accidents are caused by weakened equipment (e.g., pumps, valves). Ambient conditions play an additional role here, because temperature gradients can lead to material fatigue of industrial installations. 4% of all accidents take place during transshipment activities. Transshipment refers to loading and unloading operations. Here, management failures leading to faulty working plans indirectly cause human exposure to pressurised P_4 . Storage accidents (4%) are nearly exclusively caused by improper closure of transport drums. Thus, the protective water layer above the contained P_4 will evaporate inducing the oxidation reaction upon contact to air.

Use/Application (4%) refers to usage of P_4 products that are often handled by workers not aware of the dangerous properties of P_4 . Handling failures and improper maintenance procedures often cause individual exposure to P_4 . Due to the limited relevance of small-scale accidents such as highway accidents, school accidents, waste treatment accidents, cleaning procedures and aerial accidents, these scenarios are left out of this analysis. A table of all accidents can be found in Appendix C.

Three characteristic scenarios are identified for accidents involving P_4 :

- Human error upon maintaining and repairing procedures causes small-scale exposure to P_4 leading to chemical burns of workers on the site of the company
- Improper management and equipment failures lead to mid-scale spray releases and leakages of pressurised or atmospheric P_4 upon loading operations and subsequently to fires forming irritant clouds with subsequent exposure of workers on the site of the company
- Poor track conditions, human error or fatigue of train material induce derailment of freight trains with huge spillages out of drums or tank wagons. Subsequent pool fires form irritant clouds of P_4O_{10} and H_3PO_4 exposing third parties along with environmental contamination by P_4 or phosphorous compounds

Overall, the survey of the accident reports revealed that accidental spillages of P_4 would mostly involve continuous releases out of train wagon tanks, storage drums or transshipment devices. Such events will form a pool of P_4 which is subject to spontaneous ignition. The combustion products would form a thick cloud acting as an irritant to both workers handling P_4 and third parties at the scene. It is observed that accidents involving P_4 are among those likely to provoke large scale evacuations and hospitalisation of third parties due to airway irritation and disruption in extreme cases. Upon inhalation or mucosal tissue contact, in numerous cases hospitalisation was necessary due to intoxication with the acid mist. Fatalities due to exposure to the irritant combustion mist were not reported. Only in cases where direct skin contact to burning P_4 was involved, fatalities were observed as a result of severe chemical burns (accident no. 14, 39).

The Dutch VRW (Voorlichtingswaarde) threshold of $1 \text{ mg}\cdot\text{m}^{-3}$ for P_4O_{10} was reportedly exceeded (2 and $3.5 \text{ mg}\cdot\text{m}^{-3}$) in two cases (Accident no. 155, 162). These cases are considered particularly important for third party risk.

For example in 2003, an explosion followed by a phosphorous fire occurred in the transport depot of a plant that was specialised in phosphorus compounds producing much smoke (accident co. 155). The fire occurred during unloading procedures of a wagon carrying P_4 . The operator stopped the pumps, pushed the emergency stop button and triggered the sprinkler system, which did not work. The emergency response plan was started immediately and the fire was extinguished after 11 min, but a white cloud of smoke of 4000 m length, 200 m width and 50 m height, with a concentration of $2 \text{ mg}\cdot\text{m}^{-3}$ P_4O_{10} and higher, was formed in the valley, where a chemical plant was located. The road and train traffic was stopped for 2 hrs. 46 people were examined in a medical centre. At the time of the discharge, the P_4 was heated up to $60 \text{ }^\circ\text{C}$ by vapour injected into the containment. It was then pumped through the top of the tank car by hot water ($p \text{ max} = 3.8 \text{ bar}$). Liquid phosphorus was then extracted with a diving tube connected in a transfer line. 63 kg of P_4 escaped from a joint. The released P_4 ignited upon contact to air, emitting thick smoke. The second case is the accident described in the introduction.

In addition to the cases where the VRW was exceeded, an accidental spray release caused a 5 m high jet fire killing one person during pressurised transshipment of P_4 into a tank wagon. The burn residues contaminated the air within a range of 3 km from the source. The fire department cooled the tank wagon with water and overall the accident lasted ca. 8 hrs (accident no. 39)

Ross and coworkers (1987) reported a rare case of a railroad tank car explosion in 1978 (Accident no. 46). After roughly 7.5 hrs burning, the resulting overpressure and heat ruptured the entire steel-made vessel and scattering the explosion debris away. The analytical investigation of the accident revealed that the flammable P_4 vapour-air mixture in the gas phase led to the very harsh pressure rise within the overturned tank car causing the explosion scattering the debris over a radius of 400m. Moreover, the authors forward evidence that only a small fraction of the total energy released by the explosion reaction was sufficient to rupture the tank car with a volume of ca. 66 m^3 . They calculated that 8 lbs (approx. 3.6 kg) of the P_4 vapour-air mixture would, on rapid combustion with air, produce temperatures in the order of $2500 \text{ }^\circ\text{C}$. Visual analysis of flame pictures indicated incandescence in the flame centre linking to flame temperatures of at least $1500 \text{ }^\circ\text{C}$. Six injured people were reported.

4 Possible scenarios of P₄ accidents

Chapter 3 described major industrial activities and underlying causes of accidents involving P₄.

In this chapter the focus will be on the incorporation of the knowledge acquired from the precedent chapter with the standard scenario types stated in the Dutch Reference Manual Bevi Risk Assessments (RIVM 2009). The Reference Manual Bevi Risk Assessments defines how QRAs have to be carried out (using SAFETI-NL). It defines standard scenarios for several reservoirs, devices and transport units used in the chemical industry.

The analysis of the accident reports involving P₄ reveals that both large continuous outflow and small hole scenarios include releases from atmospheric tanks, drums, loading arms and pipelines upon external impact or due to material fatigue. Moreover in several cases small holes were reported to occur in P₄ containing railroad tank wagons with atmospheric tanks, drums and pipelines often caused by material fatigue or human error.

The study for these reservoirs revealed the following the standard scenarios based on the Reference Manual Bevi Risk Assessments (RIVM 2009) as shown in Table 1. Note that the outcome of the pipeline rupture scenario will not differ substantially from the other standard scenarios. Therefore, the subsequent analysis will incorporate this scenario into the instantaneous release scenario.

Sections 4.1 to 4.3 give a short description of the standard scenarios for different containments stated in the Reference Manual Bevi Risk Assessments. Section 4.1 highlights the instantaneous release scenario followed by chapters 4.2 and 4.3 emphasising a release of the entire contents and a continuous release from a hole. Section 4.4 presents the conclusion.

Table 1: Standard scenarios for reservoirs involved in P₄ accidents according to the Reference Manual Bevi Risk Assessments

Reservoirs according to RIVM (2009)	Standard scenario
Atmospheric tank (with a single wall)	<ul style="list-style-type: none"> • Instantaneous release of entire contents • Release of entire contents in 10 min. in a continuous and constant stream • Continuous release from a hole with an effective diameter of 10 mm
(Railroad) tank wagon with atmospheric tank	<ul style="list-style-type: none"> • Instantaneous release of entire contents • Release of entire contents from the largest connection
Loading arm	<ul style="list-style-type: none"> • Leak in loading/unloading arm or loading/unloading hose with an effective diameter of 10% of the nominal diameter, up to a maximum of 50 mm. • Full bore rupture of the loading arm/hose
Pipeline	<ul style="list-style-type: none"> • Full bore rupture of the pipeline • Leak with an effective diameter of 10% of the nominal diameter, up to a maximum of 50 mm

4.1 Instantaneous releases

According to the Reference Manual Bevi Risk Assessments (RIVM 2009), instantaneous releases of chemicals are essentially defined as scenario which describes the release of the entire contents from a reservoir within seconds and comprises the expansion from the initial conditions to atmospheric (DNV DISC Theory Document 2005). Figure 7 shows the basic principle of an instantaneous release of P_4 .

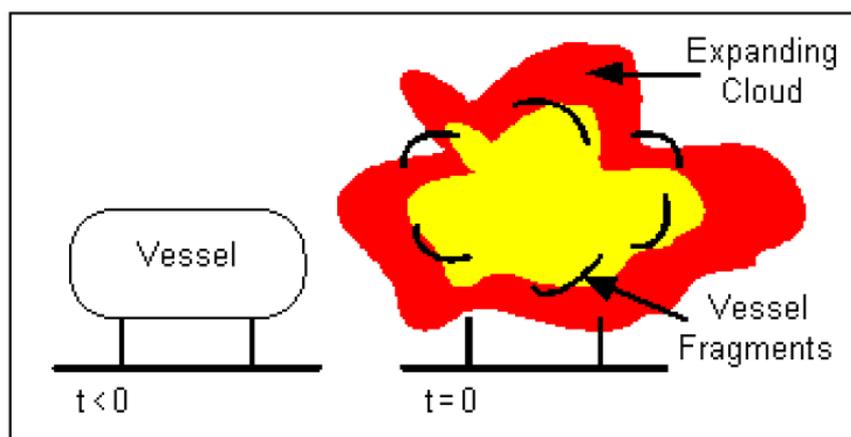


Figure 7: Scheme of an instantaneous release (adapted from DNV 2009)

Due to the relevance of the scenario for the site under consideration, the accident reports and the site visit revealed that the instantaneous release of P_4 from storage tanks is a possible outcome although reported only once after 7.5 hours burning (Ross et al 1987), because punctures often lead to an orifice rather than a full rupture of the entire containment. External events leading to tank or pipeline ruptures, fatigue of wall materials as well as failures of welds and connections are possible causes. Storage tanks are considered closed systems and are placed within tank pits that catch the entire inventory upon a LOC (Maas & Durka 2012). These pits can be filled with water in order to protect spilled P_4 from contact to oxygen. For parking of the transport containers on the premises of Thermphos International B.V., Vlissingen, to let P_4 inventories cool-down prior to transport, an instantaneous release is considered a prescribed scenario (SAVE 2011) according to legal requirements.

In the case of storage tanks where no water and no bund are available, an instantaneous release would form a huge pool of liquid P_4 , which will undergo immediate ignition. If the chemical is stored in solid state, P_4 would liquefy due to immediate ignition of the substance (unpublished observation). Therefore an instantaneous release is a possible scenario in the case of P_4 accidental releases. Given the low pressures in place, this scenario should be modelled as a pool fire.

4.2 Large continuous outflows

In contrast to instantaneous releases, large continuous outflows cover spillages where the entire contents of the containment are released in 10 min in a continuous and constant stream. Particularly, P_4 is released from the conditions in the leak orifice (e.g. storage tank or tank wagon) to atmospheric pressure with a constant release rate Q (DNV ATEX Theory Document 2005). For the largest type of continuous releases, a duration of 10 minutes is assumed in the Dutch QRA guideline. This principle is

reflected in Figure 8, which shows a schematic overview of a continuous release of the inventory (here P_4) and takes the initial vessel conditions as well the exit conditions at equilibrium into account.

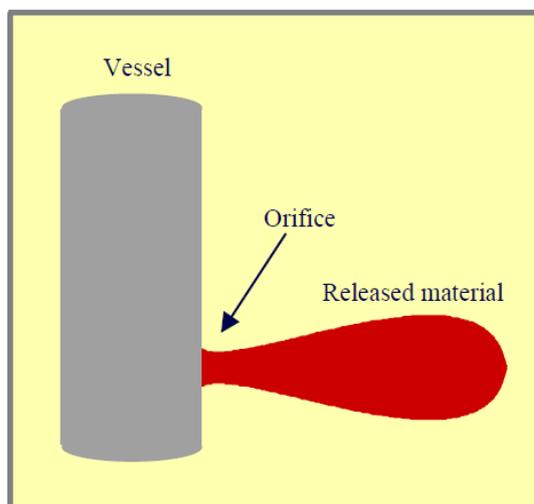


Figure 8: Scheme of a continuous outflow from a vessel (adapted from 2009)

The same storage conditions apply to large continuous releases as in the case of instantaneous releases.

In line with the instantaneous release scenario in chapter 4.1, large continuous outflows are considered relevant for reservoirs such as storage tanks and railroad tank wagons.

The survey of the accident reports revealed that the continuous releases from tank wagons and drums are among the most likely events exposing third parties to irritant clouds composed of P_4O_{10} and H_3PO_4 . The time of such accidents ranges from 1.5 to 9 hours depending on the action of emergency shutdown systems, the performance of emergency response personnel as well as reachability due the isolated location of several accidents.

Again mainly external events such as tank punctures due to goods train derailment and fatigue of train equipment materials are possible causes for large continuous outflows from tank wagons

Large continuous outflows of P_4 are possible accident scenarios and hardly differ from instantaneous releases scenarios with the exception of the time window of the event. In case of a pressurised release, it should be modelled as a jet fire as confirmed by a single accident in recent years (accident no 155). If it comes to a release from a tank at atmospheric pressure, the resulting fire should be modelled as a pool fire. Occurrence is often accompanied by the fact that mostly no bund is available to collect the spilled P_4 given the remote location of most accident.

4.3 Small hole releases

Small hole releases of substances are mostly defined as continuous releases from reservoirs through a hole with an effective diameter of 10 mm. This hole diameter is often arbitrarily chosen to equal 10 mm, which is assumed to represent the average hole diameter for the small accidents (Uijt de Haag 2012). However this value might not represent the real situation if it comes to an accident. Figure 9 emphasizes the basic idea of small hole releases from a vessel.

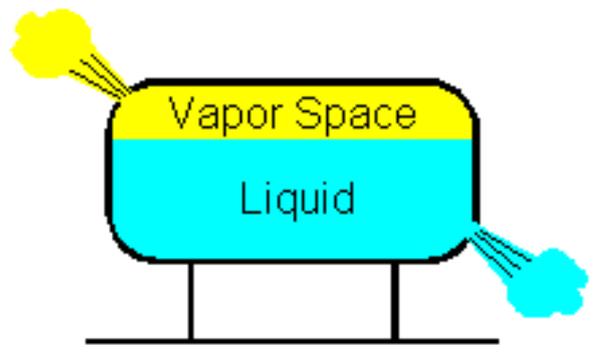


Figure 9: Scheme of a small hole release (adapted from DNV 2009)

The Reference Manual Bevi Risk Assessments (RIVM 2009) conservatively assumes small hole releases from the bottom of the reservoir in any accident. Bottom outflows release the whole inventory due to gravitational emptying in tanks maintaining atmospheric pressure.

For atmospheric tanks small hole releases are a likely scenario. Possible causes are poor sealing of tanks as well as accidents punctures of the containment with consequent small hole releases. Gravitational emptying is the common course until the flow is terminated or the fire extinguished. Often this is accompanied with sudden ignition and exposure of workers and third parties to toxic P_4O_{10} and H_3PO_4 .

Along with large continuous release scenarios, small hole releases are the most likely accident scenarios for large scale P_4 spillages.

Thus, small hole releases spilling the entire contents through a 10 mm hole from an atmospheric tank should be modelled as a pool fire. Again, if the substance is released from a pressurised system (e.g. a loading arm), the subsequent fire should be modelled as a jet fire.

4.4 Conclusion

Due to the elevated frequency of occurrence in the accident reports and the severeness of the outcome, a large continuous liquid or solid P_4 release out of a railroad tank wagon is presumed the most important accident scenario which will almost exclusively form a pool of liquid P_4 . However, the size of the pool largely differs alongside with the volume and the outflow rate of the spilled P_4 inventory. The volume and the outflow rate of spilled material are of particular importance and are determined by the actual accident scenario. In the process of spreading the pool would spontaneously ignite upon contact to ambient oxygen (O_2). However, if solid P_4 is released, oxidation will force P_4 to melt and thus the spreading rate of the pool would be considerably lower. Finally the pool of initially solid P_4 will maintain the same harsh combustion reaction endangering third parties to the toxic combustion products. Thus a pool fire of instantaneously igniting P_4 will be the most likely fire scenario. Therefore the DNV model POLF (Pool fire model) will be used to calculate input data for the subsequent sensitivity and uncertainty analysis using the DNV model UDM (Unified Dispersion Model) to predict the atmospheric concentrations of P_4O_{10} and to derive the associated concentrations of H_3PO_4 in chapter 6.

5 Results of the literature review

As noted before the model SAFETI-NL fails to calculate the atmospheric dispersion of P_4 combustion products properly.

Particularly, the current SAFETI-NL model assumes a substance-dependent area-specific burn rate for P_4 due to lacking experimental data as used in the latest QRA of Thermphos International B.V. Vlissingen (SAVE 2011). Furthermore, it fails to account for the chemical transformation from combusting P_4 to several phosphorus oxides such as P_4O_6 and P_4O_{10} (Yon et al. 1983). This is due to the fact that the model either presumes zero or full combustion reaction to form only a single combustion oxide, namely P_4O_{10} (Witlox 2012). Additionally, the Dispersion Model (Unified Dispersion Model, UDM), implemented in SAFETI-NL, fails to account for all physical and chemical processes within a moving cloud of P_4 combustion products meaning, that it will not model the reaction of P_4O_{10} and other combustion products with atmospheric moist to form H_3PO_4 .

A literature review was undertaken in order to reveal the knowledge available on the properties, toxicity as well as atmospheric dispersion of P_4 and its combustion products. The output of literature search in the MEDLINE and SCOPUS databases was 160 publications. Due to the large quantity of non-relevant literature, only 24 publications were chosen by individual judgement for further reading. For the most part, publications describing accidents and literature giving insight into the environmental fate of phosphorous compounds were proven useful in order to advance the modelling of the atmospheric dispersion of P_4 combustion products. The tables in Appendix D indicate the literature chosen for further reading including literature found using the Google search engine.

Hence section 5.1 first reflects the industrial large scale production of P_4 as well as the properties, acute toxicity and regulatory concentration thresholds for human exposure of the compounds in question. Section 5.2 puts forward information on an area-specific burn rate of P_4 which is followed by section 5.3 where physicochemical processes within a moving plume of P_4 combustion products are described. Section 5.4 puts forward the subsequent conclusions.

5.1 Properties and processes

To further understand P_4 and its combustion compounds a short overview on the industrial production process of P_4 is provided in section 5.1.1. This is followed by section 5.1.2 where the chemistry and acute toxicity of P_4 and associated compounds is explained. As phosphorus-linked fires last for a relatively short time, the focus lies on the acute toxicity of P_4 and associated compounds (P_4O_{10} and H_3PO_4). Section 5.1.3 describes the Dutch intervention values for atmospheric concentrations of P_4O_{10} and H_3PO_4 .

5.1.1 Industrial production of P_4

The information outlined below is combined input from scientific literature and the site visit on the grounds of Thermphos International B.V., Vlissingen, and The Netherlands. The industrial production of P_4 uses exclusively the electrothermal process (also called Wöhler process), which is described below (Diskowski & Hofmann 2000, Berdnikov et al 2010). Although the following information is partly linked to the specific procedures performed at the abovementioned P_4 producer and slight differences may occur globally, the overall P_4 production information can be regarded as representative for the P_4 production process worldwide. P_4 is for the most part

(83 %) an intermediate product for the production of H_3PO_4 of which 50% is used for the manufacture of phosphates for detergents (Diskowski & Hofmann 2000). Other fields of use include the production of H_3PO_4 for food products and pharmaceuticals.

First, sintered phosphate, coke and silica are transported with conveyors to bunkers which feed the electric furnace. The conveyor is equipped with automatic scales to ensure the required proportions of the raw materials.

The raw materials are made to react with silica and coke in electric furnaces at temperatures between 1,400 and 1,800 °C (Maas & Durka 2012) and exerts the following chemical reaction when using fluorapatite ($\text{Ca}_5(\text{PO}_4)_3\text{F}$):



The phosphate, quartzite and coke form a melt, in which the phosphate ion is reduced to gaseous P_4 (Diskowski & Hofmann 2000). Gaseous carbon monoxide, liquid slag and ferrophosphorus (melting of metallic electrodes) are formed as byproducts.

First, the raw materials are ground to a uniform lump form by the phosphorus producer. The grain size is homogeneous in order to ensure steady gas permeability in the furnace. After the grinding the calcium phosphate, coke and silica are mixed and filled into the furnace (see Figure 10).

The furnace consists of 3 parts, namely:

- the furnace with its electrodes, feeding equipment, vents for gas removal and tap points to take off by-products,
- the electrostatic precipitators for removal of gaseous P_4 ,
- and the condensation installation to liquefy the produced phosphorus gas

After melting, the furnace gases, containing most of P_4 , have to pass gas purification chambers to decrease the dust content to 98-99% (Diskowski & Hofmann 2000). The chambers are heated to prevent early condensation of phosphorus. The filtered furnace gas stream is then transported into a condensation installation at a temperature of 250-300 °C (Thermphos International B.V. 2001). The phosphorus gas is washed with water using either the 'hot' or 'cold' method. Both approaches process the phosphorus gas either above or under the boiling point (280.3 °C) of P_4 (Diskowski & Hofmann 2000). Upon exposing the gas to a water spray P_4 condenses as a liquid ('hot' process) or as a solid ('cold' process). The site visit at the Thermphos International B.V. premises (Maas & Durka 2012) revealed that initially condensed P_4 will be collected in vessels at 70-80 °C. After the condensation step, the intermediate product contains a mud consisting of P_4 , water and silicic acid as an impurity. The mud is therefore purified using either centrifugation or filter methods (Diskowski & Hofmann 2000). After the condensation step, P_4 is transported under overpressure (ca. 400 kPa) in pipelines on the manufacturer site into storage tanks, which operate under atmospheric pressure.

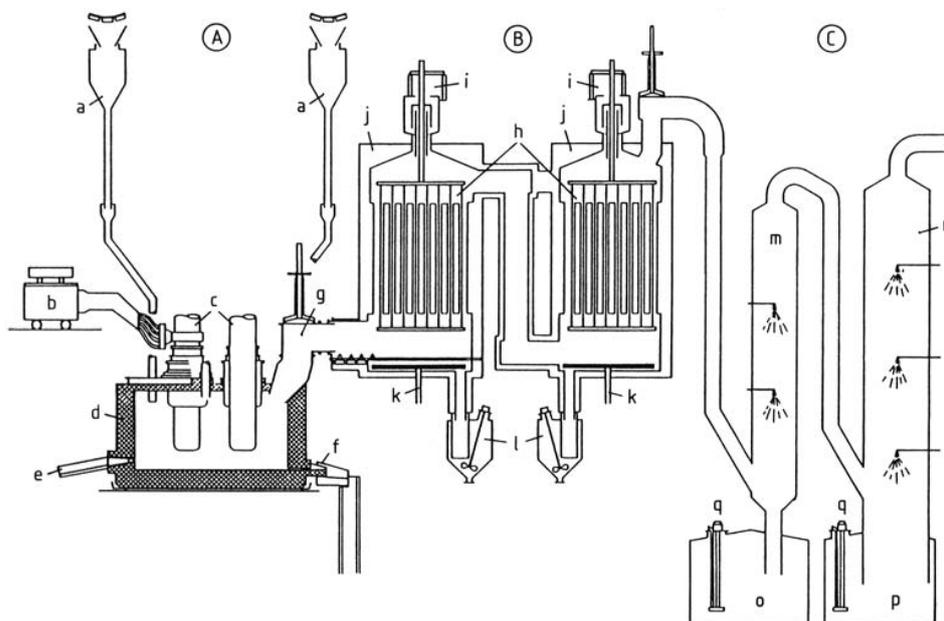


Figure 10: P_4 production installation (adapted from Diskowski & Hofmann 2001)

A) Furnace installation

- a) Raw material feed from bunkers via chutes; b) Transformers (3); c) Electrodes (3); d) Furnace casing; e) Slag tapping point; f) Ferrophosphorus tapping point; g) Furnace gas exit

B) Gas purification

- h) Electrostatic precipitators with sparking and precipitating electrodes; i) Insulated, gas-tight electrical connections; j) Heating jacket, k) Dust collection equipment; l) Containers for dust – water mixture

C) Condensation plant

- m) Hot condensation; n) Cold condensation; o) Liquid phosphorus collection zone; p) Solid phosphorus collection zone; q) Submerged pumps

Upon transshipment, heated P_4 will be transported from the storage tanks under elevated pressure (ca. 150 Pa) into containers and railway tank wagons. The filling procedure into barrels (0.2 m³) will be performed using gravitational filling. Generally, all containers will be filled with a protective water layer to prevent the P_4 load from contact to oxygen. Barrels will be sealed with a metal plug. The railway tank wagons and containers (ca. 66 m³ load capacity) are loaded in inert nitrogen (N_2) atmosphere and are sealed with metal plugs afterwards. In all cases, the transport containers will be left onsite under ambient conditions to let P_4 cool-down and harden. The filled containers are subsequently shipped to the customer by railway or road transport (Maas & Durka 2012).

5.1.2 Properties and acute toxicity

Elemental P_4

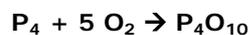
P_4 (CAS No. 7723-14-0) is a member of group 15 of the Periodic Table of Elements. All solid, liquid and gaseous forms exist as tetrahedral P_4 molecules (Diskowski & Hofmann 2000) with a molecular weight of 124 g·mole⁻¹. In its various compounds, P_4 exerts oxidation states between -3 and +5 with +5 being the most stable oxidation

state (Rayner-Canham 1996). At room temperature it is a waxy mass when stored under water. Solid P_4 has a density of 1.82 g cm^{-3} (CRC Handbook of Chemistry and Physics 2005). At $25 \text{ }^\circ\text{C}$ the vapour pressure of P_4 equals 5.3 Pa (Spangord et al 1985). The main allotropes of P_4 are white (yellow when slightly oxidized), red and black. Only the white and red forms are of large-scale industrial importance. The focus will be further on the white form of phosphorus due to its harsh reactions at ambient conditions. P_4 has a melting point of $44 \text{ }^\circ\text{C}$, boils at $280.3 \text{ }^\circ\text{C}$ and is a non-conductor. P_4 dissolves in organic solvents such as benzene, carbon disulphide or diethyl ether. P_4 ignites spontaneously at $30 \text{ }^\circ\text{C}$ in moist air and at $35\text{-}46 \text{ }^\circ\text{C}$ in dry air (ATSDR 1997). The breakdown products of P_4 are phosphorus pentoxide (P_4O_{10}), phosphorus trioxide (P_4O_6), phosphoric acid (H_3PO_4), phosphorous acid (H_3PO_3), phosphine (PH_3), and other oxides (Rivera et al. 1996).

The major hazard associated with exposure is the direct skin contact to burning P_4 . The effects include both second and third-degree burns to the skin, eye and mucosal tissues (Robles 2005). Phosphorus intoxication has been reported to occur from systemic inhalation or ingestion and is very toxic to humans and animals (Robles 2005). The lethal dose for P_4 is $1 \text{ mg}\cdot\text{kg}^{-1}$ bodyweight (Diskowski & Hofmann 2000). No data is available on P_4 acute toxicity inhalation studies (DFG 2002a). However, long-term exposure to P_4 particles in the air caused necrosis of the jaw in several subjects (DFG 2002) with long recovering periods up to two years. Workers who inhaled P_4 particles suffered persistent coughing.

Phosphorus pentoxide (P_4O_{10})

Phosphorus pentoxide (P_4O_{10} CAS No. 1314-56-3) is the major reaction product of P_4 combustion. The reaction is:



P_4O_{10} is the intermediate reaction product when P_4 combusts in excess oxygen. It cannot be further oxidised (P oxidation state +5) and has a molecular weight of $284 \text{ g}\cdot\text{mole}^{-1}$ with a density of $2.3 \text{ g}\cdot\text{cm}^{-3}$. P_4O_{10} melts at 562°C and boils at $605 \text{ }^\circ\text{C}$ (CRC Handbook of Chemistry and Physics 2005). Its vapour pressure is 100 Pa at $377.5 \text{ }^\circ\text{C}$ (CRC Handbook of Chemistry and Physics 2005). P_4O_{10} is, among phosphorous acids, responsible for the thick white cloud that is formed during P_4 combustion. Laviolette & Benson (2012) calculated the structure and thermodynamics of several phosphorus oxide caged clusters (polymers) in the gas phase. They concluded that hypothetical $P_{24}O_{60}$, P_8O_{20} , $P_{24}O_{48}$ and $P_{20}O_{20}$ molecules would all dissociate to the stable P_4O_{10} in the end. Thus, P_4O_{10} can be considered as the most stable intermediate combustion product that will be subject to reaction with atmospheric moisture to form several polyphosphoric acids and their ionic phosphates via hydrolysis given its strong desiccating properties (see Table 2). P_4O_{10} is among the most important intermediate combustion products in a P_4 fire. Various compounds are formed upon hydrolysis at later stages of the overall reaction. According to a personal communication reported to the authors of the MAK (Maximale Arbeitsplatzkonzentration) document for P_4O_{10} (DFG 2002b), P_4O_{10} smoke is noticeable, but not unpleasant in concentrations between 0.8 and $5.4 \text{ mg}\cdot\text{m}^{-3}$. In people who were not adapted to P_4O_{10} , concentrations ranging from 3.6 and $11.3 \text{ mg}\cdot\text{m}^{-3}$ lead to coughing but were tolerable by the exposed subjects (DFG 2002b). An inhalation study on humans where male subjects were exposed to time-averaged P_4O_{10} concentrations of $185\text{-}592 \text{ mg } P_4O_{10} \cdot \text{m}^{-3}$ over a period of $2\text{-}15 \text{ min}$, caused irritant effects on the respiratory tract accompanied by coughing, burning sensation and shortness of breath (DFG 2002b, IPCS 1997). Severe chemical burns can occur to the eye lids and cornea as well as to the skin upon exposure to even low amounts P_4O_{10} particles. Furthermore, inhalation studies suggest, that P_4O_{10} irritates the mucous

membranes by reacting with water in the body to form H_3PO_4 due to the desiccating properties of P_4O_{10} and exothermal reaction of P_4O_{10} to H_3PO_4 , which in turn will lead to corrosion. It is believed that the exothermal formation of H_3PO_4 exerts more serious tissue damage than H_3PO_4 itself (European Commission 1991). However, qualitatively both P_4O_{10} and H_3PO_4 implement the same health effect in humans on mucosal tissues.

Table 2: Reactions of P_4 in the environment (adapted from Rivera et al. 1996)

Material	Environmental Transformation	Environmental Fate
White phosphorus, P_4	$\text{P}_4 + 5\text{O}_2 \rightarrow \text{combustion} \rightarrow \text{P}_4\text{O}_{10}$ $\text{P}_4\text{O}_{10} + \text{atmos, H}_2\text{O} \rightarrow 4 \text{H}_3\text{PO}_4$ $\text{P}_4 + 3\text{O}_2 \rightarrow \text{combustion} \rightarrow \text{P}_4\text{O}_6$ $\text{P}_4\text{O}_6 + \text{atmos, H}_2\text{O} \rightarrow 4 \text{H}_3\text{PO}_3$	Aquatic and soil fate is oxidation to phosphate via lower oxides
Phosphorus pentoxide, P_4O_{10}	Reacts with atmospheric moisture to form polyphosphorus acids	Aquatic and soil deposition to phosphates and lower oxides
Phosphorus trioxide, P_4O_6	$\text{P}_4\text{O}_6 + \text{H}_2\text{O vapor} \rightarrow 4 \text{H}_3\text{PO}_3$	Forms H_3PO_4 , PH_3 , and phosphates
Orthophosphoric acid, H_3PO_4	$\text{H}_3\text{PO}_4 \rightleftharpoons \text{H}^+ + \text{H}_2\text{PO}_4^-$ $\text{pK}_{\text{A}1} = 2.12$ $\text{H}_2\text{PO}_4^- \rightleftharpoons \text{H}^+ + \text{HPO}_4^{2-}$ $\text{pK}_{\text{A}2} = 7.21$ $\text{HPO}_4^{2-} \rightleftharpoons \text{H}^+ + \text{PO}_4^{3-}$ $\text{pK}_{\text{A}3} = 12.32$	Aquatic and soil deposition formation of phosphate salts
Phosphine, PH_3	Oxidize to form oxy-acids of phosphorus	Oxidized or disassociated
Phosphorus acid, H_3PO_3	$\text{H}_3\text{PO}_3 \rightarrow \text{heating, } 250 - 275 \text{ }^\circ\text{C} \rightarrow 3 \text{H}_3\text{PO}_4 + \text{PH}_3$	Thermal decomposition to give H_3PO_4 , H_2 , PH_3 , and red phosphorus. It will form salts such as ammonium phosphite.

Phosphorus trioxide (P_4O_6)

When P_4 burns in an oxygen-deficient atmosphere, phosphorus trioxide (P_4O_6 , CAS No. 1314-24-5) is formed:



P_4O_6 has a molecular weight of $110 \text{ g}\cdot\text{mole}^{-1}$ with a density of $2.13 \text{ g}\cdot\text{cm}^{-3}$ (CRC Handbook of Chemistry and Physics). It has a melting point of $23.8 \text{ }^\circ\text{C}$ and boils at $173 \text{ }^\circ\text{C}$. It is further thermally unstable and decomposes to red phosphorus and other phosphorus oxides at temperatures above $210 \text{ }^\circ\text{C}$. This is likely to occur, because the initial plume temperatures of white phosphorus combustion can be assumed to exceed $500 \text{ }^\circ\text{C}$ (Witlox 2012). However, at low temperatures, P_4O_6 is hydrolysed to phosphorus acid (H_3PO_3), which will be converted to phosphoric acid (H_3PO_4) and phosphine (PH_3) (Rivera et al. 1996).

Phosphorous acid (H₃PO₃)

Phosphorous acid (H₃PO₃, CAS No. 13598-36-2) is formed from the combustion product P₄O₆ upon reaction with water:



H₃PO₃ maintains melting at 74.4 °C and boils at 200 °C. It has a molecular weight of 82 g·mole⁻¹ and a density of 1.65 g·cm⁻³ (CRC Handbook of Chemistry and Physics 2005). Pure phosphorous acid is a colourless solid and decomposes thermally to phosphoric acid, hydrogen, phosphine and red phosphorus at temperatures exceeding 250 °C. Again this is likely to occur given the temperatures in a P₄ flame (Ross et al. 1987, Witlox 2012). Several transformation reactions will give H₃PO₄ in the end.

Phosphoric acid (H₃PO₄)

Phosphoric acid (CAS No. 7664-38-2), also called orthophosphoric acid, is produced when P₄O₁₀ is hydrolysed:

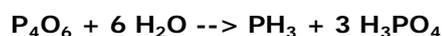


H₃PO₄ has a molecular weight of 98 g·mole⁻¹. It is a colourless and solid powder at room temperature and forms a viscous liquid upon hydrolysis. H₃PO₄ melts at 42.3 °C and boils at 213 °C. At elevated temperatures H₃PO₄ dehydrates to pyrophosphoric acid (H₄P₂O₇, Rivera et al. 1996). However, the fraction of H₃PO₄ will overexceed the H₄P₂O₇ fraction at equilibrium (Katz et al. 1981). H₃PO₄ is tribasic and exerts corrosive properties.

H₃PO₄ is, similar to P₄O₁₀, an irritant toxic substance. Inhalation of H₃PO₄ aerosols, ingestion or direct contact to skin, eyes or other mucosal tissues are possible routes of exposure (Gad & Barbare 2005). Acute toxic effects include corrosion of contact tissues as well as acidosis of the blood (Oster et al. 1978), a state of systemic pH disruption in the body. An airway toxicity study on H₃PO₄ described exposure to "hydroaerosols" at concentrations of 1.6, 7.2 or 11.0 mg H₃PO₄·m⁻³ using 15 subjects (non-smokers, 18 to 36 years old). 12 subjects indicated irritating effects at the two higher levels of the concentrations. No irritant effects occurred at 1.6 mg H₃PO₄·m⁻³; however the specified low exposure concentrations are not supported analytically (DFG 2002c). Dermal contact in low concentrations (< 25-10 Vol %) of H₃PO₄ in water (Harrison et al. 1998) lead to irritation of the skin. Higher concentrations are defined as corrosive and lead to damage of the contact tissue via chemical burns.

Phosphine

Phosphine (PH₃ CAS No. 7803-51-2) will be formed at any phosphorus oxidation reaction under oxygen deficiency conditions in the presence of water (Spanggard et al. 1983). PH₃ melts at -133.5 °C and boils at -87.4 °C (Malczewska-Toth 2001). The density equals 0.0014g·cm⁻³. PH₃ has a low-water solubility and therefore it is expected to be found in the vapours above phosphy water and certainly during P₄ combustion (Rivera et al 1996). A possible reaction is



Although PH₃ is the most toxic compound of all possible combustion products, PH₃ is unlikely to occur within P₄ combustion plumes, because the phosphine formation in relation to the total P₄ combustion reaction accounts for 0.1 % after 300 hrs

(Spanggard et al. 1985). Therefore, further analysis of phosphine formation will be dropped due to the very low fraction that this reaction accounts for.

5.1.3 Dutch intervention values for P_4O_{10} and H_3PO_4

The Dutch Ministry of Infrastructure and the Environment (formerly VROM) published three intervention values (interventiewaarden), namely Voorlichtingsrichtwaarde (VRW, Public information guide value), Alarmeringsgrenswaarde (AGW, Alarm limit value) and Levenbedreigende waarde (LBW, Life-threatening limit value). These thresholds are used to give guidelines for the protection of the population (including emergency alarming) and responders against accidents involving dangerous substances. In case of phosphorus, these values are derived from the Emergency Response Planning Guideline (ERPG) values, particularly ERPG-1, ERPG-2, ERPG-3 values (VROM 2007, AIHA 2006):

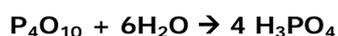
- ERPG-3 is the maximum airborne concentration below which it is believed that nearly all individuals could be exposed for up to 1 hour without experiencing or developing life-threatening health effects. Often this is the concentration at which exposed individuals begin to complain about perceiving exposure (LBW)
- ERPG-2 is the maximum airborne concentration below which it is believed that nearly all individuals could be exposed for up to 1 hour without experiencing or developing irreversible or other serious health effects or symptoms which could impair an individual's ability to take protective action (AGW)
- ERPG-1 is the maximum airborne concentration below which it is believed that nearly all individuals could be exposed for up to 1 hour without experiencing other than mild transient health effects or perceiving a clearly defined, objectionable odor (VRW)

The VRW, AGW, LBW values are given for P_4O_{10} and H_3PO_4 in $mg \cdot m^{-3}$ (Table 3). H_3PO_4 is included in this section, because P_4O_{10} is the major anhydride of H_3PO_4 and therefore relevant. Note that these values are not available for P_4 because it will at least oxidise at any ambient environmental condition to form either P_4O_{10} or finally H_3PO_4 if sufficient moisture is available in the atmosphere (Berkowitz et al 1981, Spanggard et al. 1985, DFG 2002c). Thus, given the outcome of this survey it can be concluded, that only P_4O_{10} and H_3PO_4 are important for the acute toxicity of the P_4 combustion smoke.

Table 3: Dutch intervention values for phosphorus pentoxide and phosphoric acid in $mg \cdot m^{-3}$ (adapted from VROM 2007)

	VRW	AGW	LBW
P_4O_{10}	1	10	20
H_3PO_4	1	10	50

As can be seen by the reader, the LBW for H_3PO_4 is 2.5 times higher. This factor reflects furthermore the difference in molecular weight as well as stoichiometric quantities formed in the reaction



Dividing the molecular weight of 1 mole P_4O_{10} with the molecular weight of 4 moles H_3PO_4 gives a factor of 1.7. As the system of the Dutch intervention values for atmospheric concentrations can only vary in the row ...-50-20-10-5-2-1-... (VROM 2007), the difference a factor of 1.7 can only be reflected by setting the difference in intervention values to 2.5. As P_4O_{10} and H_3PO_4 exert the same health effect, assuming that P_4O_{10} is transformed to H_3PO_4 in mucosal tissues, the difference in the LBW is of limited importance.

5.2 Burn rate

Above all, the literature survey revealed substantial information about the maximum and experimental area-specific burn rate of P_4 given in ($kg \cdot s^{-1} \cdot m^{-2}$). This area-specific burn rate can be regarded as a substance specific material flux parameter, which is crucial to predict atmospheric dispersion of combustion products and the downwind concentration of these mostly hazardous compounds in particular. The most recent QRA performed for Thermphos International B.V. Vlissingen (SAVE 2011) assumed the maximum burn-rate to be equal to ($0.025 \cdot kg \cdot s^{-1} \cdot m^{-2}$), a default for fires in chemical warehouses that do not contain flammable liquids given in the Reference Manual Bevi Risk Assessments (RIVM 2009). However this estimate is doubtful for P_4 . To further verify this area-specific burn rate, an approach using an equation available in the POLF theory manual (POLF Theory Document 2005) is used:

$$m_{\max} = 1.27 \cdot 10^{-6} \rho_L \frac{\Delta H_c}{\Delta H_v^*} \quad (1)$$

where

- ρ_L = density of the liquid ($kg \cdot m^{-3}$),
- T_b = boiling temperature (K),
- ΔH_c = heat of combustion at boiling temperature (T_b , $J \cdot kg^{-1}$),
- ΔH_v^* = modified heat of vaporisation at T_b ($J \cdot kg^{-1}$),
- C_{pL} = specific heat of liquid ($J \cdot kg^{-1} \cdot K^{-1}$).

The modified heat of vaporisation ΔH_v^* (POLF Theory Document 2005) accounts for the specific heat of liquid P_4 and is calculated using

$$\Delta H_v^* = \Delta H_v + C_{pL} (T_b) \max\{0, T_b - T_a\} \quad (2)$$

where

- ΔH_v = heat of vaporisation at T_b ($J \cdot kg^{-1}$),
- T_a = ambient temperature (K),
- C_{pL} = specific heat of liquid ($J \cdot kg^{-1} \cdot K^{-1}$).

$\Delta H_v = 4 \cdot 10^5$ at T_b is provided by the (Witlox & Woodward 1997), $C_{pL} = 849 J \cdot kg^{-1} \cdot K^{-1}$ is given in the POLF theory manual (POLF Theory Document 2005), the boiling point $T_b = 280.3 \text{ }^\circ\text{C}$ (553.45 K) is derived from the POLF theory manual and the ambient temperature $T_a = 15 \text{ }^\circ\text{C}$ (288.15 K) is added to the equation above. Thus, ΔH_v^* equals

$$\Delta H_v^* = 6.4 \cdot 10^5 \text{ J} \cdot \text{kg}^{-1}$$

Applying ρ_L of P_4 ($1528 \text{ kg} \cdot \text{m}^{-3}$) and $\Delta H_c = 2.47 \cdot 10^7$ at T_b given by Witlox & Woodward (1997) as well as ΔH_v^* from above the derived maximum area-specific burn rate m_{\max} equals:

$$m_{\max} = 0.075 \text{ kg} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$$

Experimental work conducted by P_4 manufacturer Thermphos Vlissingen B.V. revealed a temperature-dependent heat of vaporisation ΔH_v measured in $\text{cal} \cdot \text{mole}^{-1}$. This measure will be used to further validate the maximum area-specific burn rate derived from above:

$$\Delta H_v = 14713.6 - 7.7603 \cdot T + 4.9122 \cdot 10^{-3} \cdot T^2 \quad (3)$$

Where T = temperature in Kelvin (K)

The temperature will be set at the boiling temperature (T_b) of P_4 at $280.3 \text{ }^\circ\text{C}$ or 553.45 K . The new derived ΔH_v equals:

$$\Delta H_v = 1.19 \cdot 10^4 \text{ cal} \cdot \text{mole}^{-1}$$

Unit conversion to $\text{J} \cdot \text{kg}^{-1}$ reveals a value of $\Delta H_v = 4.027 \cdot 10^5 \text{ J} \cdot \text{kg}^{-1}$ and the new modified heat of vaporisation, ΔH_v^* , equals subsequently:

$$\Delta H_v^* = 6.28 \cdot 10^5 \text{ J} \cdot \text{kg}^{-1}$$

Using ΔH_v^* , new derived maximum area-specific burn rate, m_{\max} , therefore equals:

$$m_{\max} = 0.076 \text{ kg} \cdot \text{m}^{-2} \cdot \text{s}$$

Comparing this estimate with afore calculated maximum area-specific burn rate, it can be concluded that the resulting average m_{\max} equals $0.076 \text{ kg} \cdot \text{s}^{-1} \cdot \text{m}^{-2}$ given the very small differences of both estimates.

Berkowitz and coworkers (1981) indicated additional information concerning the area-specific burn rate of elemental P_4 . They carried out a single explosion of a 155 mm WP/FELT grenade. This shell contains 116 cellulose (FELT) wedges impregnated with 5980 g of P_4 (75-80% P_4 =WP) in total. FELT is defined as a cellulose matrix in which P_4 is impregnated in the various smoke munitions available. The reported burn time of 420 s was assumed to be representative for a typical shell burn. Thus the resulting burning rate m was reported to equal

$$m = \frac{5.980 \text{ kg}}{420 \text{ s}} = 0.0142 \frac{\text{kg}}{\text{s}}$$

A deeper analysis of technical ammunition data (US ARMY 1994) revealed that the WP/FELT wedges have a thickness of 1.905 cm (3/4 inch). The 116 wedges are 90°

sectored circles as shown in Figure 11. Thus $116/4 = 29$ circles with a diameter of 15.5 cm (grenade diameter) are presumed.

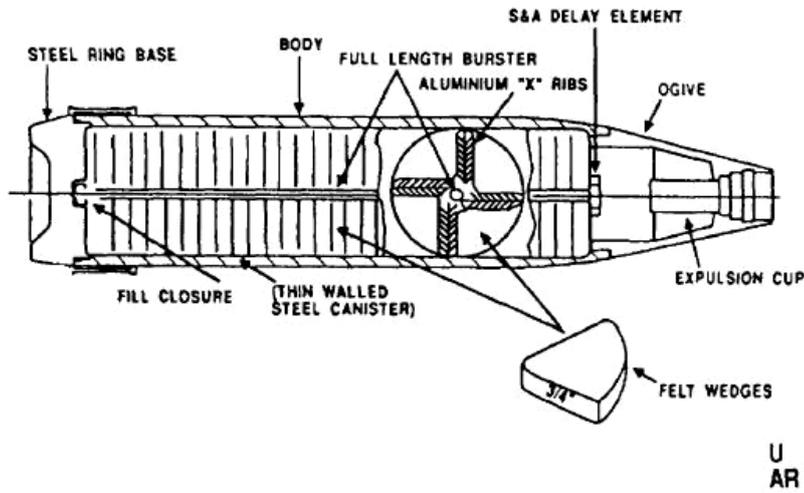


Figure 11: Design of a 155 mm WP/FELT grenade (adapted from US Army 1994)

In addition, it is assumed that the WP/WELT wedges will settle flat on the ground leading to the assumption of a single reaction surface. The wall thickness of the steel canister is assumed to equal 0.5 cm decreasing the wedge diameter by 1cm. Data on this parameter were not publicly available. Therefore the area A would then equal:

$$A = 29 * \frac{1}{4} \pi * (14.5\text{cm})^2 \approx 0.48\text{m}^2.$$

The maximum area-specific burn rate m then equals

$$m = \frac{5.980\text{kg}}{420\text{s} * 0.48\text{m}^2} \approx 3 \cdot 10^{-2} \text{kg} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$$

For consistency reasons, the area-specific burn rate calculated here will be further recalculated using the transformed formula to calculate the maximum area specific area-specific burn rate m_{max} given in the POLF theory manual (POLF Theory Document 2005).

$$m_{\text{max}} = \frac{m}{\left(1 - e^{-\frac{D}{L_b}}\right)} \quad (4)$$

where

- m_{max} = maximum area-specific burn rate ($\text{kg} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$)
- m = experimental area-specific burn rate ($\text{kg} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$)
- D = diameter of the burn surface (m)
- L_b = characteristic length of area-specific burn rate m with diameter D (m)

To give estimation for m_{\max} it is supposed that L_b equals 0 m, which is a substance-specific correlation factor for the increase of the area-specific burn rate with increasing pool diameter (DNV POLF theory 2005). This is in line with work done by Witlox & Woodward (1997) who assumed L_b to be 0 and therefore m_{\max} will asymptote the experimental burn rate m :

$$m \approx 3 \cdot 10^{-2} \frac{\text{kg}}{\text{s} \cdot \text{m}^2} \approx m_{\max}$$

Comparing the averaged m_{\max} of $0.076 \text{ kg}\cdot\text{s}^{-1}\cdot\text{m}^{-2}$, which was calculated using thermodynamical data according to the POLF theory manual, and the derived m_{\max} from the experimental data by Berkowitz et al. (1981), m equals approximately $0.03 \text{ kg}\cdot\text{s}^{-1}\cdot\text{m}^{-2}$. The results differ by a factor of ca. 2.5 which is a reasonable range given the approximations used.

However there is evidence that a significant amount of unreacted P_4 will always remain in the range 8-40%. (Katz et al. 1981, Spanggard et al 1985, Maas & Durka 2012 meaning that the kinetics of the burn rate will show a diminishing behaviour in time. Therefore the real burn rate will asymptote to a lower value until the crust of oxidation products is diminishing the combustion completely (Katz et al. 1981)

Still, it is decided to define the averaged maximum area-specific burn rate $m_{\max}=0.076 \text{ kg}\cdot\text{s}^{-1}\cdot\text{m}^{-2}$ as the base case for the subsequent sensitivity analysis in chapter 6), because m includes the uncertainty of the unknown correlation factor L_b and is therefore of limited value.

5.3 Physicochemical processes in a P_4 combustion cloud

In general a smoke plume is formed from a P_4 pool fire. As the smoke is carried by the prevailing winds, the plume rises upward due to the buoyant forces generated from the heat of combustion reactions. Ambient wind speed and atmospheric conditions that influence plume rise and expansion are important factors in determining the downwind concentration of combustion products and deposition of the particles produced from a pool fire on the ground. The type of terrain will also have a profound effect on the particle deposition of phosphorous smokes.

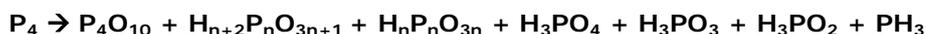
Combustion

Research on military WP/FELT smoke screens indicated that the combustion of P_4 is the result of a stepwise branching chain mechanism involving atmospheric oxygen which is a diffusion-limited process because the initial oxidation of P_4 has no activation energy. This means that the reaction has upper and lower critical O_2 partial pressures in which the reaction is very rapid and outside much slower (Spanggard et al. 1983). At atmospheric pressure and $30 \text{ }^\circ\text{C}$ ambient temperature, the oxidation in air occurs at the upper limit of combustion and is expected to be relatively slow (Spanggard et al 1983). Moreover, Melville (1932) and Fontana (1951) state that the occurrence of ozone (O_3) and inert gases (e.g. N_2) actually decrease the lower partial O_2 pressure for the "explosive" reaction of P_4 thereby accelerating the reaction velocity of P_4 oxidation. However both authors did not define the term explosion and possibly mean ignition.

Chemical reactions in the smoke plume

Later Spanggord and his colleagues (1985) concluded that a significant amount of unreacted P_4 will remain in the FELT matrix (ca. 8%) suggesting that a fraction of unburned P_4 will always remain, which was moreover confirmed by personal correspondence (Maas & Durka 2012) and by Katz et al. (1981) who reported that 40% of the WP/FELT smoke munition remained in the FELT matrix. However, poor experimental design and widely varied results make these data of limited value.

In addition to chapter 5.1.2, Spanggord et al. (1985) suggested that, besides the fact that P_4O_{10} is the major combustion product, rapid transformation of P_4O_{10} will yield a complex mixture of linear and cyclic condensed polyphosphates ($n=1-22$), phosphoric acid (H_3PO_4), phosphorous acid (H_3PO_3), hypophosphorous acid (H_3PO_2), and phosphine (PH_3).



These polyphosphates are esters of polymeric oxyanions formed from tetrahedral ($[PO_4]^{3-}$) structural units which are linked together sharing oxygen atoms (Figure 12). Spanggord and his coworkers (1985) conducted experiments with WP/FELT smoke screens by determining the composition of phosphorus smoke. Here the smoke consisted of polymers with up to 22 phosphorous molecules. The smoke consisted of 24.77% phosphorus monomers ($n=1$), 24.82% phosphorus dimers ($n=2$), 11.44% phosphorus trimers ($n=3$) and of 38.97% phosphorus polymers with more than 3 phosphorus monomers ($n>3$). Similar observations were obtained by Katz et al. (1981) after performing experimental characterisation of WP/FELT smokes.

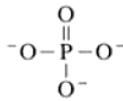
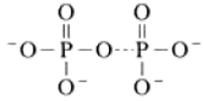
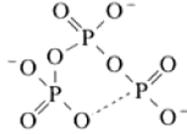
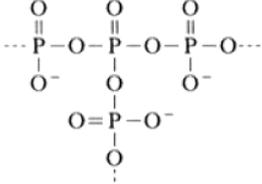
Group name	General formula	Anion structure
monophosphate (isolated PO_4 tetrahedra)	$M_3^1PO_4$	
polyphosphates (chain form)	$M_{n+2}^1P_nO_{3n+1}$	
metaphosphates (cyclic)	$M_3^1P_nO_{3n}$	
cross-linked or ultraphosphates (branched chains or rings)		

Figure 12: Different polyphosphates (adapted from Bettermann et al. 2000)

Hydrolysis of polyphosphates and other processes

Katz et al. (1981) note that higher polyphosphates in the WP/FELT munition smoke undergo transformation to lower polyphosphates "over several days". The same authors performed measurements deploying WP/FELT pieces in smoke chambers. Although the authors did not mention the humidity in the smoke chamber, Figure 14 gives an idea of the distribution of several acidic polyphosphates in the WP/FELT smoke. At neutral pH, the polyphosphates undergo slow hydrolysis with a half-life of 100 days. Yet, at low pH the polyphosphates are hydrolysed rapidly with a half-life of approximately 2 days (49 hrs, Spanggord et al. 1985) in the aerosol phase of the smoke cloud, lowering the fraction of long chain polyphosphates in time. The authors report a reaction rate of 0.0014 hr^{-1} using experimental data from two data points, 0 and 96 hrs respectively. The researchers interpreted this observation as the rate of formation of H_3PO_4 . Measurements of pH conducted by the same authors revealed that the pH value of the WP/FELT residues is 2.1 which will result in self-catalysed acid hydrolysis of the polyphosphates as long as the pH is low.

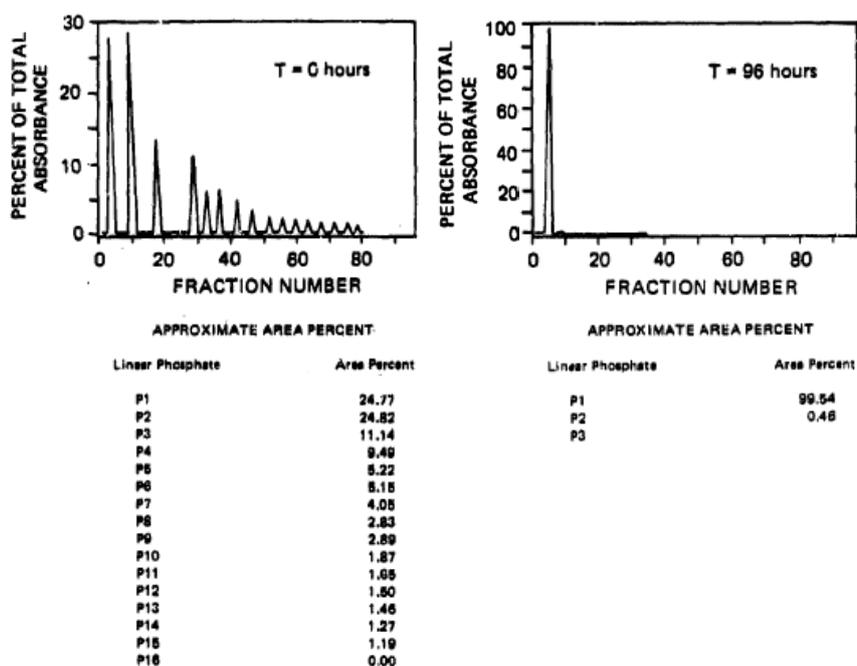


Figure 13: Mass fractions of different polyphosphates in time (modified from Spanggord et al 1985). Note that P1-P18 designate the number of P atoms per polyphosphate

The acidic character of the P_4 combustion residues was analysed by Katz et al (1981) who found evidence for the variety of phosphoric acids in the formed in the combustion reaction (see Figure 14).

The transformation of P_4 to polymeric acids is further confirmed by more recent literature (Bettermann et al 2000). Bettermann and his colleagues stated that pyrophosphoric acid (or diphosphoric acid, $\text{H}_4\text{P}_2\text{O}_7$) is a detectable compound in highly concentrated H_3PO_4 ($\geq 95\%$). Nevertheless, $\text{H}_4\text{P}_2\text{O}_7$ will be subject to conversion to H_3PO_4 .

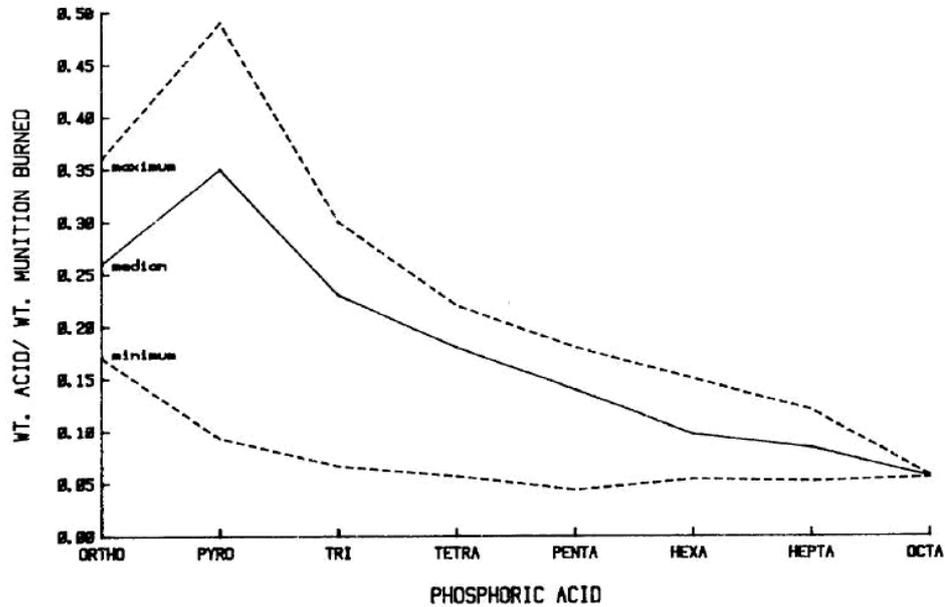


Figure 14: Weight fractions of different polyphosphoric acids in combustion residues of WP/FELT (adapted from Katz et al. 1981)

Primary polyphosphate particles in the munition smoke grow in size by coalescence (formation of bigger particles from smaller ones) as well as by polymerisation (chemical reaction of monomers to form polymers) which will also give H₂O (Spangord et al. 1985) in acid environment.

Smoke yield and humidity

Berkowitz and his colleagues calculated a yield factor of H₃PO₄ (Berkowitz et al 1981) using the model SEMM (Smoke Effectiveness Manual Model). It has to be noted here, that the authors assume that the final end product in the plume will be H₃PO₄. For example, at a relative humidity of 50% the yield factor would equal 5:1, meaning the 5 units of wet smoke mass will be produced compared to the mass of dry agent (WP/FELT) consumed (see Figure 15). The yield factor was reported to increase with increasing humidity. However, the actual total smoke yield might be higher as Figure 16 suggests.

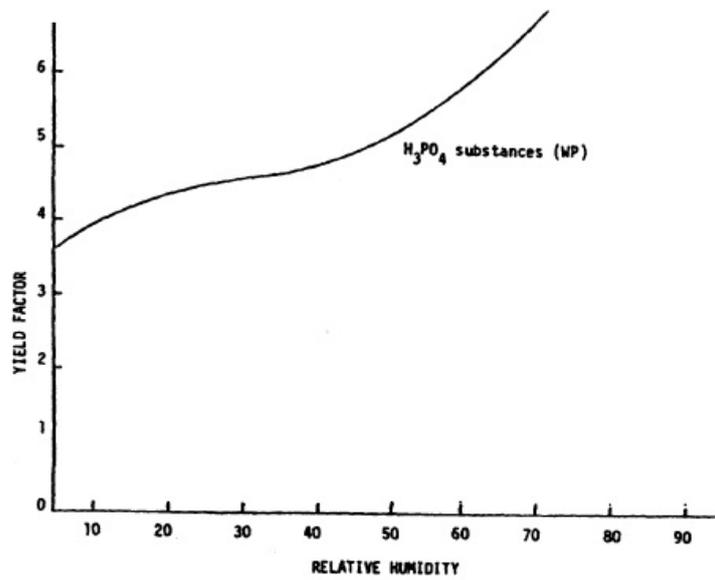


Figure 15: Yield factor of phosphoric acid as a function of relative humidity (modified from Berkowski et al. 1981)

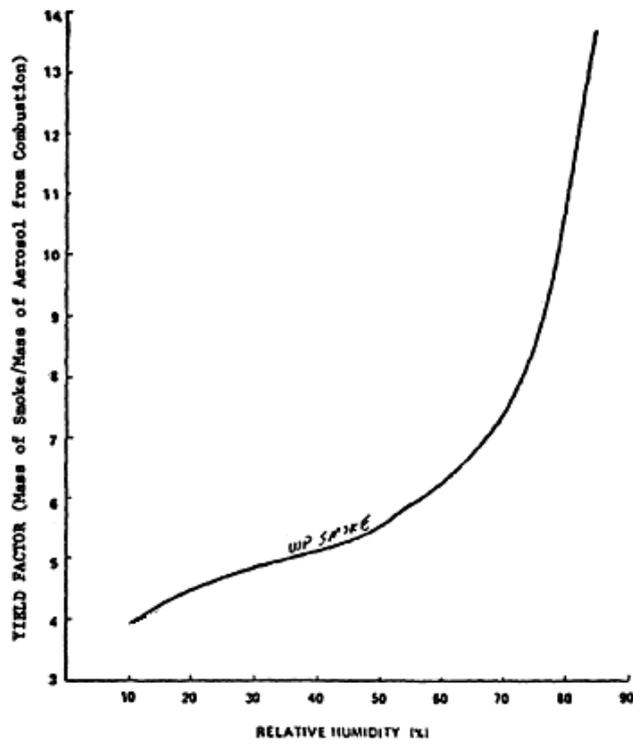


Figure 16: Yield factor of smoke mass as a function of relative humidity (modified from Berkowski et al. 1981)

Particle size

The smoke chamber experiments by Spanggord et al. (1985) furthermore revealed that there is a slight trend towards larger particles at higher relative humidities (Table 4), which is presumably due to the ability of phosphorus smoke to absorb water (P_4O_{10} is among strongest desiccating agents known) and due to coalescence as well as polymerisation processes.

Table 4: Mass median smoke particle diameters of WP/FELT smoke (modified from Spanggord et al. 1985)

Run No.	Fuel ^a	Run Time (sec)	Ambient Relative Humidity (%)	Mass Median Smoke Particle Size (μm)
14	W	1200	26	1.33 ± 0.15
12	W	1620	25	0.833
9	W	1620	39	0.955
15	W	960	52	1.32
16	W	1200	75	1.30 ± 0.11
13	W	1260	72	1.96

The particle diameter was measured to equal 1.3 μm with a geometric mean of 1.8. This diameter is slightly higher than the recommended droplet diameter of $\leq 1.1 \mu\text{m}$ by the UK Health and Safety Executive (HSE, reported in Witlox & Woodward (1997)). Spanggord et al (1985) modelled the atmospheric distribution and noted that particle size is the most important parameter, among particle growth, influencing the dispersion calculation, which was based on a formulation that was published by Gelbard and Seinfeld (1980).

Thermodynamics

Personal communication with Henk Witlox (Witlox 2012) revealed that when P_4 combusts within a pool fire, P_4O_{10} will initially be in the vapour phase when the fire temperature exceeds the boiling point of 605 °C. When the plume of combustion products moves downwind, it cools down to below the boiling point of P_4O_{10} . P_4O_{10} will condense, due to its very low vapour pressure (Fontana 1951), and may solidify when the cloud temperature drops below the melting point of P_4O_{10} (562 °C).

Regarding thermodynamics, a study by Hartley and coworkers (1963) reveals results which point to exothermic formation of P_4O_{10} and H_3PO_4 from experimental findings. Accordingly, the heat of combustion from phosphorus trioxide (P_4O_6) to P_4O_{10} , ΔH_c , gives $-2.2 \text{ MJ}\cdot\text{mole}^{-1}$. In addition the heat of formation, ΔH_f , from P_4 to crystalline P_4O_{10} was $-3 \text{ MJ}\cdot\text{mole}^{-1}$ P_4O_{10} . Moreover, the heat of formation for H_3PO_4 via the hydrolysis of crystalline P_4O_{10} is $-1.8 \text{ MJ}\cdot\text{mole}^{-1}$ H_3PO_4 . Thus, it can be concluded that the exothermic reactions lead to additional heat that is released in the smoke plume determining for some part the height of the plume depending on the ambient temperature.

Ground surface characteristics

Yon et al. (1983) mention cloud cover in addition to the modulating factors of plume behaviour reported before. Besides the atmospheric stability, which is partly defined by cloud cover, wind speed and direction of winds as well as temperature gradients, such as inversion layers, determine the atmospheric dispersion of P₄ combustion smoke. However these factors are part of the natural variability that the atmosphere entails and are therefore not of interest here. Yon and his colleagues note that trees and buildings tend to mix smoke clouds. Surface characteristics such as large hill masses and rugged terrain were assumed to cause strong crosscurrents which disperse smoke, causing holes and irregular smoke dispersion.

Deposition of smoke particles

Together with the coalescence/polymerisation of smoke particles and the water available in air, the moist reacts with the combustion products to form heavier droplets of a variety of combustion products. This process, in turn, can lead to gravitational settling (rainout) of the particles, representing mass reduction of the combustion cloud (Spanggord et al. 1985). Spanggord et al. (1985) also note, that gravitational settling of particles is thought to dominate Brownian and turbulent motion due to the particle size. Moreover, WP/FELT deployments show a trend toward higher deposition velocity with higher humidity, consistent with the trend toward larger particles with higher humidities.

The averaged deposition velocity from the same experiments in smoke chambers with WP/FELT smoke was averaged to 0.045 cm·s⁻¹ in the present study from data obtained by Spanggord et al (1985). The deposition velocity was reported to rise with increasing humidity reflecting the impact of humidity on the droplet size. Subsequently, the deposition velocity can be used to estimate the mass loss of material from a smoke plume using the time-averaged concentration, the time of interest and the plume area:

$$\Delta m = v_{\text{dep}} \cdot \text{conc}_{\text{P}_4\text{O}_{10}} \cdot t \cdot A_{\text{plume}} \quad (5)$$

where

- Δm = Loss of mass from the smoke plume (kg)
- v_{dep} = Deposition velocity (m·s⁻¹)
- conc_{air} = Concentration of P₄O₁₀ (kg·m⁻³)
- t = Time period of interest (here 3600 s [1 hr])
- A_{plume} = Area of the plume facing to the ground (m²)

In the case of a smoke plume covering an area of 85 km² (see accident no. 162), the deposited smoke mass equals ca. 3000 kg in the first hour after an accidental release when a time-averaged air concentration of 20 mg·m⁻³ (20·10⁻⁶ kg·m⁻³) is assumed. Even if only 1/3 of the total P₄ load was released (ca. 230 t), the fraction of the deposited smoke mass would be in the order of 1% for the accident in the Ukraine 2007.

Furthermore Spanggord et al. (1985) calculated deposition velocities for both a smoke mass peak at 5 μm particle diameter and mass median particle diameter equalling 1.3 μm. Thus the authors mentioned the possibility that the actual deposition velocity will be higher for the bigger particles compared to the mass median sized particles because deposition largely depends on the square of particle size. Of particular importance for the deposition is the particle growth via both coalescence and polymerisation processes which will further increase the particle size.

Here the authors emphasised the importance of the surface roughness which will have an intense effect on the deposition of combustion smoke leading to deposition differences by an order of magnitude for different types of grasses. Spanggord and his colleagues report that the mass fractions of combustion smoke deposited by 10,000 m are calculated to rise by 11 %, 29 %, 34 % in the row grass, water, gravel. Applying these values to the deposited smoke mass estimate from above, the subsequent rise would equal 3,330, 3,870, 4,020 kg in the first hour respectively.

Finally, Spanggord simulated the atmospheric dispersion P_4 combustion products and came to the conclusion that at least 50% of the aerosol remains in the atmosphere at 10,000 km downwind.

5.4 Conclusion

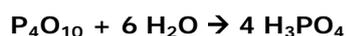
In order to improve the modelling of P_4 combustion and subsequent dispersion it can be concluded from this chapter, that some important determinants of combustion and smoke behaviour are not covered by the formulation incorporated in SAFETI-NL. Particularly the model logics do not account for the formation of H_3PO_4 , the formation of other combustion products (e.g. polyphosphates), as well as physical processes such as droplet rise and coalescence of smoke particles and deposition. Table 5 summarises the actual fire and plume characteristics and the coverage by the POLF and UDM models. Finally it is evident that the present model will overestimate the actual P_4O_{10} concentration because first complete combustion is assumed, second several other combustion products are not accounted for and third the deposition is not covered by the model logic representing loss of material from the plume.

Table 5: P_4 pool fires and coverage of intrinsic processes in SAFETI-NL

	Output	Coverage by POLF/UDM models
General	Flame characteristics	Yes, covered by POLF: Burn rate, Flame geometry, radiation data, mass fractions of combustion mixture of P_4 , which also gives output data for dispersion modelling (UDM)
	Dispersion of P_4 combustion plume	Yes, covered by UDM: E.g. cloud geometry, centre-line concentration of combustion oxide with downwind distance, plume height etc.
Chemical reactions	1st chemical reaction: P_4 to P_4O_{10}	Yes, model package assumes either zero or full reaction to P_4O_{10}
	2nd chemical reaction: P_4O_{10} to H_3PO_4	No, the model assumes combustion to only P_4O_{10}

	Other combustion products	No, model assumption is either full or zero reaction to P ₄ O ₁₀ (or possibly H ₃ PO ₄): (P ₄ O ₆), phosphorus dioxide (PO ₂), H ₃ PO ₃ , H ₄ P ₂ O ₇ , PH ₃ and red phosphorus (different allotrope of P ₄) as well as an unburned fraction of P ₄ were observed (See chapter 5.1.2).
	Polymerisation of combustion oxides to polyphosphates	Not covered, experimental finding (Spanggord et al. 1985).
	Gravitational settling of liquid/solid H ₃ PO ₄ droplets/particles	Not covered, no logic to model the loss of mass in the combustion plume by gravitational settling exists.
	Acute toxicity of combustion mist	Yes, UDM calculates time-averaged ground level concentration of the most important (acid) combustion oxide

Beyond the variety of combustion oxides, with P₄O₁₀ the most important phosphorus oxide, P₄O₁₀ is extremely hygroscopic and is therefore subject to rapid polymerisation to higher polyphosphates and hydrolysis if enough water (as mist) is available in the air. The variety of polyphosphates is extremely complex depending on the actual reaction conditions including the reaction rates. H₃PO₄ will be formed as final reaction product from the slow hydrolysis of polyphosphates (t_{1/2}= 49 hrs). Spanggord et al. (1985) considered H₃PO₄ the final combustion product for their analysis on the environmental fate of P₄ smoke screen deployment tests according to the reaction:



However for the subsequent modelling it is assumed that the reaction of P₄ combustion will form P₄O₁₀ only because the time frame of interest in this study lies within the first hour after an accidental release. Given both the time frame of emergency response and the severeness of the acute toxicity it is reasonable to consider P₄O₁₀ as the compound of interest (Berkowitz et al. 1981, Hartley et al. 1963) although it will transform into other compounds in time. In addition, the small difference of the Dutch intervention values for P₄O₁₀ and H₃PO₄ leads to the conclusion that is not really important whether the atmospheric dispersion of P₄O₁₀ or H₃PO₄ is modelled.

6 Modelling the atmospheric dispersion of phosphorus compounds

In the following chapter the focus lies on modelling using the POLF and UDM spreadsheets that use the same underlying formulations as SAFETI-NL but allow parameter-variation. Here acquired knowledge from the precedent chapters will be incorporated where applicable. Here, the pool fire scenario will be applied to perform calculations on P_4 fires under various atmospheric conditions.

First, section 6.1 will give a short introduction to the POLF and UDM models in use, which is followed by the presentation of the base case problem in section 6.2. In section 6.3 a sensitivity analysis for various parameters is carried out. In section 6.4 the output of the sensitivity analysis will be used to compare the parameters with the Dutch LBW threshold as presented in section 5.1.3. Section 6.5 gives uncertainty bounds for the model output from the sensitivity analysis. This is followed by an analysis of important parameters that are crucial for the prediction of P_4 combustion products in air in section 6.6. Subsequently the reader will be presented with a comparison of the best model estimates for atmospheric P_4O_{10} and H_3PO_4 concentrations and measurements performed at accident sites in section 6.7.

6.1 POLF and UDM model

In 1997, Witlox & Woodward developed a pool fire model (PFGEN) and performed substantial technical improvements to the UDM version at that time representing the technical base of the present study. The pool fire model itself is a model that is prior to dispersion. The unique feature of PFGEN is to link the formation of toxic combustion products in a fire to the dispersion model UDM. With the modifications made by the authors it was possible to include an accidental release with subsequent pool spread followed by a pool fire and atmospheric dispersion. The authors performed a sensitivity analysis and varied the PFGEN/UDM transition point, H_3PO_4 rate of formation, relative humidity, wind speed and spill rate.

In order to improve the modelling of atmospheric dispersion of phosphorus combustion products, a sensitivity analysis and uncertainty analysis was carried out. Here, an assortment of input parameters was chosen, which were systematically varied using the POLF and the UDM spreadsheets. The POLF model calculates the fire dimensions, such as burn rate and the surface emissive power of the fire. Upon single parameter variation of a base case, five output flame parameters are calculated by the POLF model, which are link-input for the dispersion model UDM:

- Plume-axis vertical height (m)
- Combustion mixture flow –rate ($kg \cdot s^{-1}$)
- Flame temperature (K)
- Plume velocity ($m \cdot s^{-1}$)
- Plume angle

Note that these data are taken at the transition from the POLF model to the UDM dispersion model which is at the so-called Froude flame length (H_{fr} , UDM Theory 2005). In Figure 17 the location of this transition plane is indicated. Here the combustion mixture consists of the combustion oxides, nitrogen, water and excess air and possibly unburned fuel. In most cases, the UDM theory states, that the properties

of the combustion mixture will be close to air as the mass fraction of air is ca. 90% at H_{fr} (9 m for this base case problem).

Please note that the link between POLF and UDM is not available in the generic software SAFETI-NL and PHAST (versions 6.54).

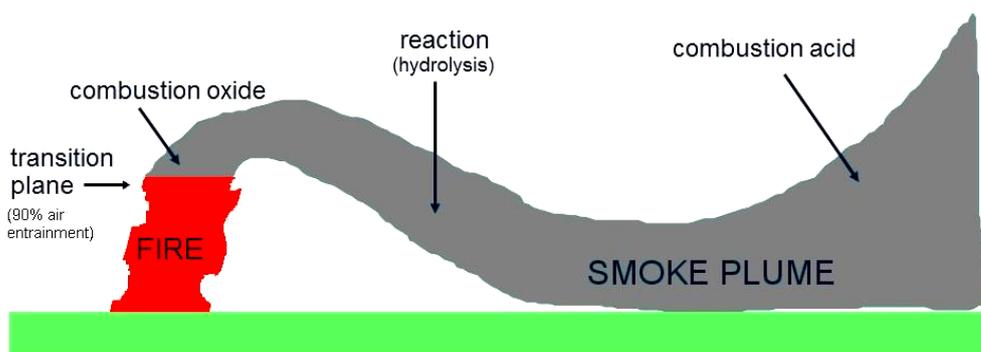


Figure 17: Scheme of a pool fire with a transition plane and subsequent dispersion (modified from POLF Theory Document 2005)

6.2 Base case problem

In line with the outcome of chapter 3 and 4, the basis of the following chapter will be the derailment of a freight train consisting of several tank wagons. Four tank wagons carrying a total load of 200 tons liquid P_4 are thought to be punctured simultaneously and the release of the inventory is assumed to be a large continuous release with release duration of 3 hours. The liquid inventory of all tank wagons is assumed to form a homogenous pool of fixed diameter which is subject to spontaneous ignition. Furthermore, it is assumed that all P_4 is converted to P_4O_{10} in the first hour after the accidental release via the combustion reaction of P_4 . As a result, the source term for P_4O_{10} is equal to the spill rate for P_4 . The smoke is then carried downwind by the major wind regime.

As can be seen by the reader, moderate ambient conditions were chosen for the base case (ambient temperature 15 °C, wind speed 4 $m \cdot s^{-1}$, humidity 0.6). Due to the harsh reactions of dried P_4 with ambient oxygen (Berkowitz et al 1981, DFG 2002 a) the combustion efficiency was set to 1. The substance-specific heat of combustion for P_4O_{10} was reported by Witlox & Woodward (1997) and subsequently incorporated into the POLF spreadsheet.

The pool temperature was set at 70 °C, a common process temperature in the installations at Thermphos Vlissingen B.V. (Maas & Durka 2012). Furthermore, the spill rate of 18.52 $kg \cdot s^{-1}$ was derived from the dividing the assumed total outflow of 200,000 kg P_4 by the release time of 3 hrs (10,800 s):

$$\frac{200,000kg}{10,800s} \approx 18.52kg \cdot s^{-1}$$

The elevation of the pool fire was set for the actual location in Vlissingen (NL). The pool diameter was set to 7 m, which is realistic assumption given accident footage from accident no 162.

The burn rate input ($kg \cdot s^{-1}$) for a pool with a diameter of 7 m was calculated from the maximum area-specific burn rate ($kg \cdot m^{-2} \cdot s^{-1}$) by multiplying the maximum area-specific burn rate with the area of the pool according to

$$\frac{0.076\text{kg}}{\text{m}^2 \cdot \text{s}} * \frac{1}{4} \pi * (7\text{m})^2 \approx 2.91\text{kg} \cdot \text{s}^{-1}$$

The base case is described by the input parameters to the POLF spreadsheet in Table 6.

Table 6: Input parameters for the base case

Ambient wind speed (m·s⁻¹)	4
Ambient temperature (K)	288.15 (15 °C)
Humidity (fraction)	0.6
Ambient pressure (Pa)	101325
Combustion efficiency of P₄ (fraction)	1
Specific heat of P₄O₁₀ (J·kg⁻¹·K⁻¹)	500
Pool temperature (K)	343.15 (70 °C)
Spill rate (kg·s⁻¹)	18.52
Elevation of pool fire (m)	0
Is the pool fire on land? (flag)	TRUE
Pool diameter (m)	7
Total burn rate of P₄ (kg·s⁻¹) (derived from 0.076 kg·m ⁻² ·s ⁻¹)	2.91

The base case was further fitted for the use in the UDM spreadsheets. Besides the same ambient input data, data to account for the flame characteristics calculated by the POLF model were incorporated (Table 7).

Table 7: Input data for the base case in the UDM

Pasquill stability class (flag)	7 (D: neutral)
Ambient wind speed (m/s)	4
Ambient temperature (K)	288.15 (15 °C)
Humidity (fraction)	0.6
Ambient pressure (Pa)	101325
Dispersing surface type (flag)	1 (land)
Temperature of dispersing surface (K)	288.15 (15 °C) Note: This is the temperature of the surface underneath the dispersing plume
Temperature of pool surface (K)	343.15 (70 °C)
Bund diameter (m)	7

Initial modelling using the POLF spreadsheet revealed that, when P₄ combusts, plume temperatures of ca. 550 °C can be assumed at the transition plane from the flame tip to atmospheric dispersion. Upon further downwind moving, the cloud will cool down

and its temperature will approximate to the ambient temperature. Thus, P_4O_{10} is thought to occur for the most part either as liquid droplets or vapour depending on the plume temperature.

6.3 Sensitivity analysis

Table 8 finally indicates the parameter inputs for the sensitivity analysis. This analysis is based on the variation of input parameters of the base case. Within the analysis, a single parameter was varied to include superior and inferior values of the base case with every other input parameter unchanged. In the spill rate and burn rate cases, input of these parameters was only feasible in the POLF spreadsheet. Still, the variation of these parameters was accounted for due to different POLF output, which was subsequently incorporated in the UDM model (see Table 8). An important restriction to the variation of spill rate applies: The underlying assumption of the POLF model is that for a steady-state release without a bund the steady-state spill rate S_{pool} ($kg \cdot s^{-1}$) should never be lower than the total burn rate Q ($kg \cdot s^{-1}$).

Therefore it is assumed for consistency reasons that the spill rate will be higher than the total burn rate in any case and the pool diameters were fitted accordingly.

The variation of the Pasquill stability class was performed in the UDM spreadsheet. This makes sense, as atmospheric stability (e.g. insolation, height of atmospheric boundary layers) is hardly relevant for P_4 pool fires taking place at ground level. In all other cases the variation of the parameters was carried out in both the POLF and UDM spreadsheets.

Table 8: Input data of the sensitivity analysis. Note that base case values included as bold data. Mp= melting point, bp=boiling point

Parameter	Range	Input in POLF	Input in UDM	Notes
Spill rate ($kg \cdot s^{-1}$)	9.26 11.11 13.89 18.52 27.78 55.56	Yes	No	Derived from the initial released 200 tons P_4 and different release times: 1, 2, 3 , 4, 5, 6 hrs respectively. Note restrictions in the text.
Pool diameter (m)	3 6 7 9 12 15	Yes	Yes	
Burn rate ($kg \cdot s^{-1}$)	0.38 1.92 2.91 5.77 9.62 16.57	Yes	No	Total area-specific maximum burn rates correspond to the variation of m_{max} in relation to a pool with $D=7m$: 0.01 (lower limit), 0.05, 0.076 , 0.15, 0.25, 0.43 $kg \cdot m^{-2} \cdot s^{-1}$ (upper limit)
Wind speed ($m \cdot s^{-1}$)	1.5 5.5 4 7.5 9.5 11.5	Yes	Yes	Annual average wind speed in Vlissingen: $6.4 m \cdot s^{-1}$ in (KNMI 2011)

Pasquill stability class (flag)	A B C D E F	No	Yes	A: Very unstable B: Unstable C: Slightly unstable D: Neutral E: Slightly, stable F: Stable
Ambient temperature (K)	278.15 283.15 288.15 293.15, 298.15 303.15	Yes	Yes	5 °C 10 °C 15 °C 20 °C 25 °C 30 °C
Humidity (fraction)	0.2 0.4 0.6 0.8 1	Yes	Yes	
Pool temperature (K)	278.15 317.3 343.15 400 500 553.5	Yes	Yes	5 °C 44.15 °C (mp P ₄) 70 °C 126.85 °C 226.85 °C 280.35 °C (bp P ₄)

Figure 19 to Figure 30 contain predictions for the centre-line height, downwind centre-line mass concentration as well as downwind off-centre-line mass concentration underneath the centre-line at ground level (height = 0 m) of P₄O₁₀ for an averaging time of 1 hr. The centre-line concentration is the concentration in the centre-line of the plume at a specific location. In addition, the ground level off-centre-line concentration is the concentration underneath the centre line at ground level. Note, that the centre-line concentration at centre-line height will be considerably higher than the ground level off centre-line concentration prior to touchdown of the plume on the ground. Figure 18 gives an indication on this issue.

Overall, only the parameters pool diameter, burn rate, Pasquill stability class and wind speed caused the UDM model to react sensitive to the single parameter variation. The UDM is not sensitive for the variation of humidity, ambient temp and spill rate given the design of the present study.

The P₄O₁₀ downwind centre-line mass concentrations at ground level were derived from the P₄O₁₀ mass fractions of the combustion mixture at the transition plane using both POLF and UDM output data.

For clarification, the plots presented in this section could be further extended to include plume position, plume width and centre-line concentrations of P₄O₁₀ as well as the centre-line angle.

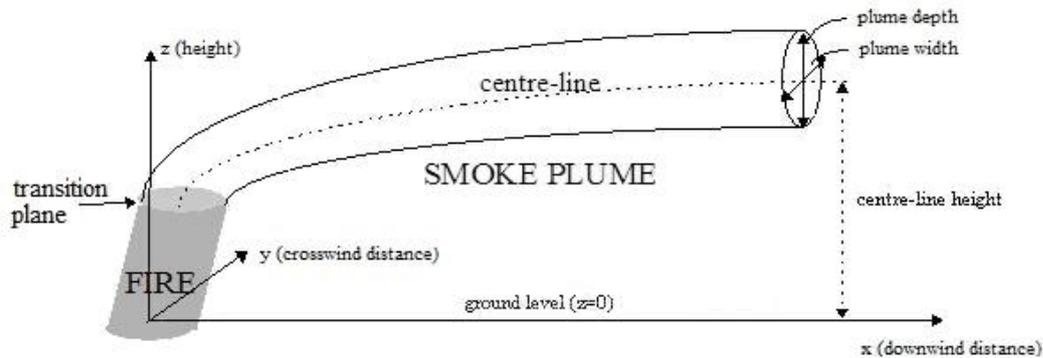


Figure 18: Basic plume geometry (adapted from Witlox & Woodward 1997)

Pool diameter

Figure 19 to Figure 21 contain outcomes of the UDM model for various pool diameters. At this point it is observed that for larger pool diameters the transition from the POLF pool fire to the UDM is initiated further downwind. However, this difference is very small and ranges between 0.016 and 0.019 m downwind distance. The UDM calculation further revealed different centre-line heights of the combustion plume (see Figure 19). Here, higher pool fire diameters lead to higher reaction heat and therefore to higher initial plume rise. As an inherent property of the Gaussian plume model, which was incorporated into the UDM, gives the indication that the concentration of combustion products decrease from the centre-line to the upper and lower flanks of the plume. At this point it is indeed observed that with increasing pool diameters the centre-line heights increase and thereby decrease the 1 hr-averaged ground level mass concentrations of P_4O_{10} until ca. 2000 m downwind distance, because higher plumes give lower concentrations of combustion products at ground level (Figure 21). After approaching equilibrium beyond this point, Figure 21 suggests that the time-averaged downwind concentrations will be higher for higher pool diameters. Moreover, the UDM calculation predicts that the larger the pool diameter the higher the calculated centre-line concentrations of P_4O_{10} which vary by nearly 1 order of magnitude (Figure 20). This observation can be explained by higher burn rates due to an increased combustion reaction surface (pool diameter) which in turn gives more combustion product per time unit. Given the logic to derive the total burn rate Q ($kg \cdot s^{-1}$).

$$Q = m_{\max} * \frac{1}{4} * \pi * D^2 \quad (6)$$

with

m_{\max} =maximum area-specific burn rate ($kg \cdot m^{-2} \cdot s^{-1}$)

D =pool fire diameter (m)

it can be seen that the model will react in a similar way to the variation of m_{\max} in comparison to the variation of D^2 giving output in the same order of magnitude (see Table 7 for input values of D and m_{\max}).

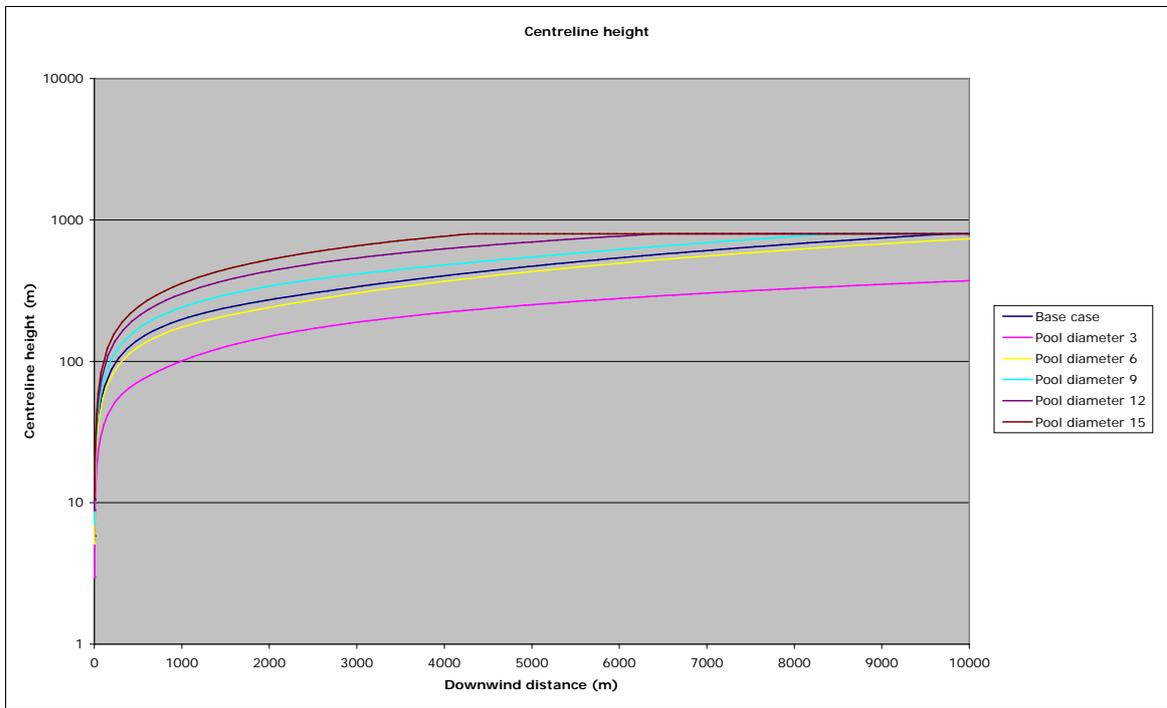


Figure 19: UDM centre-line height for pool diameter variation (in m).
 Note that the base case is 7 m.

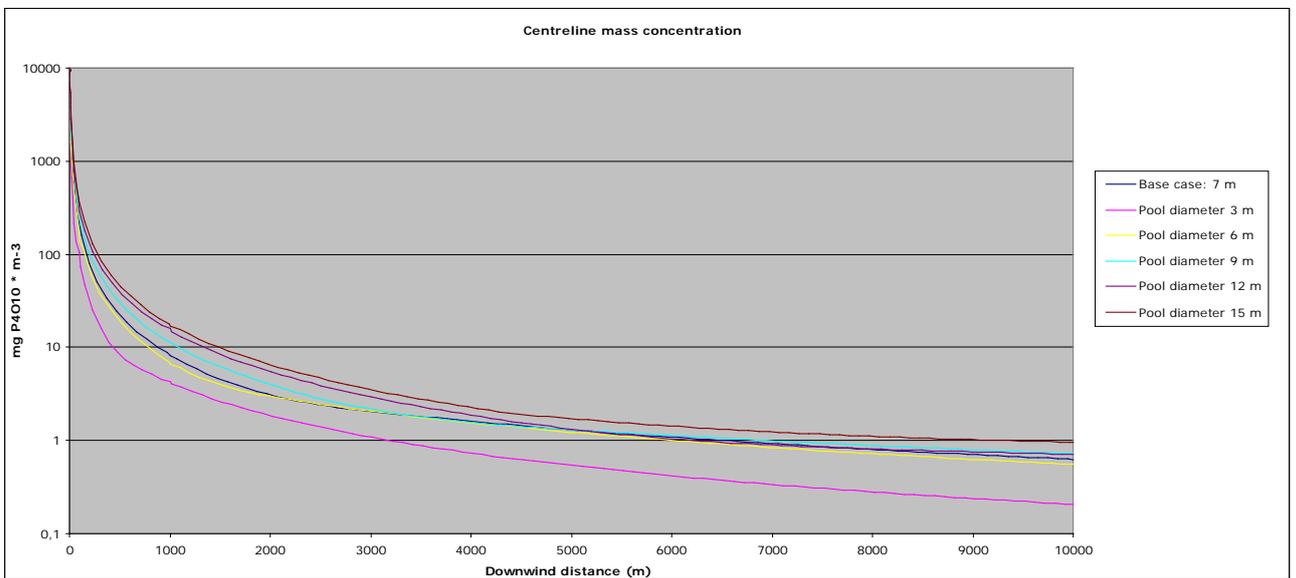


Figure 20: UDM P_4O_{10} centre-line mass concentrations for pool diameter variation

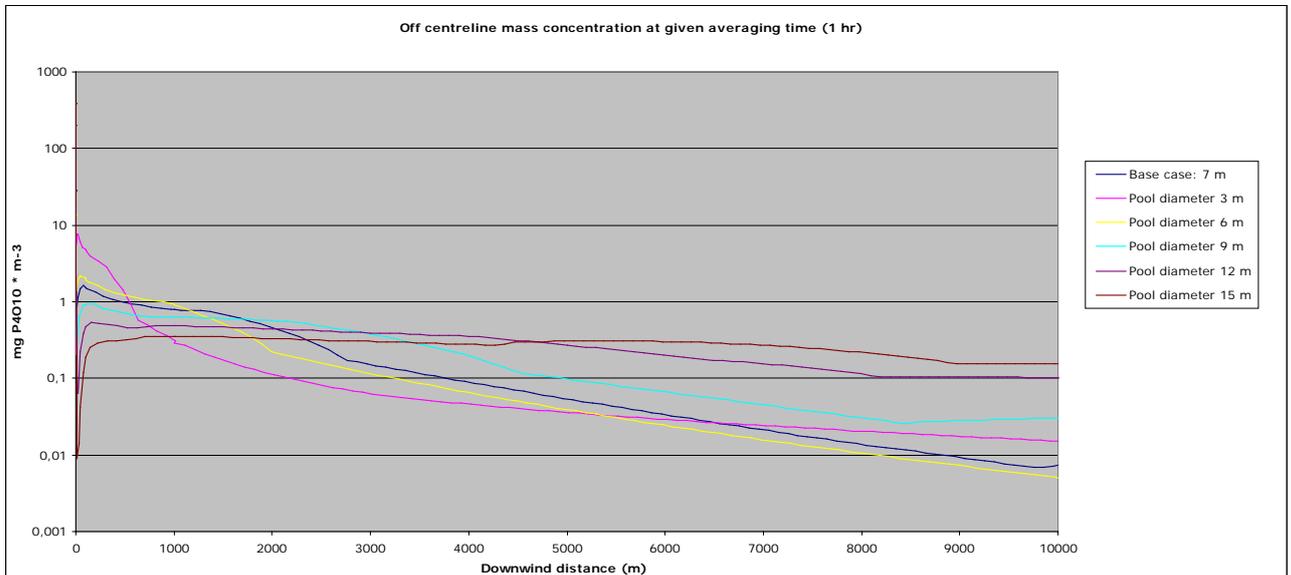


Figure 21: UDM P_4O_{10} 1 hour-averaged off-centre-line mass concentrations at ground level for pool diameter variation

Burn rate

Figure 22 to Figure 24 reflect the effect of the maximum area-specific burn rates which were modified to total burn rates as model input accounting for the base case pool diameter (7 m). From the centre-line height data it is obvious, that with increasing burn rate input the overall height of the plume will increase (see Figure 22). The scatter of the centre-line height is about 0.5 orders of magnitude for the different burn rate cases. However, this difference decreases with downwind distance giving a range of 500 to 800 m centre-line height. Figure 23 indicates that the P_4O_{10} downwind centre-line concentrations are larger for higher burn rates and diminish with downwind distance from the pool fire. At 10,000 m downwind distance, the concentrations of P_4O_{10} differ by one order of magnitude, ranging between 0.16 and $1.44 \text{ mg } P_4O_{10} \cdot m^{-3}$ depending on the burn rate. The UDM output data for the 1 hour-averaged mass concentration of P_4O_{10} gives again an insight into the relationship between ground level concentration and centre-line height of the combustion plume. Due to the considerably high variation of the plume height at initial stages of the atmospheric dispersion, it is shown that the ground level concentrations differ accordingly. Interestingly, burn rates in the lower range of the burn rate values give higher concentrations at ground level due to lower centre-line height of the pertinent combustion plume, which is in line with observations made in the sensitivity analysis of the pool diameter. The last QRA report for Thermphos International B.V., Vlissingen revealed that the downwind distance between 100 and 1,000 m downwind distance are the most relevant for the risk contours calculated by SAFETI-NL, which uses the output of the UDM to calculate the risk of fatalities in line with weather data. In this range, the UDM output reveals that the 1 hr-averaged ground level concentration gives a range of 0.0012 and $23 \text{ mg } P_4O_{10} \cdot m^{-3}$ at 100 m as well as 0.015 and $0.95 \text{ mg } P_4O_{10} \cdot m^{-3}$ at 1,000 m downwind distance. Here the difference of burn rate inputs lies in the range of 0.38 and ca. $17 \text{ kg} \cdot s^{-1}$. A higher burn rate will lead to more heat formation by the pool fire. Therefore the initial plume height is higher decreasing the concentration of smoke particles at ground level. At roughly 2500 m downwind distance, the UDM output tends to give an inverted relationship between burn rate and downwind ground level concentration. This observation means that higher burn rate input will give higher ground level concentrations, because the mixing layer caps the

vertical dispersion leading to a more uniform distribution of the plume with downwind distance. This will give higher ground level concentrations for a given burn rate in the end (Figure 24). The reason for this observation is the uniform distribution of the combustion mixture over the mixing layer in the atmosphere at a certain downwind distance.

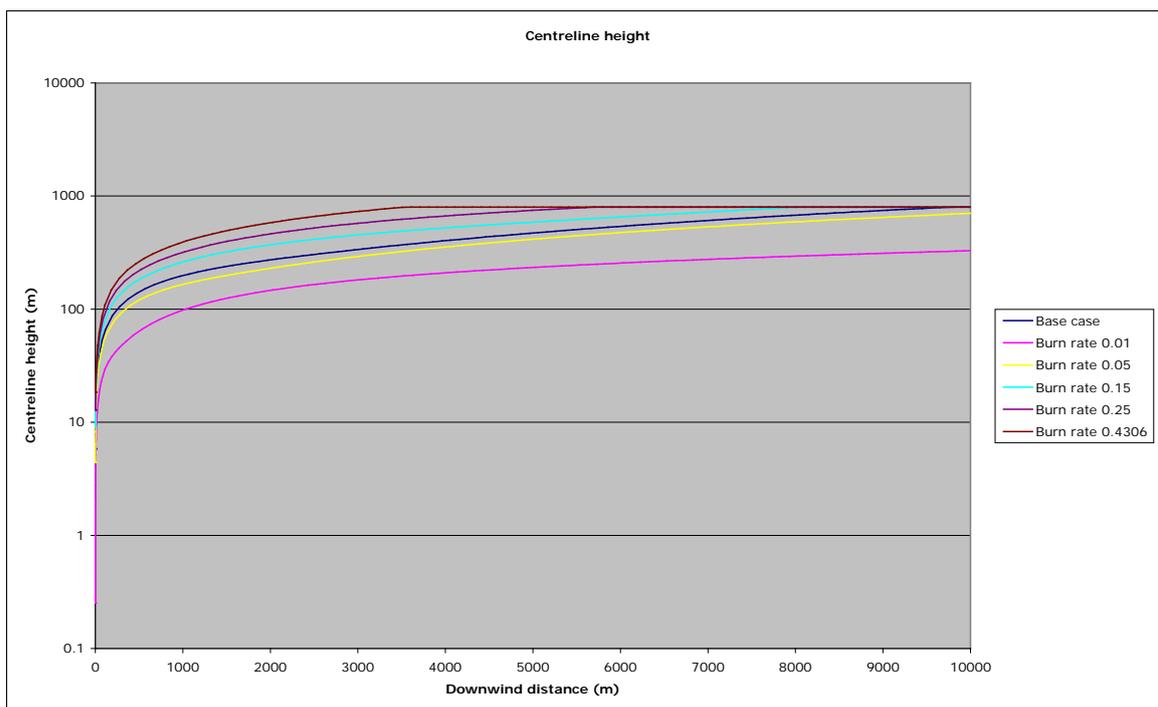


Figure 22: UDM centre-line height for area-specific burn rate variation (in $\text{kg}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$). Note that the base case is $0.076 \text{ kg}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$

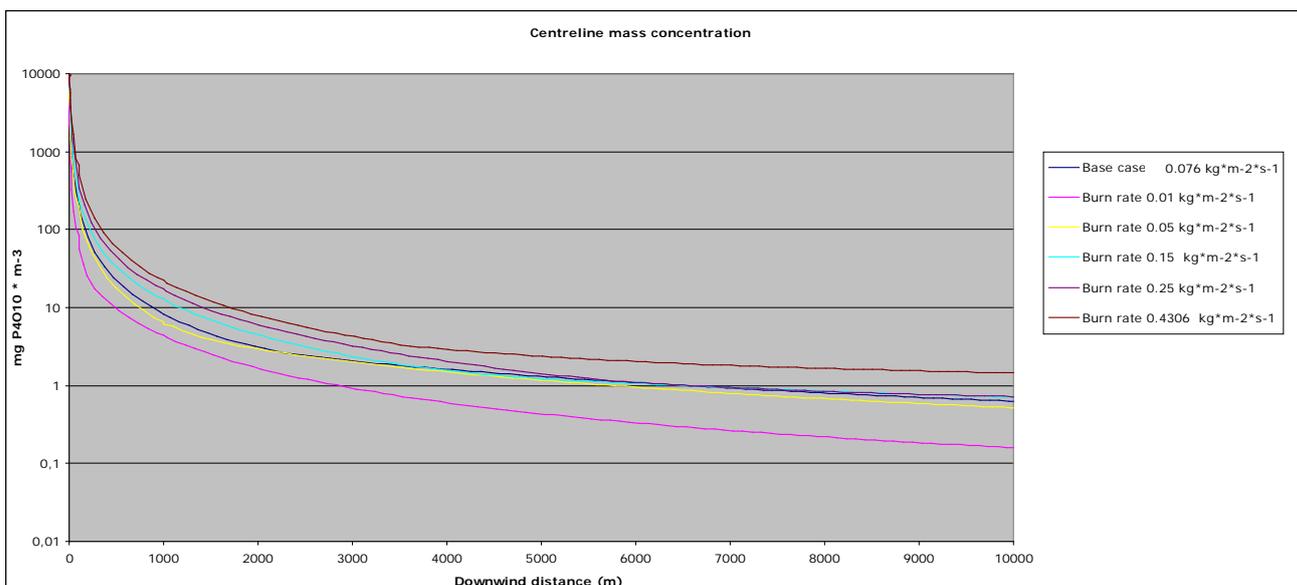


Figure 23: UDM P_4O_{10} centre-line mass concentrations for maximum area-specific burn rate variation

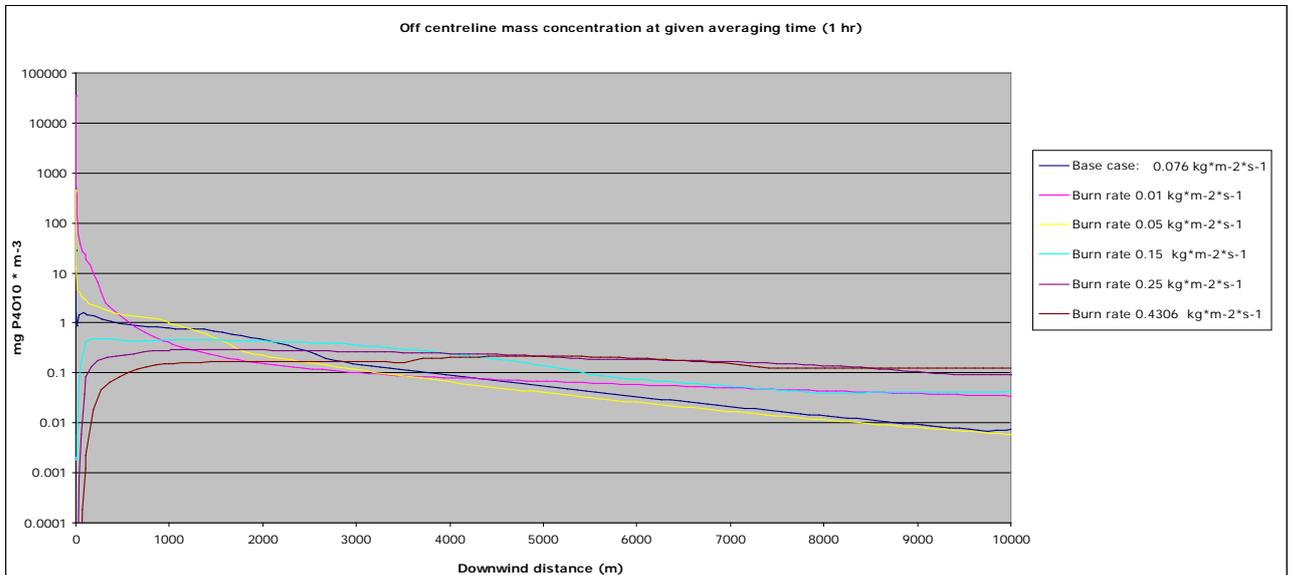


Figure 24: UDM P_4O_{10} 1 hour-averaged off-centre-line mass concentrations for maximum area-specific burn rate variation

Pasquill stability class

In Figures 25 to 27 the effect of the variation of the Pasquill stability classes is demonstrated. From class A to F the stability is increasing i.e. by means of increasing temperature gradients amounting to positive temperature gradients in Pasquill stability class F (inversion, Pasquill 1961). In the row A to F the centre-line height roughly decreases with increasing stability, which reflects the fact that the height of the mixing layers is fixed for a certain Pasquill stability class (DNV UDM Theory Document 2005). This observation can be readily seen in Figure 25 reflecting the default UDM mixing layer heights (100, 400 and 800 m respectively) in the F, E and C cases. In all other cases, the centre-line heights will be capped by the mixing layer height downwind of 10,000 m.

The downwind centre-line concentrations of P_4O_{10} will be higher in more stable conditions due to the decreased depth and width of the combustion plume with higher atmospheric stability (see Figure 18 and Figure 26). Here the UDM output undeniably reflects the reversed relationship between plume cross section area and centre-line concentration due to ongoing dilution of the combustion oxide with increasing cross section area.

In Figure 27 it is observed that two regimes affect the UDM calculation of the off-centre-line mass concentration at ground level. First, it can be concluded that lower atmospheric stability will give higher ground level concentration due to turbulent dilution in the vicinity of the source affecting the ground. However, when the plume rises and moves downwind, the model gives an inverted relationship between ground level concentration and atmospheric stability, which can be seen from ca. 1,000 m downwind distance in Figure 27. This observation can be partly explained by the fact that the plume is capped by the top of the mixing layers in several Pasquill stability class cases (classes F, E, C). At this point, the total mass of P_4O_{10} is not further diluted in vertical direction.

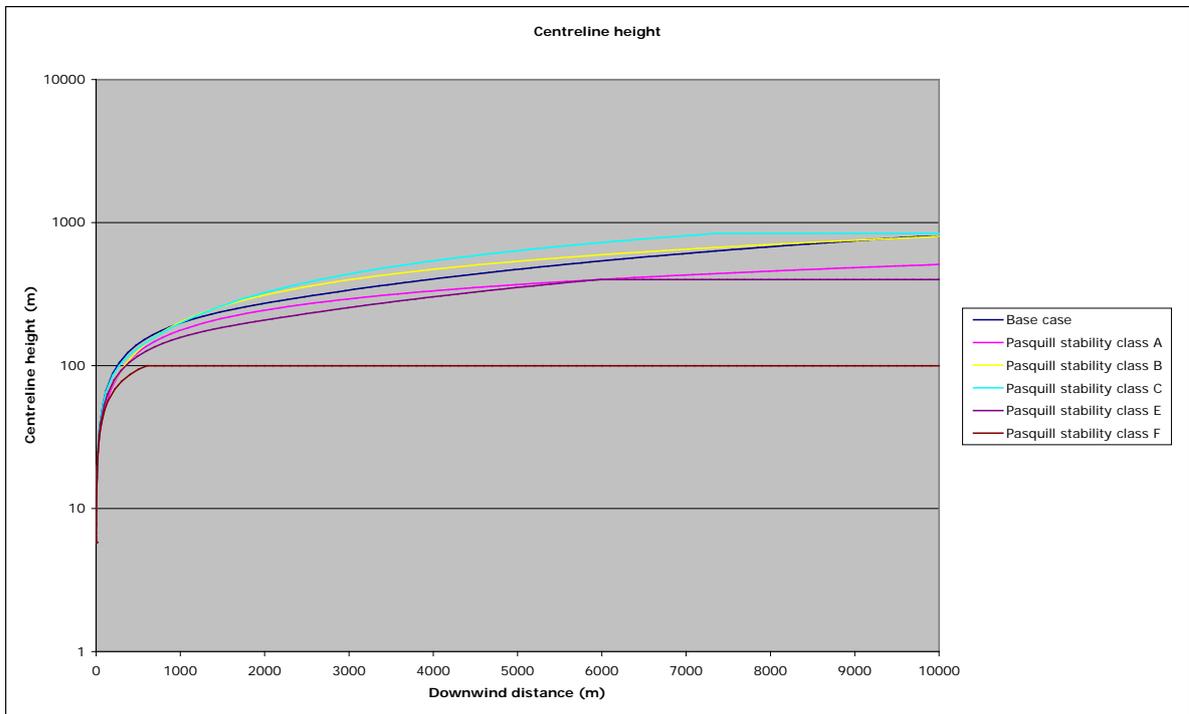


Figure 25: UDM centre-line height for variation of Pasquill stability classes. Note that the base case is Pasquill stability class D

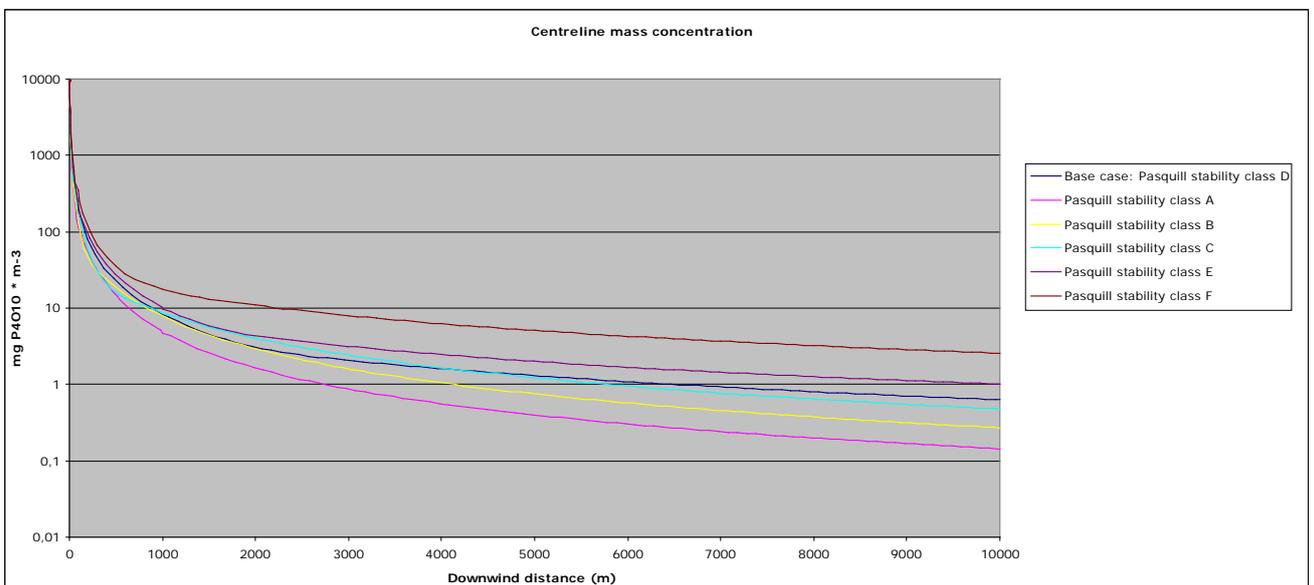


Figure 26: UDM P_4O_{10} centre-line mass concentrations for the variation of Pasquill stability classes

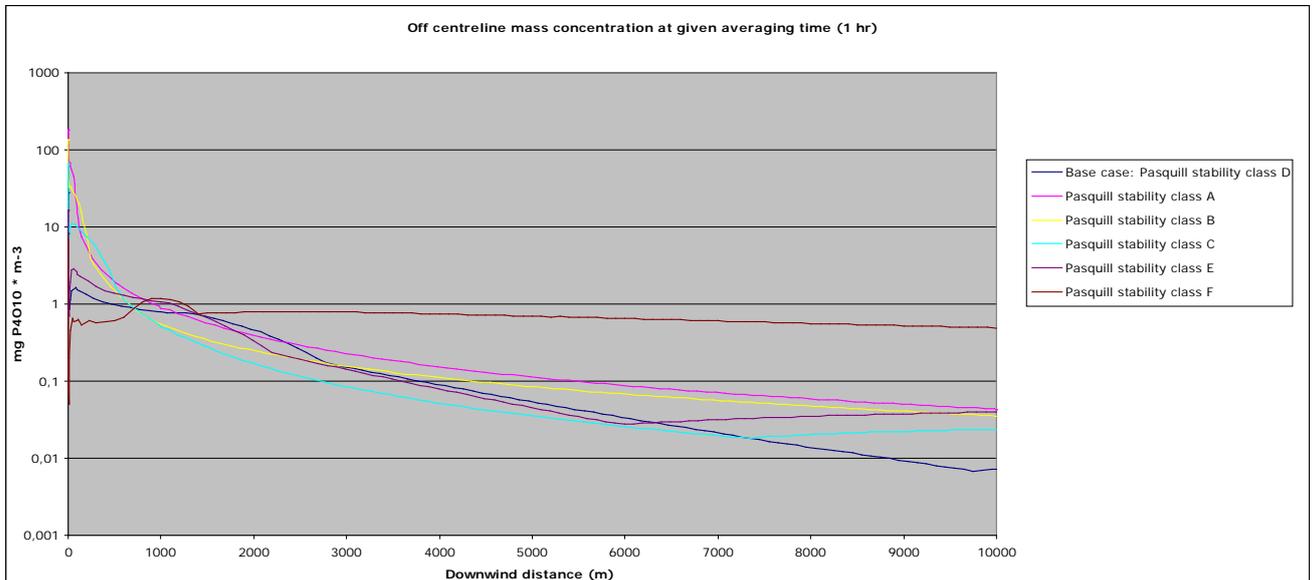


Figure 27: UDM P_4O_{10} 1 hour-averaged off-centre-line mass concentrations for the variation of Pasquill stability classes

Wind speed

Figure 28 to Figure 30 show results with a variation of the wind speed. Referring to Figure 28 and to Figure 29, it is obvious that wind speed has no significant impact on the centre-line height of the plume as well as on the centre-line concentration of P_4O_{10} . However, as can be seen in Figure 30, the ground level concentrations in the vicinity of the fire differ by 0.5 orders of magnitude at ca 50m downwind distance. This can be partly explained by the fact that the flame centre-line and therefore the transition plane is leaned to the ground with increasing wind speed, thus increasing the concentration of P_4O_{10} (DNV UDM Theory Document 2005)

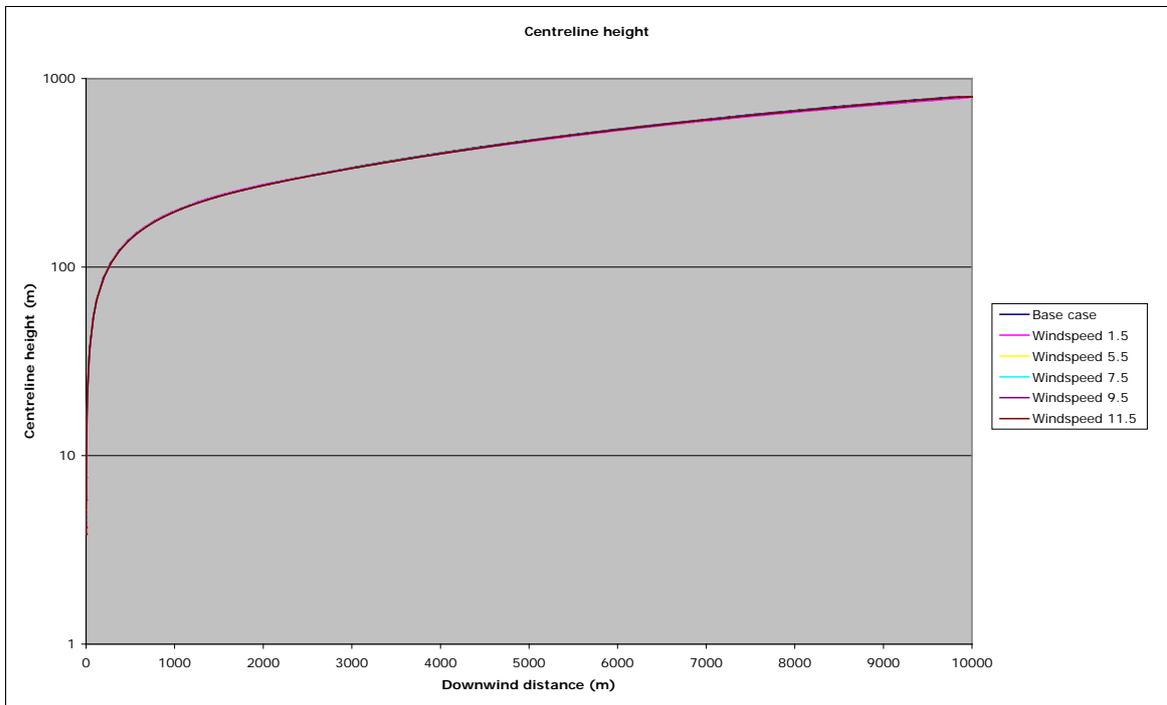


Figure 28: UDM centre-line height for wind speed variation (in $m \cdot s^{-1}$) Note that the base case is $4 m \cdot s^{-1}$

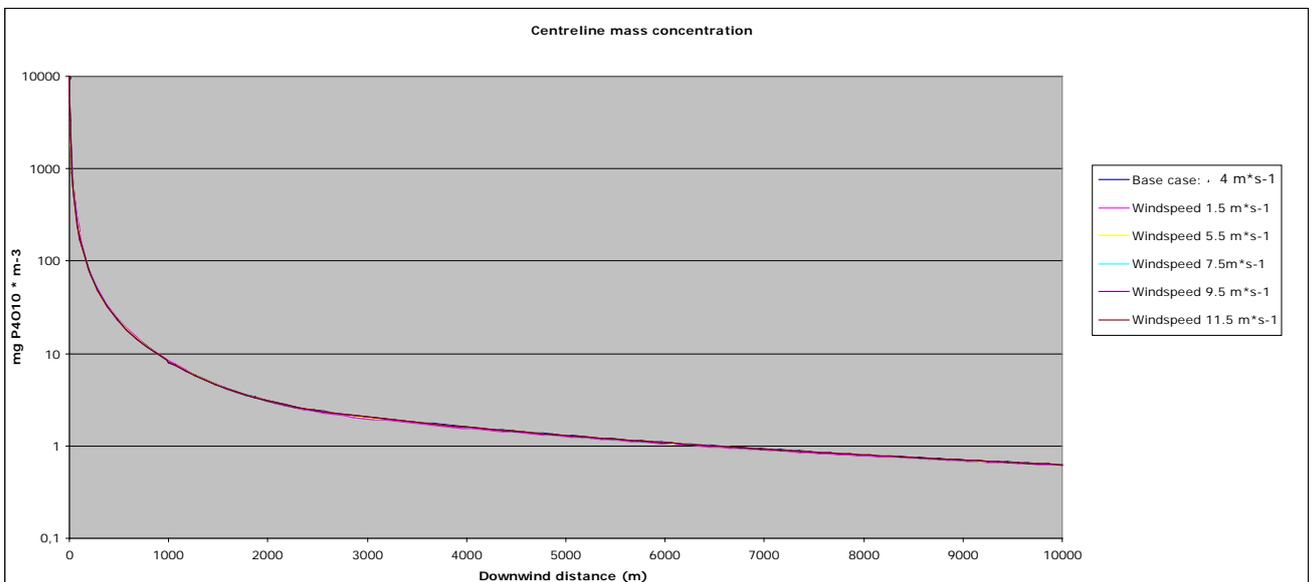


Figure 29: UDM P_4O_{10} centre-line mass concentrations for wind speed variation

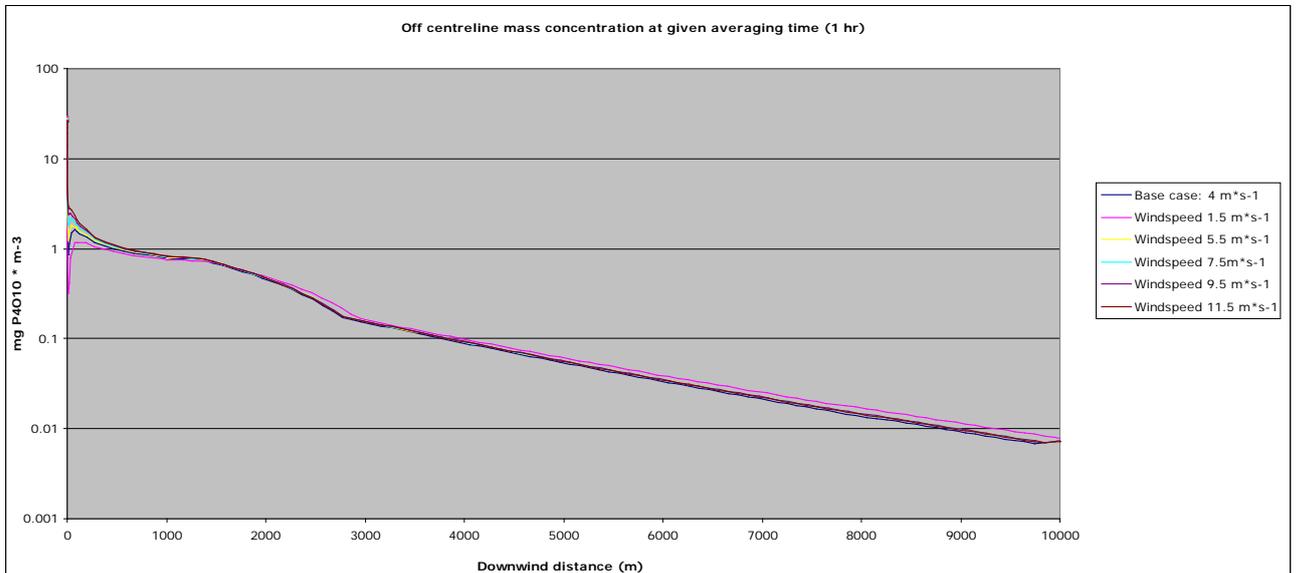


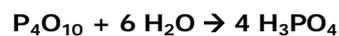
Figure 30: UDM P_4O_{10} 1 hour-averaged off-centre-line mass concentrations for wind speed variation

Derivation of H_3PO_4 off-centre-line mass concentrations at ground level

The UDM model predictions for P_4O_{10} were further analysed for H_3PO_4 formation in the combustion plume.

According to Witlox and Woodward (1997), all water in the air can be expected to react immediately with P_4O_{10} to form H_3PO_4 . As outlined above, formation of only H_3PO_4 is assumed and chemical reaction to polyphosphates, phosphorous oxides as well as step-wise reaction to the end product will be ignored.

Relating to



a theoretical H_3PO_4 off-centre-line mass concentration at ground level in $mg \cdot m^{-3}$ will be calculated using the P_4O_{10} downwind off-centre-line mass concentration at ground level in mg/m^3 with the assumption that all P_4O_{10} will be converted into H_3PO_4 :

$$Conc_{H_3PO_4} = Conc_{P_4O_{10}} * f_{moles} * \left(\frac{M_{H_3PO_4}}{M_{P_4O_{10}}} \right)$$

with

- $Conc_{P_4O_{10}}$ = mass concentration of P_4O_{10} ($mg \cdot m^{-3}$)
- $Conc_{H_3PO_4}$ = mass concentration of H_3PO_4 ($mg \cdot m^{-3}$)
- f_{moles} = molar ratio of H_3PO_4 to P_4O_{10} (4:1)
- $M_{P_4O_{10}}$ = molecular weight of P_4O_{10} ($284 g \cdot mole^{-1}$)
- $M_{H_3PO_4}$ = molecular weight of H_3PO_4 ($98 g \cdot mole^{-1}$)

$Conc_{P_4O_{10}}$ is a calculated UDM output parameter for any case of the sensitivity analysis, which was incorporated in the abovementioned equation to give the H_3PO_4 off-centre-line mass concentration at ground level. The maximum yield factor of H_3PO_4 equals 1.38 and is independent of the distance.

Figure 31 to Figure 34 include only predictions for the downwind off-centre-line mass concentration at ground level (height = 0 m) in $mg \cdot m^{-3}$ of H_3PO_4 for an averaging time

of 1 hr and do not include centre-line heights and centre-line concentrations, because the H_3PO_4 data do not differ from P_4O_{10} data. According to the yield factor, the actual H_3PO_4 concentrations at ground level shift upwards by a factor of 1.38 with the plots showing the same qualitative characteristics as outlined for P_4O_{10} .

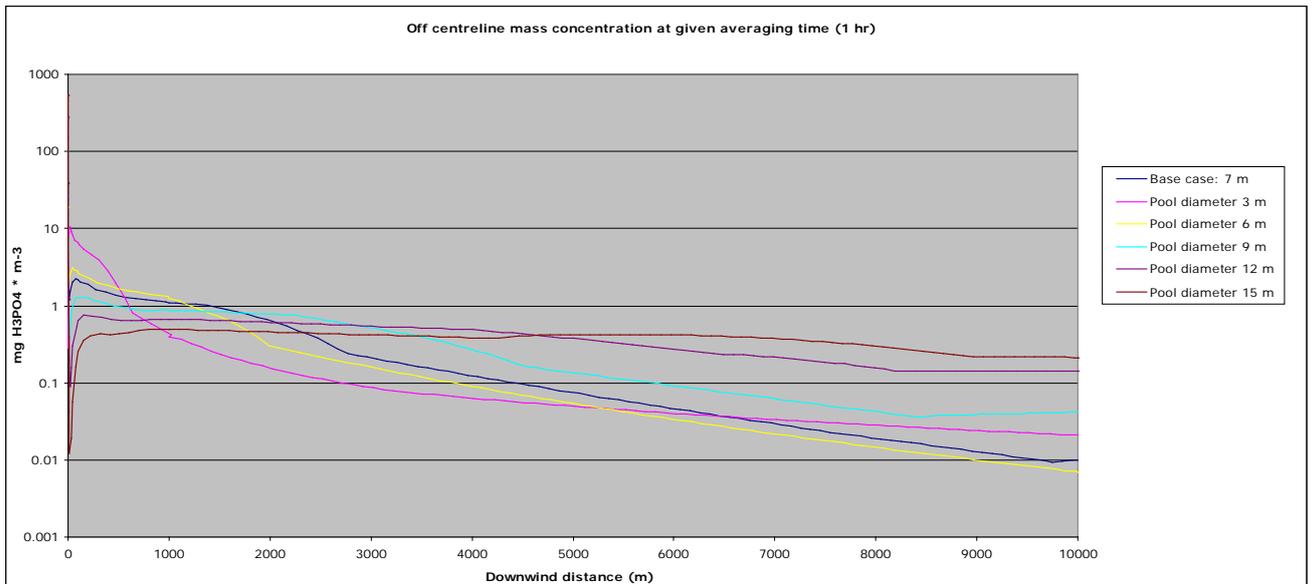


Figure 31: UDM H_3PO_4 1 hour-averaged off-centre-line mass concentrations for pool diameter variation

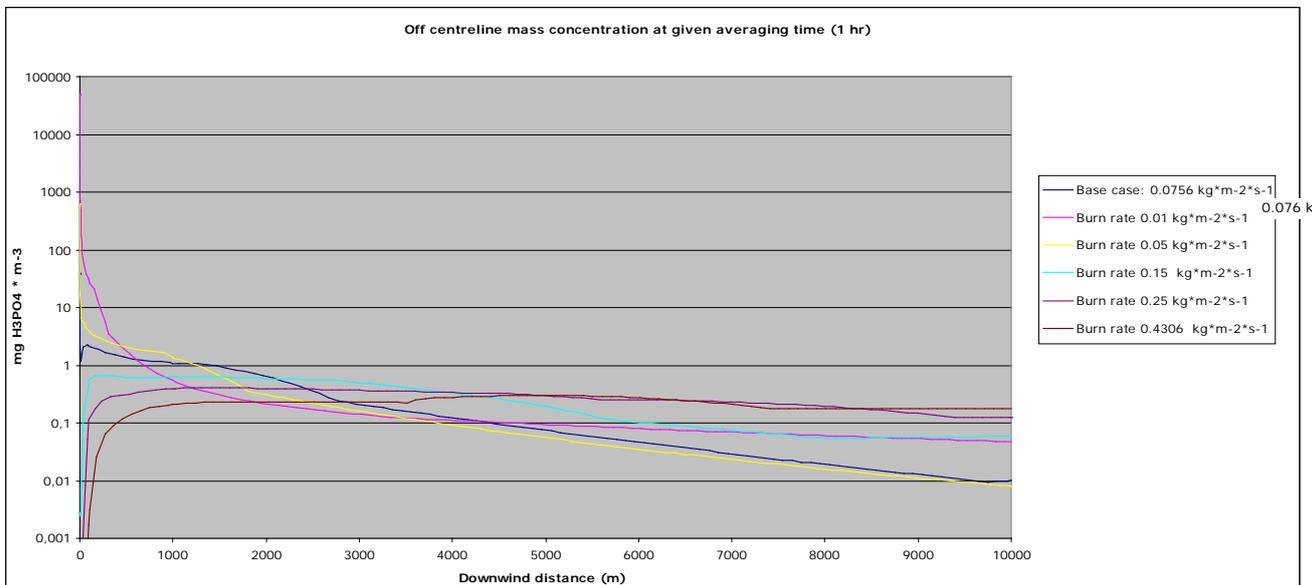


Figure 32: UDM H_3PO_4 1 hour-averaged off-centre-line mass concentration for area-specific burn rate variation

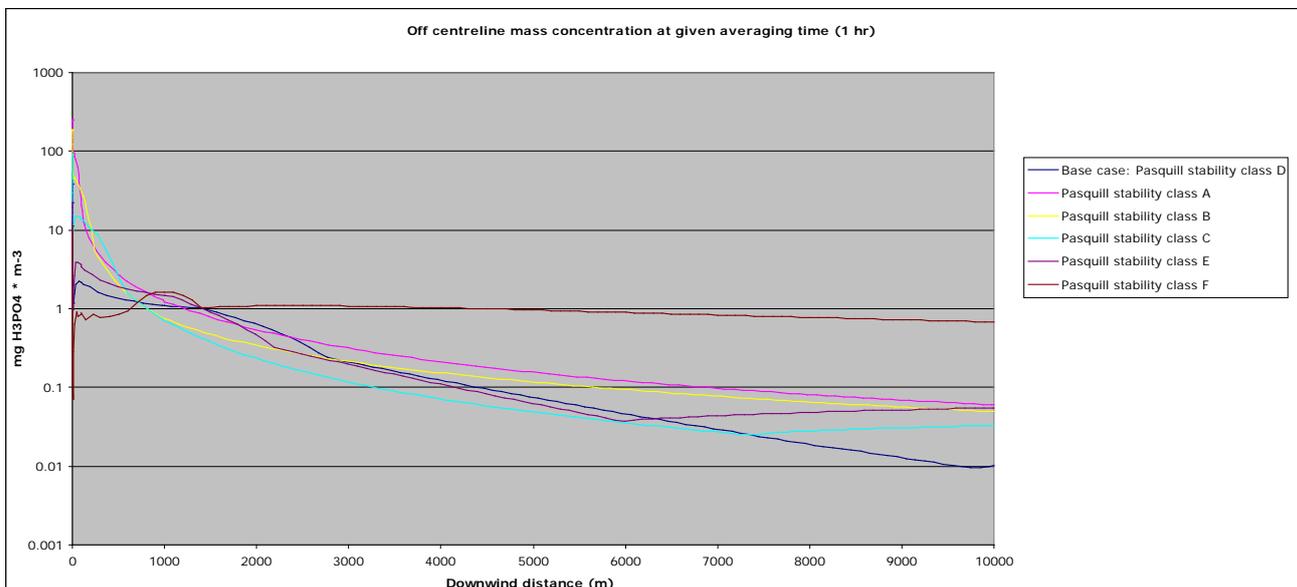


Figure 33: UDM H₃PO₄ 1 hour-averaged off-centre-line mass concentrations for variation of Pasquill stability classes

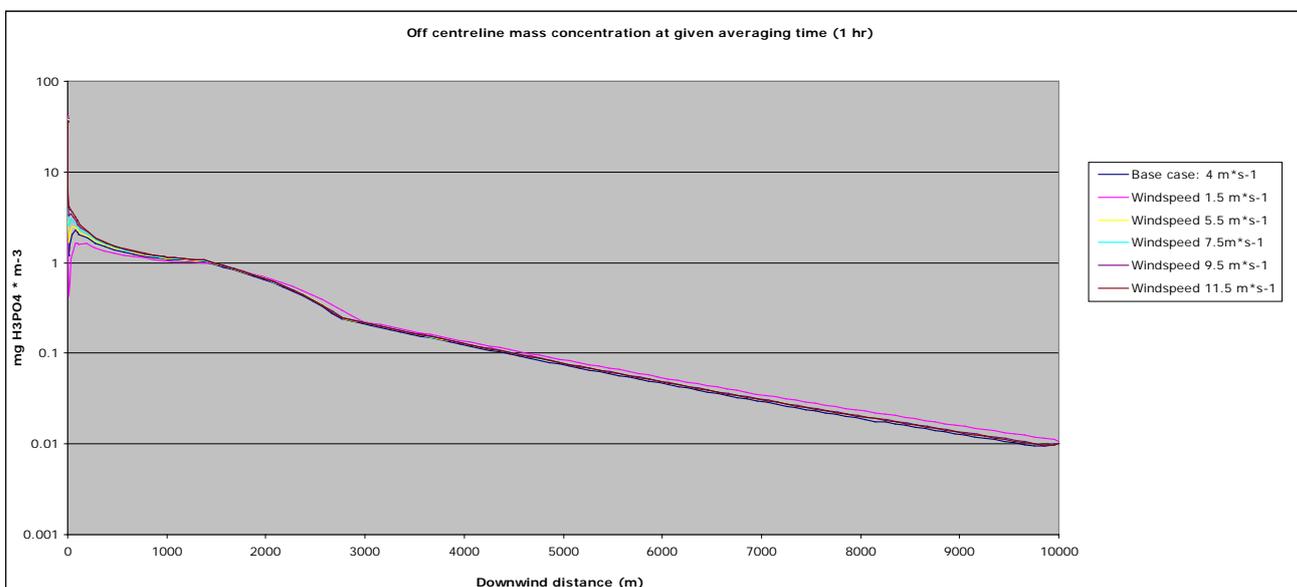


Figure 34: UDM H₃PO₄ 1 hour-averaged off-centre-line mass concentrations for wind speed variation

6.4 Comparison with the Dutch LBW

The P_4O_{10} and H_3PO_4 downwind off-centre-line mass concentration at ground level (height = 1 m) will be compared with the Dutch LBW intervention value (levensbedreigende waarde, life-threatening intervention value) in this section. This section focuses on the LBW because ultimately, for QRAs in the Netherlands the VRW and AGW thresholds are not of interest for the individual risk of mortality. Note that the LBW represents the threshold concentration for death or irreversible health effects occurring after exposure of 1 hr.

Moreover, a comparison is carried out for any case at downwind distances of 100, 1,000 and 10,000 m. As discussed in the previous section, the possible effect of deposition is not considered.

The comparison reveals that the calculation with Pasquill stability class B will exceed the LBW for P_4O_{10} at a downwind distance of 100 m. In this study the UDM calculates an off-centre-line mass concentration at ground level of ca $23 \text{ mg } P_4O_{10} \cdot \text{m}^{-3}$ whereas the relevant LBW is $20 \text{ mg} \cdot \text{m}^{-3}$ (bold values in Table 9). This stability class is unstable (along with class A), allowing vertical dilution of the combustion mixture. The initial combustion mixture will approach the ground and consequently increase the off-centre-line P_4O_{10} concentration at ground level. Moreover the calculation with a area-specific burn rate of $0.01 \text{ kg} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$ gives an exceedence of the LBW. The value for the off-centre-line mass concentration at ground level is $22 \text{ mg } P_4O_{10} \cdot \text{m}^{-3}$. Higher area-specific burn rates will initially lead to higher combustion plumes and subsequently to even lower concentrations at ground level. Further downwind the Gaussian plume model reflects dilution processes due to ongoing dispersion of the plume. The exceedence of the P_4O_{10} LBW threshold observed herein are in the order of 10 to 15 % at 100 m downwind distance under the conditions of this study. No exceedence can be reported for downwind distances at 1,000 and 10,000 m.

It can be concluded from the above that the LBW is likely to be exceeded by a low burn rate and an unstable atmosphere. Moreover it is noted, that downwind distances $\geq 1,000$ m downwind distance are hardly important for fatalities under the conditions investigated in this study.

Table 9: Comparison of UDM output and LBW thresholds

Case	Case parameter	Off-centre-line-P ₄ O ₁₀ / H ₃ PO ₄ conc. at ground level (mg·m ⁻³)			LBW value P ₄ O ₁₀ (mg·m ⁻³)	LBW value H ₃ PO ₄ (mg·m ⁻³)
		100	1,000	10,000		
Base case	See above	1.6/2.14	0.79/1.1	7.3·10 ⁻³ /1.0·10 ⁻³	20	50
Pool diameter (m)	3	4.8/6.7	0.29/0.40	1.5·10 ⁻² /2.1·10 ⁻³		
	6	1.9/2.6	0.89/1.23	5.0·10 ⁻³ /6.9·10 ⁻³		
	9	0.92/1.3	0.63/0.88	3.0·10 ⁻² /4.2·10 ⁻²		
	12	0.47/0.65	0.48/0.67	0.10/0.14		
	15	0.19/0.26	0.35/0.49	0.15/0.21		
Area-specific burn rate (kg·m ⁻² ·s ⁻¹)	0.01	23/31	0.41/0.56	3.4·10 ⁻² /4.7·10 ⁻²		
	0.05	2.9/4.01	0.96/1.31	5.7·10 ⁻³ /7.9·10 ⁻³		
	0.15	0.41/0.56	0.46/0.63	4.2·10 ⁻² /5.8·10 ⁻²		
	0.25	0.084/0.12	0.28/0.39	9.0·10 ⁻² /0.12		
	0.43	1.2·10 ⁻³ /1.7·10 ⁻³	0.15/0.21	0.13/0.17		
Pasquill stability class	A	15/21	0.88/1.2	4.3·10 ⁻² /5.9·10 ⁻²		
	B	22/31	0.55/0.76	3.5·10 ⁻² /4.9·10 ⁻²		
	C	10/13	0.50/0.69	2.4·10 ⁻² /3.3·10 ⁻²		
	E	2.4/3.4	1.06/1.5	4.0·10 ⁻² /5.5·10 ⁻²		
	F	0.61/0.84	1.2/1.6	0.49/0.68		
Wind speed (m·s ⁻¹)	1.5	1.2/1.6	0.76/1.04	7.7·10 ⁻³ /1.1·10 ⁻²		
	5.5	1.6/2.3	0.80/1.1	7.4·10 ⁻³ /1.0·10 ⁻²		
	7.5	1.8/2.5	0.81/1.1	7.3·10 ⁻³ /1.0·10 ⁻²		
	9.5	1.9/2.6	0.82/1.1	7.3·10 ⁻³ /1.0·10 ⁻²		
	11.5	2.1/2.9	0.83/1.2	7.3·10 ⁻³ /1.0·10 ⁻²		

6.5 Uncertainty analysis

The following section deals with giving uncertainty bounds for the downwind off-centre-line mass concentration at ground level (height = 0 m) of P_4O_{10} . The data in this section is derived from the UDM model output in line with the sensitivity analysis in the previous section. Moreover, the data is only given for sensitive cases of the UDM parameter variation. Table 10 shows the results for P_4O_{10} and constitutes a reflection of the minimum and maximum values of the graphs of the sensitivity analysis. Note that minimum and maximum values are given for 100, 1,000 and 10,000 m downwind distances only. The numbers in brackets represent the pertinent input parameter case of the sensitivity analysis with the unit given in the case row. As the actual values for H_3PO_4 concentrations are only shifted by a factor 1.38, it is decided not to include a table for H_3PO_4 .

Table 10: Minimum and maximum values for off-centre-line mass concentrations at ground level as calculated by the UDM

Case	Downwind distance	Off-centre-line P_4O_{10} conc. at ground level (in $mg \cdot m^{-3}$)		
		Min	Base case	Max
Pool diameter (m)	100	0.19 (15)	1.6 (7)	4.8 (3)
	1,000	0.29 (3)	0.79	0.89 (6)
	10,000	$5.0 \cdot 10^{-3}$ (6)	$7.3 \cdot 10^{-3}$	0.15 (15)
Area-specific burn rate ($kg \cdot m^{-2} \cdot s^{-1}$)	100	$1.2 \cdot 10^{-3}$ (0.43)	1.6 (0.076)	23 (0.01)
	1,000	0.15 (0.43)	0.79	0.96 (0.05)
	10,000	$5.7 \cdot 10^{-3}$ (0.05)	0.0073	0.13 (0.43)
Pasquill stability class	100	0.61 (F)	1.6 (D)	22 (B)
	1,000	0.50 (C)	0.79	1.2 (F)
	10,000	$7.3 \cdot 10^{-3}$ (D)	$7.3 \cdot 10^{-3}$	0.49 (F)
Wind speed ($m \cdot s^{-1}$)	100	1.2 (1.5)	1.6 (4)	2.1 (11.5)
	1,000	0.76 (1.5)	0.79	0.83 (11.5)
	10,000	$7.3 \cdot 10^{-3}$ (11.5)	$7.3 \cdot 10^{-3}$	$7.7 \cdot 10^{-3}$ (1.5)

Overall it can be concluded that the UDM calculates huge differences in the vicinity of the pool fire. As the plume moves downwind, the differences in ground level concentration diminish in the 1,000 to 2,000 m downwind distance, depending on the parameter. In distances approaching 10,000 m, the model again calculates higher differences in ground level concentrations. This observation is shown in Table 11, where the difference in the minimum and maximum values per parameter is given as a factor. As can be seen, the area-specific burn rate gives a factor of 19,000 at 100 m downwind distance, which indicates the crucial function of a realistic burn rate value

for P_4 . Moreover, the difference in the pool diameter and Pasquill stability class cases is quite low being in the same order of magnitude (25 and 36 respectively). As noted above, these differences diminish with downwind distance but rise again approaching 10,000 m. Here the difference lies in the same order of magnitude for the pool diameter, area-specific burn rate and Pasquill stability class cases (30, 22 and 67 respectively). Finally, the analysis of the wind speed case gives hardly any difference in ground level concentrations. However, the variation at 100 m downwind distance is slightly increased (factor 2) due to the pushing impact of increasing wind speed on the flame, therefore increasing the ground level concentration in the surrounding area of the fire.

The physicochemical processes in the smoke plume, namely polymerisation, coalescence and therefore aerosol growth are important to improve the modelling with the UDM logic. Larger droplets will rain out due to their size and will therefore increase the deposition velocity (see Section 5.3.). This observation will decrease the actual P_4O_{10} concentration in the smoke plume. However, if it comes to human exposure to the acid smoke, including the deposition in the UDM logic might be of limited value due to the small fraction that is deposited as estimated in chapter 5.3).

Still, if no incorporation of these processes were considered, the uncertainty of the dispersion calculation will increase because these processes will decrease the P_4O_{10} concentration in air.

Table 11: Difference of minimum and maximum values with downwind distance

	Downwind distance	Factor
Pool diameter	100	25
	1,000	3
	10,000	30
Area-specific burn rate	100	19,000
	1,000	6
	10,000	22
Pasquill stability class	100	36
	1,000	2
	10,000	67
Wind speed	100	2
	1,000	1
	10,000	1

6.6 Important parameters to predict P₄ combustion products in air

Given the outcome of the personal correspondence with several stakeholders, the literature study in chapter 5 and the sensitivity analysis in the POLF and UDM spreadsheets the following key parameters to predict the behaviour of phosphorous compounds can be characterised. The focus of the following observations will be in the intrinsic behaviour of P₄ and its combustion products in air. The impact of atmospheric conditions on the dispersion calculation of combustion plumes is undeniable and was shown in chapter 6.2.3, however this is already extensively studied elsewhere (Gifford 1976, Hanna et al. 1982, Pasquill & Smith 1983, UDM Theory document 2005) and will not be part of the following chapter. From the integrated review of the SAFETI-NL theory manuals and the literature as well as the accident reports it can be judged that the following parameters are important:

- **Fire scenario:** As noted before, accident no. 39 (see Appendix C) reveals that not only pool fires are likely outcomes. If it comes to a pressurised release (e.g. due to a failure in the loading arm) of spontaneously combusting P₄, a resulting jet fire will readily discharge combustion products into the air. In the single case of a jet fire the combustion products were detected in 3 km downwind distance and the overall accident lasted 8 hrs. Therefore the incorporation of a jet fires is necessary. The railroad tank car explosion reported by Ross et al. (1987) is not considered here as the explosion happened after 7.5 hrs burning.
- **Diameter of the pool:** The diameter of a liquid pool of combusting P₄ determines the reaction surface of the combusting substance. Given the harsh reaction of P₄ at ambient conditions, a lack of oxygen in the air surrounding the pool is likely decreasing the reaction rate given observations that a lack of oxygen leads to the formation of an oxygen-deterring crust on WP/FELT wedges (Katz et al. 1981, Spanggard et al. 1985). It is not known if this observation is true for P₄ pools. However information is lacking, whether this mechanism is overcompensated by the effect of an increasing pool diameter on the area-specific burn rate, because the POLF logic (Equation (4)) is based on the assumption that the actual area-specific burn rate asymptotes the maximum area-specific burn rate with increasing pool diameter (see sensitivity analysis of pool diameter in chapter 6.3).
- **Reactivity of P₄:** In line with the above, the reactivity of P₄ can be designated as the maximum area-specific burn rate, i.e. the amount of fuel burned per unit of time and area. In this case, the reactivity of P₄ is very high compared to other substances and it is likely that this parameter exceeds the recommended default maximum area-specific burn rate of 0.025 kg·m⁻²·s⁻¹ (RIVM 2009), as given the analysis in chapter 6.1. where a value of 0.076 kg·m⁻²·s⁻¹ was calculated. The reactivity finally determines the formation of hazardous combustion products and the subsequent release into the air.
- **Density of the cloud:** The cloud density is crucial for the fate of combustion products at ground level. First dispersing compounds and the cloud temperature modulate the cloud density. The cloud density finally determines if the cloud is heavier than the surrounding air. The plume is likely to touch the ground, increasing the ground level concentration of hazardous combustion products and putting third parties at danger. However if the cloud density is lower than that of the surrounding air, the less people are exposed to a toxic cloud. The modelling using the UDM spreadsheet revealed that the centre line density of the plume is lower to the density of the atmosphere.

- Chemical reactions in the plume:** Within the first hour of an accidental release of P_4 , rapid conversion to P_4O_{10} will follow. This reaction will be accompanied by the formation of linear and cyclic polyphosphates besides other compounds forming a complex mixture of combustion products. P_4O_{10} will undergo hydrolysis to form H_3PO_4 depending on the humidity in the atmosphere (see below). The polyphosphates maintain polymerisation reactions to higher polyphosphates and form droplets that grow in size with downwind distance by both polymerisation and coalescence.
- Humidity/Rain:** Given the extent of the impact of atmospheric humidity on the fate of P_4 combustion products (see section 5.3), humidity modifies the chemical reactions within the smoke plume over literally the whole range of atmospheric humidities possible in the environment. The higher the humidity, the higher the size of smoke particles in the plume. Moreover, if rain is accompanying an accidental release, the combustion residues are subject to wash out from the plume leading to a substantial mass loss of the plume and decreasing the ground level concentration in air. This is particularly relevant because of the inorganic nature and water-solubility of P_4 combustion products. Contrary to that, if very little moist were available in the atmosphere, chemical reactions will slow down due to the intrinsic reactivity of P_4 combustion products with water, shifting the equilibrium of the chemical reactions to non-water reacting compounds such as P_4O_{10} and polyphosphates rather than H_3PO_4 in the time frame of a few hours after the accidental release.
- Initial plume height/Cloud temperature:** The plume of combustion products rises until the point where the density of the plume is equal to the air density. The height where this condition prevails before it moves further downwind can be considered initial plume height. The initial plume height is determined for the most part by the released heat of the combustion reaction as well as by the release height (UDM Theory Document 2005). Considering a release at ground level, the initial plume height is of relevance for the ground level concentration. A higher plume height will therefore decrease concentration of the combustion mixture at ground level and vice versa
- Physicochemical processes:** Most importantly the physicochemical process within a moving cloud of phosphorus combustion products influence the plume behaviour to a large extent. First the literature survey revealed a polymerisation reaction maintained by phosphates in the initial combustion mixture. As the plume moves downwind, both polymerisation and coalescence within the smoke plume will lead to a rise in droplet diameter, which is further enhanced by the presence of moist in the atmosphere.
- Deposition:** Generally, deposition is distinguished in wet and dry deposition. Wet deposition is settling of an atmospheric pollutant due to the reaction with rain. Dry deposition is settling of pollutant particles due to sedimentation or adherence of smoke particles. It is indeed observed by Spanggard et al. (1985) that gravitational settling of solid and liquid acid particles is an important process to improve the modelling using the UDM logic due to the fact that gravitational settling represents a mass loss in the plume. This process is predominantly dependent on the extent of polymerisation of polyphosphate monomers, coalescence and atmospheric humidity leading to a rise in droplet size (Spanggard et al. 1985), which is further increasing the rate of droplet formation.

6.7 Comparison of the model estimates with accident observations

This chapter is intended to give a comparison of the UDM estimates for the 1 hour-averaged ground level concentrations of P_4O_{10} and H_3PO_4 with actual air measurements performed after accidental releases and air concentrations given in toxicity studies.

Air measurements after accidental releases were rarely undertaken given the unexpected nature of these events. However Badyugin (2009) measured the atmospheric concentration of “phosphoric anhydride” (P_4O_{10}) 1 day after the accident in Lviv area in 2007 (Ukraine) and reported a value $3.5 \text{ mg } P_4O_{10} \cdot \text{m}^{-3}$. Without mentioning the location relative to the accident site. Moreover Badyugin mentioned a sharp decrease in air concentrations of P_4 combustion products after the fire was extinguished by fire fighting personnel meaning that there was no smoke plume on the day of the measurement.

The P_4 fire that happened in 2005 (accident no. 155, see Appendix C) formed a smoke cloud with 4000 m in length, 200 m in width and 50 m in height in a valley, where the chemical plant was located. The authors measured concentration of $2 \text{ mg } P_4O_{10} \cdot \text{m}^{-3}$. However in both cases the authors fail to mention the height at which the measurements were performed as well as the specific downwind distances. Moreover the authors in the second case did not give a time estimate explaining whether P_4 was still burning. Still the air measurements will be incorporated in Table 12.

Table 12: Comparison off-UDM concentration ranges with post-accident measurements and inhalation studies of P_4O_{10} and H_3PO_4

Distance	UDM GL conc. range in $\text{mg } P_4O_{10} \cdot \text{m}^{-3}$ (H_3PO_4)	Accident measurements ($\text{mg } P_4O_{10} \cdot \text{m}^{-3}$)	Major health effect of acidic smoke
100	0.0012 -23 (0.0017 -32)	2-3.5	Irritation of respiratory tract, problems speaking, Irritation of eyes
1,000	0.15-1.2 (0.21-1.6)		
10,000	0.0050-0.49 (0.0050-0.68)		

The comparison the model estimates with measurements undertaken at accident scenes are of limited value due a lacking number of experiments and poor experimental design. The two measurements mentioned do not reflect the time variation of atmospheric concentrations, concentration heights and the effect of dilution by noting the downwind distance.

The study of the accident reports revealed that in some cases, hospitalisation of people was necessary. This fact indicates that victims suffered serious symptoms which impaired the individual’s ability to take protective action to the exposure. Given the definition of the ERPG values in section 5.1.3, it can be assumed that the ERPG-2 value for both P_4O_{10} and H_3PO_4 was readily exceeded at the locations where hospitalised people resided at the time of exposure (AIHA 2011), given that the exposure time is in the order of one hour. If the exposure time is much higher or lower, the corresponding concentration is lower/higher. Consequently, it can be considered that in several cases the time-averaged concentrations were at least equal to the ERPG-2 for P_4O_{10} ($10 \text{ mg} \cdot \text{m}^{-3}$) and H_3PO_4 ($30 \text{ mg} \cdot \text{m}^{-3}$) in accident cases 127, 162, 164. In the first two cases, the unknown authors mentioned an affected area of

51 and 86 km² respectively. Very roughly assuming a circular combustion plume moving in wind direction from the source, it can be concluded that the affected victims were located within 8 to 10 km (circle diameter) downwind distance relative to the accident site. However this affected distance will increase or decrease depending on the atmospheric conditions such as wind speed. Due to lacking data the application of a Gaussian plume area was not feasible.

As no fatalities were reported, the actual time-averaged concentrations in air were possibly lower than the ERPG-3 value for P₄O₁₀ and H₃PO₄ respectively (50 and 150 mg·m⁻³) in the same radius. This means that the victims have been exposed to time-averaged concentrations ranging between 10-50 mg·m⁻³ and 50- 150 mg·m⁻³ for P₄O₁₀ and H₃PO₄. Having these estimates in mind. Comparing these rough estimates with time-averaged concentrations of the UDM model it is obvious that the results of the UDM are one to two orders of magnitude lower than the ERPG values presented.

The findings presented herein have a large uncertainty due to the quality data. Emergency air measurement data and the specific locations of hospitalised victims are crucial for the assessment of downwind concentrations. Therefore the comparison of the model estimates remains inconclusive.

7 Discussion

The present study revealed that 144 P_4 accidents occurred between 1967 and 2012. 77% of these accidents involve derailment of goods trains leading to accidental releases of P_4 from tank wagons. Most accidents are small-scale spillages and near-misses. A large-scale release from an atmospheric tank leads mainly to P_4 pool fires giving an acid combustion plume, which exposes third parties to a complex mixture of irritant combustion products. The study goal was to determine the means by which the modelling of the behaviour of such a combustion plume using POLF/UDM models can be improved. A large release from a pressurised tank will yield a jet fire with irritant combustion products.

The main difficulty was the lack of experimental data on the release behaviour and the behaviour of hazardous combustion products in air. The findings and recommendations presented herein are based on actual case reports and experimental work that was conducted under controlled laboratory conditions. The findings and recommendations help to validate the POLF and UDM models regarding additional fire scenarios, P_4 area-specific burn rate, the fraction of unburned P_4 , as well as the chemical reactions in the smoke plume. This is further compared with the presentation of post-accident P_4O_{10}/H_3PO_4 air concentrations using the output of a POLF/UDM sensitivity analysis.

From an extensive literature survey it is evident, that other fire scenarios such as jet fires and tank car explosions can occur (Ross et al 1987, accident no. 46) although these scenarios are rare compared to cases involving small spills. Moreover the combustion of P_4 yields an unburned fraction ranging between 8 and 40 % (DFG 2002a, Katz et al 1981), which was the result of an oxygen-deterring crust on the reaction surface of WP/FELT wedges. Still P_4 can be considered to maintain a high area-specific burn rate and it is therefore recommended to use $0.076 \text{ kg}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$.

Chemical reactions in the P_4 combustion plume include most importantly

- polymerisation of initially formed monophosphates to acid polyphosphates ($\text{pH}\approx 2.1$),
- hydrolysis of polyphosphates to yield mainly H_3PO_4 ,
- coalescence of polymers,
- aerosol diameter growth by both polymerisation and coalescence of polymers and
- deposition of smoke aerosols via gravitational settling towards the ground ground (dry deposition) or wash out (wet deposition).

The comparison of the model output with inhalation studies and actual measurements at the scene revealed values in the same order of magnitude. The UDM ground level concentrations for P_4O_{10} are may exceed the Dutch LBW threshold for this compound at downwind distances within 100 m from the scene, which is also the case for H_3PO_4 ground level concentrations as the ground level mass concentration differ only by a factor of 1.38. Furthermore, this is the radius in which serious health effects to the human pulmonary tract are likely to occur given the results of inhalation studies with P_4O_{10} and H_3PO_4 .

Interestingly, the PFGEN/UDM model used by Witlox & Woodward included a formulation for the synthesis of H_3PO_4 (reaction of P_4O_{10} with moisture) was available in the UDM at that time, which is also recommended herein to be re-included for a more realistic picture of smoke dispersion if time frames > 2 days after the accidental release of P_4 are important. This is closely related to the fact that the past UDM gave sensitive results for the variation of relative humidity by giving an estimate for the

zero-order decrease rate of the mass fraction of water ($dw_{R2}/dt = -k_1$) for the hydrolysis reaction from P_4O_{10} to H_3PO_4 , for time frames of one to a few hours. This is not the case in the UDM version of the present study. However, as time periods >2 days are important, a lower reaction rate should be applied in the future.

Moreover, the authors noted that for very large wind speeds the fire cylinder will touch the ground. Therefore the same implication applies for the UDM, which will give higher ground level mass concentrations just beyond the transition from the pool fire model for very large wind speeds. This observation is confirmed in this study, due to the fact that the initiation of the POLF/UDM transition was calculated further downwind for increasing wind speeds. The authors also emphasised the spill rate as a crucial determinant of the UDM behaviour. This finding can be indirectly confirmed here, because the pool diameter logic largely depends on the spill rate. The results of this study indicate higher centre-line concentrations with increasing pool diameter. However the spill rate variation in this study was limited by a constant pool diameter over all spill rate cases to ensure consistency with the variation of the area-specific burn rate. The reason for this is the fact that the highest area-specific burn rate case should always be lower than the spill rate of the base case to beware a decreasing pool diameter with increasing area-specific burn rate.

The MAK publication on P_4O_{10} casts doubt concerning the experimental determination of P_4O_{10} and H_3PO_4 (DFG 2002b). Here, P_4O_{10} hydrolysis was reported to readily occur upon P_4O_{10} sampling and in P_4O_{10} test chambers and therefore published concentrations of P_4O_{10} (e.g. from inhalation studies) should be considered with caution. However, regarding the small difference in intervention values for P_4O_{10} and H_3PO_4 , this observation might be of minor importance.

The area-specific burn rate (m) that was derived from the smoke grenade deployment performed by Berkowski et al (1981) ($m = 0.03 \text{ kg} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$) was assumed to equal the maximum area-specific burn rate m_{\max} (Equation (4)) via $L_b = 0$. This value is at least not contradicting the derived m_{\max} ($m_{\max} = 0.076 \text{ kg} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$) which is approximately 2.5 times higher than the area-specific burn rate (m) derived from Berkowski and coworkers in 1981.

The limitation of this approach is the assumed value of 0 m for the correlation factor L_b . If $L_b = 0$ m, the area-specific burn rate m will always equal the maximum area-specific burn rate m_{\max} . However, the L_b values for e.g. propane or kerosene are 2 m and 10 m respectively (POLF Theory Document 2005) leading to lower values for m than m_{\max} . Combining the area-specific burn rates and the wedge diameter of the WP/FELT wedges presented in this study and transforming equation (4), L_b equals 0.29 m which is substantially lower than the values for aforementioned hydrocarbons. This is further confirmed by the fact that the cellulose fraction in the WP/FELT wedges is used as a burn rate modifier to markedly optimise the smoke generation upon deployment in military operations (Lombardi 2012). The cellulose matrix comprises a fraction of 15-20 % (Berkowitz et al. 1981, Spangord et al. 1985) and allows a higher packing density in the smoke grenade limiting the value of the burn rate derived from this experiment, because elemental P_4 was not analysed in the study by Berkowski et al. (1981).

On the other hand, this observation puts forward evidence in favour of the area-specific burn rate ($0.076 \text{ m}^{-2} \cdot \text{s}^{-1}$) that was derived from the POLF Theory Document (2005) and that is still 3 times higher than the area-specific burn rate for hazardous products in chemical warehouses without flammable liquids (RIVM 2009). This is supported by the fact that P_4 ignites instantaneously and maintains harsh reactions over the entire burn time (unpublished observation).

An additional limitation is the assumption of a constant pool diameter in section

Besides the recommendations that will follow in chapter 8 further refinements should include the determination of the unburned fraction of P_4 , which ranges between 10-40% (Katz et al. 1980, DFG 2002a) and could be validated in experiments. However, these values are derived from deployments of WP/FELT munitions and may not reflect

the behaviour of elemental P_4 , although it is certain that a fraction of unburned P_4 will always remain (Maas & Durka 2012)

Additional refinements may be developed for a link between a jet fire scenario and smoke dispersion as suggested by Witlox & Woodward (1997). The investigation of the accident analysis indeed revealed that a P_4 jet fire is a possible outcome. The rail road tank car explosion mentioned in this study should not be included as an additional scenario due the precedent pool fire in this case.

Improvements of the UDM could include significant further testing of m_{\max} ($0.076 \text{ m}^2 \text{ s}^{-1}$) and experimental validation of this value is of importance.

It could be further judged whether the present models over- or underestimate the ground level concentrations of P_4O_{10} before incorporating the present findings into the models.

An additional refinement of the H_3PO_4 formulation from section 6.3 can be considered. Consequently, this formula presumes that all P_4O_{10} is converted to H_3PO_4 . A more advanced approach could be to make f_{moles} time-dependent with the value 4 being the maximum:

$$f_{\text{moles}} = 4 \cdot (1 - e^{-at})$$

in which a accounts for the half life time of the reaction and t for the time of interest. The parameter a in the exponent could furthermore depend on the air humidity.

Further improvements that were raised by Witlox and Woodward (1997) could comprise reactions for other compounds like ammonia (NH_3), sulphuric compounds and chlorine (e.g. SO_3 and Cl_2), because goods trains are often composed of tank wagons with different inventories.

8 Recommendations to improve the modelling in the future

The review of the literature, the study of accident reports as well as the modelling using the POLF/UDM spreadsheets finally leads to recommendations by what means the modelling of P_4 fires using the POLF/UDM spreadsheets can be improved. Moreover, the focus of the subsequent analysis will be on the first hour after an accidental release of P_4 to qualify the future RIVM CV (Centrum Veiligheid) department for giving advice on P_4 fires in the field of emergency response.

The flame characteristics including the fire dimensions, fractions in combustion mixture, flow rate of the combustion mixture, fire temperature and the area-specific burn rate input are well covered by the POLF logic if it comes to a pool fire of P_4 . It is advised to use the pool fire scenario for scenarios involving accidental releases from tank wagons, drums, road tankers and pipelines. If an accidental release from a pressurised loading arm is considered, the application of the jet fire model with a subsequent link to the dispersion model UDM, which is not available so far.

The dispersion of the combustion mixture can be applied using Gaussian dispersion formulations, which are incorporated into the UDM logic. The UDM gives endpoint data such as plume geometry, centre-line height, centre-line and off-centre-line concentrations of P_4O_{10} with downwind distance as well as other dispersion data.

The intermediate reaction from P_4 to P_4O_{10} is presumed to be very important in timeframes of 1 hr after a chemical accident. Given a half-life of 49 hrs for the conversion of smoke residues to H_3PO_4 (Spanggard et al. 1985), P_4O_{10} is recommended to be the compound of interest with a LBW threshold of $20 \text{ mg}\cdot\text{m}^{-3}$. Although P_4O_{10} and H_3PO_4 exert the same health effects, P_4O_{10} has a lower LBW threshold than H_3PO_4 ($50 \text{ mg}\cdot\text{m}^{-3}$), which can be explained by the fact that the mass of 1 mole P_4O_{10} is a factor 1.7 less than the mass of 4 moles H_3PO_4 . Less molecules of P_4O_{10} are necessary to exert the same health effect. The use of H_3PO_4 as compound of interest is only recommended for time frames exceeding 49 hours (or 2 days) after an accident and if equilibrium conditions are presumed.

The reflection of the whole range of compounds present in the complex combustion mixture is not feasible to apply in the UDM model and therefore in SAFETI-NL. As the combustion mixture will be hydrolysed in the air to form H_3PO_4 , using P_4O_{10} as endpoint is reasonable given the fact that P_4O_{10} will be hydrolysed upon contact to mucous tissues of humans as well as the limited time frame of interest. Therefore, the use of P_4O_{10} only will also reflect a conservative modelling approach, because there will always be a fraction of less reactive compounds in the combustion mixture (Katz et al 1980, Berkowitz et al 1981, Spanggard et al. 1983, 1985) exposing humans to a less dangerous combustion mixture in real life situations, considering P_4O_{10} , H_3PO_4 and polyphosphates and other phosphorous acids.

Polymerisation in the smoke plume will add to a changing composition of the cloud in time and space. In addition, monophosphates which are formed as a result of the combustion reaction, maintain polymerisation to polyphosphates within the first hour of an accidental release (Spanggard et al 1985). The polymerisation reaction will lead to an increase of aerosol diameter (mass median diameter $\approx 1.3 \mu\text{m}$, Spanggard et al. 1985) by both polymerisation and coalescence. The subsequent increase in aerosol mass will lead to a loss of mass in the smoke plume due to gravitational settling (dry deposition) (Spanggard et al. 1985). It is therefore recommended to implement a polymerisation/coalescence logic in the dispersion formulation to account for the increase of aerosol diameters. Nevertheless, if no implementation of such logic takes place, the model is presumed to overestimate the ground level concentration, because the deposited fraction of the combustion mixture is included in the calculation of the

ground level concentration. From the literature it is hard to judge at which downwind distance this observation will have effect.

The effect of atmospheric humidity in the reaction within the smoke plume of P_4 combustion products is undeniable given the role of water for the fate of the compounds in question. Spanggord et al (1985) found relative humidity to have a profound effect on the aerosol diameter with a slight trend towards larger particles with increasing relative humidity. Moreover, the fraction of deposited aerosols as a function of aerosol diameter differed largely at 10,000 m downwind distance for aerosol diameters ranging from 0.5 to 5 μm (Spanggord et al. 1985). The amount of smoke formed rises also exponentially with relative humidity. Moreover, the past PFGEN/UDM model incorporated a zero-order decrease rate of the mass fraction of water ($dw_{R2}/dt = -k_1$) for the hydrolysis reaction from P_4O_{10} to H_3PO_4 which should be updated for time frames >2 days. It is therefore strongly recommended to incorporate the effect of humidity on particle growth, H_3PO_4 formation and consequently deposition into the UDM logic. If the effect of humidity is not incorporated in the UDM, the ground level concentration will be underestimated, because smoke generation largely depends on relative humidity, showing exponential growth with increasing humidity. However the P_4O_{10} concentration will be overestimated if the effect of humidity is not taken into account.

Gravitational settling of smoke aerosols was found to dominate deposition via Brownian and turbulent motion (Spanggord et al 1985). This is particularly true for increasing relative humidity. The deposition of aerosols via gravitational settling depends on the particle diameter and therefore on the particle area, which increases by the square of the particle diameter.. The averaged deposition velocity was calculated to $0.045 \text{ cm}\cdot\text{s}^{-1}$ in the present study from data obtained by Spanggord et al (1985). In the case of a smoke plume covering an area of 85 km^2 (see accident no. 162), the deposited smoke mass lies in the range of 3000 kg in the first hour after an accidental release if a uniform time-averaged ground level concentration of $20 \text{ mg } P_4O_{10}\cdot\text{m}^{-3}$ is assumed. However applying higher time-averaged concentrations would lead to more loss of material for huge smoke plumes in the order of 85 km^2 . It is thereby recommended to implement a deposition formulation to account for gravitational settling. Here, the DNV model HGSYSTEM can be considered, which is feasible to be applied for dry deposition. If no implementation is considered, the UDM will slightly overestimate the ground level concentration because the deposited fraction is not taken into account by the UDM logic.

Table 13 summarises the precedent recommendations.

Table 13: Features in P₄ fires and combustion plumes and coverage by POLF/UDM model

	Output	Coverage by model package SAFETI-NL (POLF/UDM)	Recommendation
General	Fire type	Yes, covered by POLF (Pool Fire Model): Flame geometry, mass fractions of combustion mixture of P ₄ , which also gives output data for dispersion modelling (UDM)	Use of POLF model or jet fire model (JFSH) with UDM link
Chemical reactions	Fraction of unburned P ₄	Yes, a fraction of unburned P ₄ can be incorporated via the definition of the combustion efficiency in POLF, but its use limited to due deficiencies in the formulation. Katz et al (1980) and DFG (2002a) report a fraction of 40% and 10% unburned P ₄ on WP/FELT	Set combustion efficiency to 1
	Chemical reaction: P ₄ to P ₄ O ₁₀	Yes, model package assumes either zero or full reaction to P ₄ O ₁₀	Use of P ₄ O ₁₀ as compound of interest within the first hour after an accidental release
	Chemical reaction: P ₄ O ₁₀ to H ₃ PO ₄	No, immediate transformation from P ₄ to H ₃ PO ₄ is possible to presume in POLF but not necessary given the time frame of 1 hr after an accident as well as the half-life of 2 days or the hydrolysis reaction of polyphosphates to form H ₃ PO ₄ (Spanggard et al.1985)	Use of H ₃ PO ₄ if post-accident times ≈2 days are important
	Other combustion products	No, model assumption is either full or zero reaction to P ₄ O ₁₀ (or possibly H ₃ PO ₄): Linear/cyclic condensed polyphosphates (n=1-22), H ₃ PO ₄ , H ₃ PO ₃ , hypophosphorous acid (H ₃ PO ₂), H ₄ P ₂ O ₇ , PH ₃ and red phosphorus (different allotrope of P ₄) are formed as well	Use of P ₄ O ₁₀ as compound of interest within the first hour after an accidental release
	Polymerisation of monophosphates to polyphosphates	No, the reaction of acidic monophosphates to form polyphosphates results in increase of droplet diameter. This will result in gravitational settling (Spanggard et al. 1985)	Implementation of polymerisation/coalescence logic in UDM or no implementation if overestimation of ground level concentration is desired
	Coalescence of smoke aerosols	No, coalescence of smoke aerosols was found to increase the particle diameter and leads to deposition via gravitational settling (Spanggard et al. 1985)	
	Humidity and rise in droplet size	Not covered, increasing humidity leads to increased diameter of smoke aerosols	Implementation of reaction rate of the mass fraction of water as done for PFGEN/UDM. Implementation of logic for particle diameter growth
	Gravitational settling of smoke aerosols	Not covered, gravitational settling is an important process leading to a substantial loss of material from the smoke plume (depending on aerosol diameter)	Implementation of deposition logic necessary. Use of DNV model HGSYSTEM

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Figures

Figure 1: Date accessed 01/11/2013
<http://www.rferl.org/content/article/1077823.html>

Figure 2: Date accessed 01/11/2013
<http://ukraine-gdp.blogspot.nl/2007/07/ukrainians-accident.html>

Figure 3: Date accessed 01/11/2013
<http://www.rferl.org/content/article/1077659.html>

Appendix A

Model description SAFETI-NL

The knowledge presented herein is intended to support the reader in understanding the use of certain models and the chronology of calculation steps that are incorporated into the SAFETI-NL model package. Figure 35 comprises the base for the following analysis.

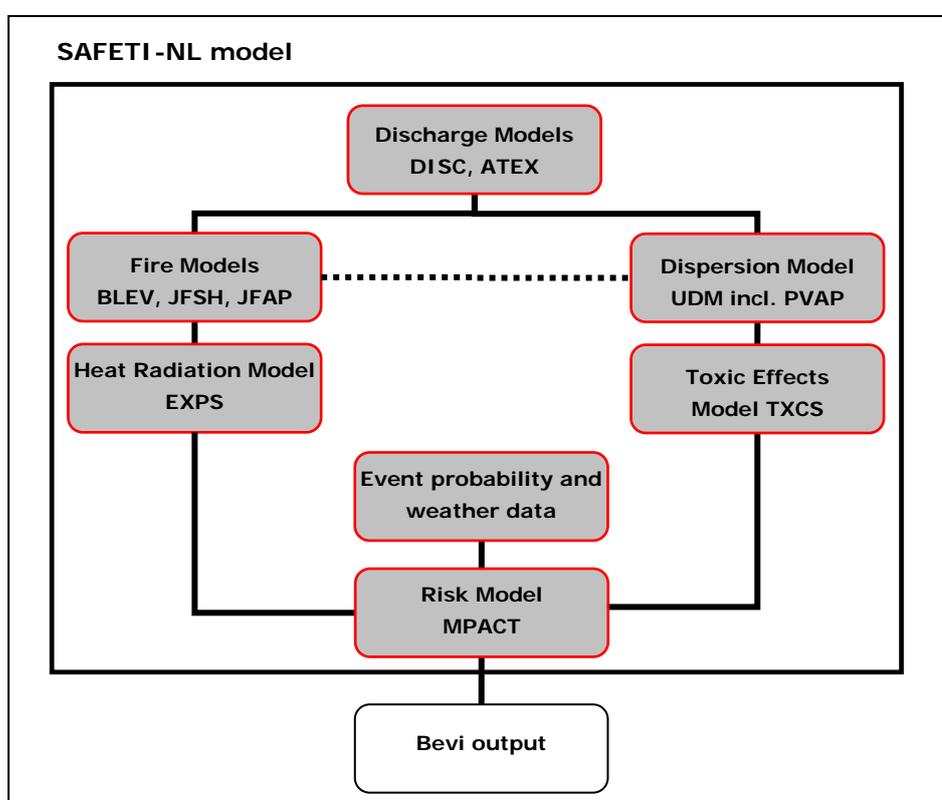


Figure 35: Model structure of SAFETI-NL model package (simplified for this study)

The loss of containment (LOC) definition step is processed by the material properties, the process conditions under which the chemical is kept, risk data, scenario data, elevation and direction of the discharge. The scenario type constitutes the type of discharge (e.g., leakage from a pipeline or instantaneous release from a vessel). Due to production process requirements, a vessel carrying the chemical can be elevated above the ground, which is of importance for the initial plume rise if it comes to discharge into the atmosphere. If one imagines a release of a chemical, it is assumed, that the release angle can range between 90° (vertical) and 0° (horizontal).

The discharge model step uses the release type scenario to calculate the mass flow rate, temperature of the discharge, liquid fraction of the chemical, velocity of the release and droplet size (DNV DISC and ATEX Theory Documents 2005).

The output of the discharge model is used by the dispersion model to predict the cloud development with distance downwind and calculates its geometry as well as the concentration of the chemical with downwind distance. If a horizontal and elevated

discharge is assumed, evaporating droplets move away from the plume centre-line to the ground. When droplets reach the surface, complete rain out is assumed, leading to the formation of a spreading liquid pool. This pool will represent a secondary source of vapour (DNV UDM Theory Document 2005). The dispersion model calculates passive, turbulent and heavy plume dispersion. Following an elevated, horizontal discharge of a pressurised chemical, the release is modelled as a circular cross section, which levels off to the ground and tends to flatten into an ellipse. The cloud may lift-off until constrained by the atmospheric mixing layer. The centre-line velocity decays with downwind distance until either the heavy gas or passive dispersion become dominant. Turbulent dispersion of a cloud is characterised by rapid pressure and velocity changes with a low diffusion momentum (Davidson 2004). The concentration of aerosols may vary in time at a specific point x in downwind direction, resulting from either time-varying releases or time-varying wind regimes (DNV UDM Theory Document 2005). Ultimately, the dispersion model will give a concentration profiles for time-varying releases well as width and length estimates to describe the geometry of the plume. The dispersion post processing step produces concentration plots, concentration contours, foot prints and plume side views. Moreover it calculates the probability of death for a given position and substance. If the chemical is flammable this step calculates immediate ignition effects using either BLEVE (boiling liquid in a vessel expands leading to explosion), pool fire (ignition of a pool) or jet fire (fire of a continuous spray release) models, depending on the scenario. Delayed ignition effects are applied if the user wants to include delayed ignition of a substance, i.e. when an evaporation cloud passes a downwind ignition source. This step calculates the flammable mass of the cloud as well as the probability for delayed ignition (DNV MPACT Theory 1997). In addition, the dispersion post-processing model approximates the cloud boundary in which a cloud can ignite (LFL fraction boundary) represented by an ellipse.

The subsequent risk model calculates individual and societal risks in line with the Dutch legislation. For individual risk, SAFETI-NL calculates an array of individual risk for a specific location totalled over all events and weather conditions in question. Societal risk is estimated by accounting for the number of people affected by the outcome of an event.

The risk ranking of individual and societal risks constitutes the contribution of an event to the risk at a limited number of locations within the risk contours. The risk ranking is included to compare the relative importance of different events, which are subject of the QRA (DNV MPACT Theory 2005). In the risk calculation, the analysed events will have a cumulated frequency of occurrence F , and a predicted number of persons harmed, N . The output of this analysis is a F/N curve, which displays N (x-axis) against F (y-axis) with a mostly negative slope (CCPS 2009). The F/N curve designates the development and impact of an accident for a given combination of weather conditions (wind speed and weather stability) and wind direction. If one thinks of four weather conditions and eight wind directions, an accidental release would be calculated with 32 outcomes.

The potential life lost (PLL) is an integrated measure to simplify the risk analysis that accounts for the population exposed to the risk. It can be either based on individual or societal risk estimates. In the first case, the individual risk is multiplied with the number of persons probably harmed (N). The PLL can be further based on societal risk calculations. Here, all probabilities of fatal accidents are summed.

The risk integral (RI) is an additional risk measure to further simplify the output of the risk analysis. It accounts for the greater societal aversion to accidents with increasing values of harmed people (N).

Finally, SAFETI-NL provides risk contours, F/N curves, population counting, and risk ranking for both individual and societal risk estimates. Risk contours account for the orientation of an event and the location being considered for individual risk. Thus, the distribution of individual risk over an area is the output of interest, which is displayed

as risk contour or array. Together with the individual risk ranking results, the risk contours constitute the societal ranking results which account for the number of people affected by an event. Together with societal ranking results, the F/N curves will represent the societal output of the risk calculation. Thereby SAFETI-NL calculates the risk outcome as prescribed in the Bevi. Further information on the underlying assumptions and equations can be found in the SAFETI-NL technical documentation.

Appendix B

1st search in MEDLINE and SCOPUS databases

- 1 (phosphorus or phosphoric acid* or phosphorous acid* or sodiumdihydrogenphosphate or disodiumhydrogenphosphate or phosphorus gas or phosphorus pentoxide or diphosphoruspentoxide or sodiumtripolyphosphate or phosphine).ti. (14615)
- 2 *phosphorus/ or *phosphoric acids/ or *phosphorus pentoxide/ or *phosphine/ (15227)
- 3 (7723-14-0 or 7664-38-2 or 1314-56-3 or 7758-29-4 or 7803-51-2).rn. (30948)
- 4 1 or 2 or 3 (38614)
- 5 (accident* or accident* or event or (loss adj3 containment) or release or leakage or rupture or fire or fires or explosion* or gaseous pollution or toxic clouds or liquid pools).ti. or (gaseous pollution or toxic clouds or liquid pools).ab. (182619)
- 6 4 and 5 (296)
- 7 (process conditions or aggregate state or pressure or temperature or ignition or flammability or chemical reaction*).ti. (184642)
- 8 4 and 7 (257)
- 9 (dispersion or air or plume or distance or humidity or moisture or water content or reaction rate or wind speed or thermodynamic* or spill behavi* or pool behavi*).ti. (77442)
- 10 4 and 9 (186)
- 11 (exposure or toxic* or physical effects or fatalities or injuries or burns or burning or burn rate or burn injuries or blast injury or heat-radiation).ti. (256613)
- 12 4 and 11 (585)
- 13 (risk assessment or risk analysis or risk factors).ti. (58167)
- 14 4 and 13 (48)
- 15 6 or 8 or 10 or 12 or 14 (1350)

Due to the amount of non-relevant literature and possibly missing compounds a modification of the search strategy was considered. Additional Boolean logic of compounds in the search strategy included "disodiumtripolyphosphate", "*polyphosphates", "tetraphosphorus decaoxide" and "pentasodiumtriphosphate". Furthermore, "quantit*" and "amount" were included to account for quantities of chemical released. Broader terms linking to the atmosphere like "weather conditions", "wind direction" and "wind speed" were additionally incorporated into the new search strategy. The term "heat radiation" was added to include more results linked to physical effects of phosphorus fires. The search strategy was therefore modified (2nd search).

2nd search in MEDLINE and SCOPUS databases

- 16 (phosphorus or phosphoric acid* or disodiumtripolyphosphate or polyphosphates or phosphorus gas or tetraphosphorus decaoxide or phosphorus pentoxide or diphosphoruspentoxide or pentasodiumtriphosphate or phosphine).ti. (15232)
- 17 *phosphorus/ or *phosphoric acids/ or *phosphorus pentoxide/ or *phosphine/ or *polyphosphates/ (16071)
- 18 (7723-14-0 or 7664-38-2 or 1314-56-3 or 7758-29-4 or 7803-51-2 or 16752-60-6).rn. (30966)

- 19 16 or 17 or 18 (39899)
20 (accident* or accident* or event or (loss adj3 containment) or release* or leakage or rupture or fire or fires or explosion* or gaseous pollution or toxic clouds or liquid pools).ti. or (gaseous pollution or toxic clouds or liquid pools).tw. (189879)
21 accidents/ or chemical hazard release/ or accidents, occupational/ or disaster planning/ or explosions/ or burns/ or burns, chemical/ or fires/ or smoke/ (88680)
22 19 and (20 or 21) (489)
23 (process conditions or aggregate state or pressure or temperature or ignition or flammability or chemical reacti* or (quantit* adj5 released) or (amount adj5 released) or modulating factors).ti. (185143)
24 19 and 23 (272)
25 (dispersion or air or plume or distance or humidity or moisture or water content or reaction rate or weather conditions or wind speed or wind direction or thermodynamic* or thermochem* or thermal behaviour or spill behavi* or pool behavi*).ti. (78582)
26 19 and 25 (197)
27 (exposure or toxic* or physical effects or fatalities or injuries or burns or burning or burn rate or burn injuries or blast injury or heat radiation).ti. (257992)
28 19 and 27 (601)
29 (risk assessment or risk analysis or risk factors).ti. (58193)
30 19 and 29 (48)
31 22 or 24 or 26 or 28 or 30 (1524)
32 31 not 15 (174)
33 from 32 keep 18,35,55,80,96,113,141,143,152,166,168 (11)

Additional search term using GOOGLE

"phosphor* AND white AND environmental fate AND air AND acid AND pentoxide AND combustion"

Appendix C

The search in the ARIA database included the terms "PHOSPHORUS AND NOT CHLORIDE", because the database accounts for many accidents involving phosphorus trichloride (PCl₃). Due to the fact, that this compound maintains very different chemical reactions, it was left out of the search. The query in the MARS database was simply "PHOSPHORUS" to miss as few information as possible. In the German ZEMA database, the term "PHOSPHOR" was used due to different spelling of P₄ in the German language.

The search term in the FACTS database was modified for the following database flags:

- PHOSPHORUS YELLOW
- PHOSPHORUS WHITE
- PHOSPHORUS PENTOXIDE
- PHOSPHORUS WASTE
- PHOSPHORUS (N.O.S. [not other specified])

Here, all results for "PHOSPHORUS YELLOW" were flagged as "PHOSPHORUS WHITE". The search in the PHMSA accident database was "PHOSPHORUS WHITE", because using only "PHOSPHORUS" gave too much non-relevant literature.

Finally the analysis in the Disasters Database of the United Nations Environmental Program (UNEP) showed no results using "PHOSPHORUS" as search query.

Table 14: List of accidents involving elemental phosphorus and related substances

No.	Year	Country	Activity	Location	Chemical	Fatalities	Injuries	Summary
1.	1967	D	PROC	CHEMF	WATER PHOSPHORUS N.O.S.	5	9	Slag douche for cooling slag failed and water entered phosphorus furnace forming detonating gases (P ₄ , CO and H ₂) which exploded causing fire and 14 casualties
2.	1971	USA	RAILT	RAILW	PHOSPHORUS WHITE, IN WATER	0	0	
3.	1971	USA	RAILT	RAILW	PHOSPHORUS WHITE, IN WATER	-	-	
4.	1971	USA	RAILT	RAILW	PHOSPHORUS WHITE, IN WATER	-	-	
5.	1971	USA	RAILT	RAILW	PHOSPHORUS WHITE DRY	-	-	
6.	1971	USA	RAILT	RAILW	PHOSPHORUS WHITE , IN WATER	-	-	
7.	1972	USA	RAILT		PHOSPHORUS WHITE, IN WATER	-	-	-
8.	1973	NL	RAILT	RAILY	PHOSPHORUS WHITE	-	-	Smoke emission out of an empty freight wagon due to self-ignition of yellow phosphorus residues.
9.	1973	USA	RAILT		PHOSPHORUS WHITE, IN WATER	-	-	
10.	1973	USA	RAILT		PHOSPHORUS WHITE, IN WATER	-	-	
11.	1973	USA	RAILT		PHOSPHORUS WHITE, IN WATER	-	-	
12.	1973	USA	RAILT		PHOSPHORUS WHITE, IN WATER	-	-	

13.	1973	NL	USE/APP	CHEMF	PHOSPHORUS WASTE	-	3	At an acid processing plant, a measuring device of the warm water supply for a phosphorus-dosing tank clogged. After analysing the clog, the gauge was removed out of the pipe. The gauge had not been removed entirely and was still attached to the pipe by one bolt. The clogged flowmeter was then removed and the operators did not bother to clean the line even though they knew phosphorus might be in there. While the gauge was being removed completely, phosphorus sludge splashed onto three operators and caught fire leading to burn injuries.
14.	1973	NL	CLEAN	CHEMF	PHOSPHORUS WASTE	1	-	In a phosphorus-using chemical factory, an employee tried to clean a pipe system in which warm water was mixed with phosphorus. However, the operator did not open the valves, which had to be opened for this cleaning step. The entire pipe system was put under a pressure of 600 kPa. In order to make the water stream he opened a valve, which got subsequently loose, atomising the phosphorus sludge and burning the operator to death.
15.	1974	USA	RAILT		PHOSPHORUS WHITE, IN WATER	-	-	
16.	1974	USA	RAILT		PHOSPHORUS WHITE, IN WATER	-	-	
17.	1974	USA	RAILT		PHOSPHORUS WHITE, IN WATER	-	-	
18.	1974	USA	RAILT		PHOSPHORUS WHITE, IN WATER	-	-	
19.	1974	USA	RAILT		PHOSPHORUS WHITE, IN WATER	-	-	
20.	1974	USA	RAILT		PHOSPHORUS WHITE, IN WATER	-	-	
21.	1974	USA	RAILT		PHOSPHORUS WHITE, IN WATER	-	-	
22.	1974	USA	RAILT		PHOSPHORUS WHITE, IN WATER	-	-	
23.	1975	USA	RAILT		PHOSPHORUS WHITE, IN WATER	-	-	
24.	1975	USA	RAILT		PHOSPHORUS WHITE, IN WATER	-	-	

25.	1975	USA	RAILT		PHOSPHORUS WHITE, IN WATER	-	-	
26.	1975	USA	RAILT		PHOSPHORUS WHITE, IN WATER	-	-	
27.	1975	USA	RAILT		PHOSPHORUS WHITE, IN WATER	-	-	
28.	1976	USA	RAILT		PHOSPHORUS WHITE, IN WATER	-	-	Volume of spillage: 1 liquid gal
29.	1976	USA	RAILT		PHOSPHORUS WHITE, IN WATER	-	-	Volume of spillage: 1 liquid gal
30.	1976	USA	RAILT		PHOSPHORUS WHITE, IN WATER	-	-	Volume of spillage: 1 liquid gal
31.	1976	USA	RAILT		PHOSPHORUS WHITE, IN WATER	-	-	
32.	1976	USA	RAILT		PHOSPHORUS WHITE, IN WATER	-	-	Volume of spillage: 1 liquid gal
33.	1976	USA	RAILT		PHOSPHORUS WHITE, IN WATER	-	-	Volume of spillage: 5 liquid gal
34.	1976	USA	RAILT		PHOSPHORUS WHITE, IN WATER	-	-	Volume of spillage: 1 liquid gal
35.	1976	USA	RAILT		PHOSPHORUS WHITE, IN WATER	-	-	Volume of spillage: 1 liquid gal
36.	1976	USA	RAILT		PHOSPHORUS WHITE, IN WATER	-	-	Volume of spillage: 1 liquid gal
37.	1976	USA	RAILT		PHOSPHORUS WHITE, IN WATER	-	-	Volume of spillage: 1 liquid gal
38.	1976	USA	RAILT		PHOSPHORUS WHITE, IN WATER	-	-	Volume of spillage: 1 liquid gal
39.	1977	CH	TRANSS	RAILY	PHOSPHORUS WHITE	1	-	During transfer of P ₄ into a tank wagon, an accidental spray release caused a 5m high jet fire killing one person. The burn residues contaminated the air within a range of 3 km from the source. The fire department cooled the tank wagon with water. Overall, the accident lasted for ca. 8hrs.
40.	1977	USA	RAILT		PHOSPHORUS WHITE, IN WATER	-	-	Volume of spillage: 1 liquid gal
41.	1977	USA	RAILT		PHOSPHORUS WHITE, IN WATER	-	-	Volume of spillage: 1 liquid gal
42.	1977	USA	RAILT		PHOSPHORUS WHITE, IN WATER	-	-	Volume of spillage: 1 liquid gal

43.	1977	USA	RAILT		PHOSPHORUS WHITE, IN WATER	-	-	Volume of spillage: 300 liquid gal
44.	1977	USA	RAILT		PHOSPHORUS WHITE, IN WATER	-	-	Volume of spillage: 12532 liquid gal
45.	1977	USA	RAILT		PHOSPHORUS WHITE, DRY	-	-	Weight of spillage: 1 solid lb
46.	1978	USA	RAILT	RAILW	PHOSPHORUS WHITE	-	6	A draw bar of an eastbound freight train with 99 tank cars got loose, ripping up some sleepers of the railroad line. Damage of a wheel led to derailment of the 32nd tank car. A tank car with 76.34 m ³ molten P ₄ was overturned and punctured releasing some inventory. The spill caught fire with a flame height of 15 m forming of a plume of phosphorus pentoxide. 6 adjacent freight wagons loaded with lumber and 1 freight car loaded with paper bags were set on fire. An explosion of the P ₄ tank car occurred due to very high pressure within the tank car after burning for several hours. It is thought that the water layer in the tank car boiled and established pressure. Fragments were scattered within a range of 400m of the accident site. In total, the accident caused 6 injuries.
47.	1978	NL	USE/APP	CHEMF	PHOSPHORUS WHITE	-	1	Two operators working on a phosphorus sludge drain pipe under steam pressure (343.2 kPa) were exposed to molten phosphorus sludge. The protective clothing of one of the operators was too small not protecting his legs. Upon rupture of the drain pipe this worker suffered severe chemical burns on the skin not covered by protective clothing.
48.	1978	USA	RAILT		PHOSPHORUS WHITE, DRY	-	-	Volume of spillage: 7000 liquid gal
49.	1978	USA	RAILT		PHOSPHORUS WHITE, IN WATER	-	6	Volume of spillage: 17310 liquid gal
50.	1978	USA	RAILT		PHOSPHORUS WHITE, DRY	-	-	
51.	1978	USA	RAILT		PHOSPHORUS WHITE, IN WATER	-	-	Weight of spillage: 196624 solid lb
52.	1978	USA	RAILT		PHOSPHORUS WHITE, IN WATER	-	-	
53.	1978	USA	RAILT		PHOSPHORUS WHITE, DRY	-	-	Weight of spillage: 10 solid lb

54.	1978	USA	RAILT		PHOSPHORUS WHITE, IN WATER	-	-	Volume of spillage: 1 liquid gal
55.	1979	NL	RAILT	RAILY	PHOSPHORUS WHITE	-	-	While filling a tank wagon with yellow phosphorus some of the chemical was spilled into a drip cup. The spilled chemical self-ignited and the fire department was called.
56.	1979	USA	RAILT		PHOSPHORUS WHITE, DRY	-	7	
57.	1979	USA	RAILT		PHOSPHORUS WHITE , DRY	-	-	
58.	1979	USA	RAILT		PHOSPHORUS WHITE , DRY	-	-	
59.	1979	USA	RAILT		PHOSPHORUS WHITE, IN WATER	-	-	Volume of spillage: 1 liquid gal
60.	1979	USA	RAILT		PHOSPHORUS WHITE, IN WATER	-	-	Volume of spillage: 1 liquid gal
61.	1979	USA	RAILT		PHOSPHORUS WHITE, IN WATER	-	-	
62.	1979	USA	HIGHW		PHOSPHORUS WHITE, DRY	-	116	Volume of spillage: 2670 liquid gal
63.	1979	USA	RAILT		PHOSPHORUS WHITE, DRY	-	1	
64.	1979	USA	AIR		PHOSPHORUS WHITE, DRY	-	-	
65.	1979	USA	RAILT		PHOSPHORUS WHITE, IN WATER	-	-	
66.	1979	USA	RAILT		PHOSPHORUS WHITE, IN WATER	-	-	Volume of spillage: 1 liquid gal
67.	1979	USA	RAILT		PHOSPHORUS WHITE, IN WATER	-	-	Volume of spillage: 1 liquid gal
68.	1979	USA	RAILT		PHOSPHORUS WHITE, IN WATER	-	-	Volume of spillage: 1 liquid gal
69.	1979	USA	RAILT		PHOSPHORUS WHITE, DRY	-	-	Volume of spillage: 1 liquid gal
70.	1979	USA	RAILT		PHOSPHORUS WHITE, IN WATER	-	-	
71.	1979	USA	RAILT		PHOSPHORUS WHITE, IN WATER	-	-	Volume of spillage: 1 liquid gal
72.	1979	USA	RAILT		PHOSPHORUS WHITE, IN WATER	-	-	Volume of spillage: 1 liquid gal

73.	1979	USA	RAILT		PHOSPHORUS WHITE, IN WATER	-	-	
74.	1979	USA	RAILT		PHOSPHORUS WHITE, IN WATER	-	-	Volume of spillage: 1 liquid gal
75.	1979	USA	RAILT		PHOSPHORUS WHITE, IN WATER	-	-	Volume of spillage: 1 liquid gal
76.	1979	USA	RAILT		PHOSPHORUS WHITE, IN WATER	-	-	Volume of spillage: 10 liquid gal
77.	1979	USA	HIGHW		PHOSPHORUS WHITE, IN WATER	-	-	Volume of spillage: 1 liquid gal
78.	1979	USA	RAILT		PHOSPHORUS WHITE, IN WATER	-	-	Weight of spillage: 10 solid lb
79.	1979	USA	RAILT		PHOSPHORUS WHITE, IN WATER	-	-	Volume of spillage: 15 liquid gal
80.	1979	USA	Water		PHOSPHORUS WHITE, IN WATER	-	-	
81.	1980	USA	RAILT	RAILW	PHOSPHORUS WHITE WATER	-	-	The covering water layer in a drum filled with solid P ₄ vaporised leading to self-ignition of the inventory onboard a freight train driving through a desert. The freight train consisted of two wagons loaded with 104 drums (208 l inventory per drum). The subsequent fire spread onto 4 drums damaging eight other drums onboard the train. The fire department prevented the fire from further spreading by extinguishing the fire with excessive amounts of water. The train was moved to a remote area afterwards. Subsequent safety measures included cooling the drums with 75 ice blocks (136 kg each).
82.	1980	NL	USE/APP	FACTORY	PHOSPHORUS WHITE	-	1	A worker in an ammunition factory accidentally screwed a detonator too far on a shell releasing liquid P ₄ onto the worker who immediately jumped into a water basin. However the worker did not wear a protective mask exposing his eyes to P ₄ . The worker was taken to hospital.
83.	1980	USA	RAILT		PHOSPHORUS WHITE, IN WATER	-	-	Volume of spillage: 1 liquid gal
84.	1980	USA	RAILT		PHOSPHORUS WHITE, IN WATER	-	-	
85.	1980	USA	RAILT		PHOSPHORUS WHITE, IN WATER	-	-	Volume of spillage: 1 liquid gal

86.	1980	USA	RAILT		PHOSPHORUS WHITE, IN WATER	-	-	Volume of spillage: 1 liquid gal
87.	1980	USA	RAILT		PHOSPHORUS WHITE, IN WATER	-	-	Volume of spillage: 1 liquid gal
88.	1980	USA	RAILT		PHOSPHORUS WHITE, DRY	-	-	Volume of spillage: 1 liquid gal
89.	1980	USA	RAILT		PHOSPHORUS WHITE, DRY	-	-	Volume of spillage: 1 liquid gal
90.	1980	USA	RAILT		PHOSPHORUS WHITE, IN WATER	-	-	Volume of spillage: 55 liquid gal
91.	1980	USA	RAILT		PHOSPHORUS WHITE, IN WATER	-	-	
92.	1981	NL	USE/APP	CHEMF	PHOSPHORUS WHITE	-	1	At a chemical factory a defective pump had to be replaced. In order to clean the pump, it was transported with a truck to the local wastewater installation. After working on the pump for 1.5 hrs the worker screwed a plug out of the pump, P ₄ spilled onto his leg forcing him to jump into the water which limited the magnitude of his burns.
93.	1981	USA	RAILT		PHOSPHORUS WHITE, IN WATER	-	-	Volume of spillage: 1 liquid gal
94.	1981	USA	RAILT		PHOSPHORUS WHITE, DRY	-	-	Volume of spillage: 1 liquid gal
95.	1981	USA	RAILT		PHOSPHORUS WHITE, IN WATER	-	-	
96.	1981	USA	RAILT		PHOSPHORUS WHITE, IN WATER	-	-	
97.	1981	USA	RAILT		PHOSPHORUS WHITE, IN WATER	-	-	
98.	1981	USA	RAILT		PHOSPHORUS WHITE, IN WATER	-	-	
99.	1981	USA	RAILT		PHOSPHORUS WHITE, IN WATER	-	-	Weight of spillage: 50 solid lb
100.	1981	USA	RAILT		PHOSPHORUS WHITE, IN WATER	-	-	Volume of spillage: 1 liquid gal
101.	1981	USA	RAILT		PHOSPHORUS WHITE, DRY	-	-	
102.	1983	USA	RAILT		PHOSPHORUS WHITE, IN WATER	-	-	Volume of spillage: 1 liquid gal

103.	1983	USA	RAILT		PHOSPHORUS WHITE, DRY	-	-	Volume of spillage: 60 liquid gal
104.	1983	USA	RAILT		PHOSPHORUS WHITE, IN WATER	-	-	Volume of spillage: 1 liquid gal
105.	1983	USA	RAILT		PHOSPHORUS WHITE, IN WATER	-	-	Volume of spillage: 1 liquid gal
106.	1983	USA	RAILT		PHOSPHORUS WHITE, IN WATER	-	-	Weight of spillage: 1 solid lb
107.	1983	USA	RAILT		PHOSPHORUS WHITE, DRY	-	-	Weight of spillage: 300 solid lb
108.	1984	USA	RAILT		PHOSPHORUS WHITE, DRY	-	-	
109.	1985	NL	WASTE-TREATMENT	LAB	PHOSPHORUS WASTE	-	-	An explosion of a bottle in a school laboratory filled with phosphorus residues led to a fire and to traffic interruptions for a limited time period.
110.	1985	USA	RAILT		PHOSPHORUS WHITE, IN WATER	-	-	Volume of spillage: 1 liquid gal

111.	1986	USA	RAILT	RAILW	PHOSPHORUS WHITE TALLOW SULPHUR MOLTEN PAPER	-	166-569	<p>The 24th wagon of a 44 wagon freight train derailed while crossing a small bridge. The next 14 wagons also derailed including 3 tank wagons with P₄, molten sulphur and tallow. The derailment was caused by a lateral misalignment (76 mm) of the railway track due to the high ambient temperature (32 °C). All tank wagons released some of their contents and the P₄ spontaneously ignited because of the ambient temperature. The derailment caused a large fire, which also involved a freight wagon with paper. The fire was just 2m off the tank wagon with molten sulphur. These conditions were very dangerous because sulphur can react with phosphorus and form toxic gases, especially when phosphorus pentasulphide is formed. About 12,000 people were evacuated from the nearby town. The next day, the fire was almost extinguished and people returned to their homes, although the evacuation had not been lifted. At 1804 pm the tank wagon with the P₄ fell 1.5 m downhill due to erosion caused by water from fire fighting. The fire reignited to form a phosphoric acid cloud with the moist in air. A thick smoke was approaching the town afterwards outing 30,000 people at risk. All citizens were evacuated in two hours to avoid exposure to the phosphoric acid cloud.</p> <p>Subsequently, the fire department left the P₄ inventory burning for 3 days until the fire had almost ended. Afterwards, they moved the tank wagon to a wet sand pit to extinguish the fire completely. This accident caused fish death over 25 km of the river and the financial damages was estimated to equal 3,540,000 USD.</p>
112.	1986	NL	RAILT	RAILY	PHOSPHORUS WHITE AMMONIA	-	-	<p>A freight train consisting of 16 tank cars derailed in a rural area. 2 of the 9 derailed wagons overturned carrying ammonia and yellow phosphorus. 45 m³ of ammonia were pumped to another tank wagon in order to secure the inventory. The overall operation lasted for 7hrs.</p>
113.	1986	USA	RAILT		PHOSPHORUS WHITE, IN WATER	-	-	Volume of spillage: 0.0630 liquid gal

114.	1986	USA	RAILT		PHOSPHORUS WHITE, IN WATER	-	-	
115.	1986	USA	RAILT		PHOSPHORUS WHITE, IN WATER	-	-	
116.	1987	USA	RAILT		PHOSPHORUS WHITE, IN WATER	-	-	Weight of spillage: 112000 solid lb
117.	1987	USA	RAILT		PHOSPHORUS WHITE, IN WATER	-	-	Weight of spillage: 8 solid lb
118.	1987	USA	RAILT		PHOSPHORUS WHITE, DRY	-	-	Weight of spillage: 800 solid lb
119.	1987	USA	RAILT		PHOSPHORUS WHITE, DRY	-	-	
120.	1987	USA	RAILT		PHOSPHORUS WHITE, DRY	-	-	Weight of spillage: 40 solid lb
121.	1987	USA	RAILT		PHOSPHORUS WHITE, DRY	-	-	Weight of spillage: 40 solid lb
122.	1988	USA	RAILT		PHOSPHORUS WHITE, DRY	-	-	Weight of spillage: 1 solid lb
123.	1988	USA	RAILT		PHOSPHORUS WHITE, IN WATER	-	-	Weight of spillage: 8 solid lb
124.	1988	USA	RAILT		PHOSPHORUS WHITE, DRY	-	-	Weight of spillage: 110752 solid lb
125.	1988	USA	RAILT		PHOSPHORUS WHITE, IN WATER	-	-	Weight of spillage: 8 solid lb
126.	1988	USA	RAILT		PHOSPHORUS WHITE, IN WATER	-	-	

127.	1988	USA	RAILT	RAILW	PHOSPHORUS WHITE	-	3	At approximately 7 pm the driver of a 99-121 car freight train exceeded the speed limit leading to a 36 car derailment. The tank wagon containing P ₄ overturned ignited releasing a white cloud of phosphorus pentoxide fumes over a large, sparsely populated area. The plume was 121 m high and 91.4 m wide. The plume forced the local officials to evacuate 2300 residents living in an area of 51 km ² . The fire was allowed to burn entirely because the fire department feared that water usage might cause toxic run off contaminating the local groundwater. Officials banned all aircraft from the air space over the affected area. At 730 pm the next day, the overturned P ₄ -containing tank wagon was set upright. The inventory reignited which formed a new plume of irritant pentoxide. The reignition forced the evacuation of 15,000 residents. Three people were sent to hospital for throat irritation. The responsible company was fined with 720 USD.
128.	1989	NL	RAILT	LEVELCR	CHEMICAL N.O.S.. PESTICIDE N.O.S.. PHOSPHORUS WHITE	-	-	7 wagons of a 29-car freight train derailed due to a loosened brake block upon crossing a railroad crossing. One of the derailed wagons was filled with P ₄ which was covered with water by the fire department. Other tank wagons containing other chemicals overturned but showed no leakage. Over a distance of 300 m the railway overhead line was damaged.
129.	1989	USA	RAILT		PHOSPHORUS WHITE, DRY	-	-	Weight of spillage: 1 solid lb
130.	1989	USA	RAILT		PHOSPHORUS WHITE, IN WATER	-	-	Weight of spillage: 40 solid lb

131.	1990	GB	STOR	WAREH/D EP	PHOSPHORUS WHITE	-	-	<p>Drummed yellow phosphorus ignited 21 July 1990 in a warehouse at a chemical factory producing elemental phosphorus and its derivatives. The probable cause was the corrosion of the inner surface of the drums. The accident occurred 0300 am. In total 580 120 l drums were stored in the warehouse equalling 115,000 kg of yellow phosphorus. The drums were grouped in three separate stacks in order to avoid spreading in case of a fire. The fire was detected by security personnel upon routine patrol with no warning from the automatic detection system. One drum was on fire and was dealt with by site personnel. However, another 67 drums have been affected by the fire and were put into 200 l salvage drums which were filled with water, sealed and removed from the building which was returned to normal operations at 1 pm the same day. No injuries were reported. A subsequent inspection of the burned drum revealed extensive corrosion of the inner surface of the drum showing holes in the drum wall. Phosphoric acid was considered to attack the mild steel in the water phase protecting the yellow phosphorus in the drum due to poor sealing of the drums allowing oxygen to enter. This was further enhanced by the hot weather at that time reaching temperature exceeding the melting point of yellow phosphorus (44 °C). It was considered to investigate the remaining drums but before that a second fire occurred at 0804 am 03 August 1990 within the following days of the accident. The Institution of Chemical Engineers (IChemE) recommended best practices to store drums with elemental phosphorus after this accident:</p> <ul style="list-style-type: none"> • Controlling the pH using Disodiumhydrogenphosphate (Na_2HPO_4) in the water layer • Use of tight head drums to prevent breathing of the drums • Strict stock rotation of the drums and periodical inspections of drums for signs of corrosion and pH fall • Closed-circuit television to be installed (CCTV)
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132.	1990	GB	STOR	WAREH	PHOSPHORUS WHITE	-	-	<p>Linking to accident no 131, the fire on 03 August 1990 was indicated by the fire alarm system between 0630 and 0640 am. The day before, the ambient temperature rose to 36 °C, possibly exceeding the melting point of elemental phosphorus due to greenhouse effect. Multiple explosions occurred in line with intense yellow flashes together with what appeared to be the drum lids ejected through the roof. The flashes were reported to be fireballs rising to up to 15 m above the rooftop. At 0830 am the fire was extinguished except for small deposits. At 0930 clean-up was performed lasting for several days. All drums were removed and a number of burnt drums were put under water in order to recover the material.</p> <p>A cloud of smoke was travelling away from the fire. Complaints were received from a town some 16 km in south-westerly direction. The probability of formation of phosphine and phosphorus trioxide was said to be very low. Approximately 30,000 kg of yellow phosphorus were consumed in the fire (= 150 drums). No injuries or fatalities were reported.</p>
133.	1990	USA	RAILT		PHOSPHORUS WHITE, DRY	-	-	Weight of spillage: 1 solid lb
134.	1990	USA	HIGHW		PHOSPHORUS WHITE, IN WATER	-	-	Weight of spillage: 0.6250 solid lb. Costs: 225 USD
135.	1990	USA	RAILT		PHOSPHORUS WHITE, IN WATER	-	-	Weight of spillage: 8 solid lb. Costs: 505 USD
136.	1990	USA	RAILT		PHOSPHORUS WHITE, IN WATER	-	-	Weight of spillage: 16 solid lb. Costs: 925 USD

137.	1991	MAL	PROC	FACTORY	CHEMICAL N.O.S. FIREWORK/FIRECRACKER LEAD OXIDE BARIUM NITRATE BARIUM CARBONATE BARIUM CHLORIDE PHOSPHORUS WHITE	>26	60-112	During mixing of chemicals to test an assortment of fireworks an explosion occurred. The experiment was performed in the canteen rather than on a special testing site. The explosion trapped 150 people in the building, killing at least 26 people and wounding at least 60 people. Nearby wooden houses were destroyed. Residents within a range of 1 km were evacuated 26 hrs later, as an explosion was feared to occur in an underground storage facility. Due to heavy rainfall that day, the site in question was flooded with water damaging six drums filled with yellow phosphorus. The spillage led to a chemical reaction releasing a toxic cloud over an area with a radius of 11km. The damage amounted to a value of 1,000,000 MYR (approx. 252,371.38 EUR)
138.	1991	T	STOR	WAREH	PHOSPHORUS N.O.S. METHYL BROMIDE TRICHLOROISOCYANURIC ACID PHOSPHORIC ACID	15	>1	Sacks of phosphorus stored outside a chemical warehouse caught fire and spread over four other warehouses and nearby slums. 3250 people lost their homes. A fireball and toxic emissions were reported. The fire was brought under control after 9 hrs. At least 15 people were killed by the explosion and the subsequent fire. Days after the blaze the slum dwellers began complaining of itching as a result of exposure to the chemicals stored in the warehouses.

139.	1991	USA	RAILT	RAILW	PHOSPHORUS WHITE	-	-	At 1110 am, 29 cars of a 119 car-freight train derailed upon rupture of a wheel. Four cars were filled with yellow phosphorus. The yellow phosphorus load equalled 84,000 kg and one tank wagon was punctured releasing some inventory and exposing it to ambient oxygen. About 1.9 m ³ of phosphorus leaked and ignited spontaneously. Hazardous waste crews worked to plug a hole in the toppled wagon containing yellow phosphorous. Officials worried that a shift in wind could carry fumes to a nearby village of about 100 people. Fire crews used foam to extinguish a fire in the leaking car which did not end the hazard. The yellow phosphorous caught fire and a toxic cloud was released from the punctured tank wagon. Railroad officials expanded the evacuation area near the site while salvage crews pulled two tankers filled with a toxic chemical to the opposite side of the tracks. 350 people were evacuated from the nearby villages. A second car also suffered cracks but the holes in the two railroad tanker cars were patched two days later. Emergency crews attached cables to the disabled cars dragging them along a trench dug across the tracks in order to lift the tankers onto a flatbed car. The leak was stemmed by welding boxes onto cars with breaches. The damage to the second tank was less severe and the attached box was filled with sand and fitted with a lid.
140.	1991	USA	RAILT		PHOSPHORUS WHITE, IN WATER	-	-	
141.	1991	USA	RAILT		PHOSPHORUS WHITE, IN WATER	-	-	Weight of spillage: 1000 solid lb. Costs: 1,108,365 USD
142.	1992	USA	RAILT		PHOSPHORUS WHITE, IN WATER	-	-	Weight of spillage: 1 solid lb. Costs : 5 USD
143.	1992	USA	RAILT		PHOSPHORUS WHITE, IN WATER	-	-	Weight of spillage: 8 solid lb. Costs: 500 USD
144.	1995	NL	RAILT	RAILW	PHOSPHORUS WHITE	-	-	An empty train wagon (before the accident containing a phosphorus-solution) still had remaining product left in the receptacle of the filling point. This receptacle started to leak, which caused pollution of air and soil. After discovering the leak the receptacle was cleaned.

145.	1995	USA	TRANSS	WAREH	PHOSPHORUS N.O.S	-	-	Port operations at a pier were shut down for about 4 hrs due to a phosphorus fire in a tank container. Clean-up crews attended the next day.
146.	1996	D	STOR	WAREH	WATER PHOSPHORUS WHITE PHOSPHORUS WASTE	-	-	At a former phosphorus production site phosphorus residues were stored in phosphorus mud pits. These residues were covered with water, according to the rules of P ₄ handling instructions. 22 February 1996, the water cover froze and a subsequent thaw period with sunlight reduced the water cover. Thus, an area of max. 40 x 40 m phosphorus was exposed to the surface. Due to intense sunlight, white/yellow phosphorus pit inventory ignited around noon. Work at the adjacent construction site was forced to stop for 1 h. Thick white to grey cloud of resulting phosphorus pentoxide covered neighbouring farms and nearby roads.
147.	1996	D	STOR	WAREH	WATER PHOSPHORUS WHITE PHOSPHORUS WASTE	-	-	In order to clean the phosphorus pits after the fire on 22 February 1996 (Accident No. 146) the sludge from the pits was loaded to a special container using an excavator. The container was placed in the phosphorus pit and was filled half with water. After several loading procedures, the phosphorus waste on the shovel spontaneously ignited during excavation. The burning sludge in turn, caused a thick cloud phosphorus pentoxide. The cloud moved over the area and briefly obscured a road. The fire and emergency response personnel on the site immediately extinguished the fire. Subsequently containers and pits were filled with a protective water layer.

148.	1998	D	TRANSS	RAILY	PHOSPHORUS WHITE	-	-	<p>During normal heating of a tank wagon with yellow phosphorus a spontaneous release of phosphorus occurred. The heating of the tank wagon is a preparation for the unloading sequence. After 6 hrs of heating a release occurred through an open nozzle. The phosphorus immediately ignited when brought into contact with the air. Contrasting usual procedure the tank wagon had a second rising tube next to the one used for the unloading. This rising tube was not recognisable as such from the outside. During heating, the nozzle on the rising tube was opened in order to make temperature measurements inside the wagon. Meanwhile, the wagon was spooled with nitrogen because phosphorus expands strongly when heated. The rising tube was locked and pressure rose inside the tank wagon. The pressure was relieved after fully melting the contents of the tank wagon over the second rising tube, in which phosphorus was released with the flow. All safety equipment worked as intended. All emergency personnel carried out the emergency plan. The company fire department arrived shortly after the accident was communicated. The fire was extinguished. The tank wagon heating was switched off and the area was cordoned off. Outside the factory area neighbouring companies were warned while measurements were performed. Damages included the phosphorus unloading site as well as the tank wagon.</p>
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149.	1998	D	PROC	CHEMF	CHLORINE PHOSPHORUS N.O.S. PHOSPHORUS TRICHLORIDE	-	-	<p>A short release of phosphorus trichloride occurred from a phosphorus trichloride plant. In a phosphorus furnace liquid phosphorus and chlorine gas are burnt to form phosphorus trichloride. The furnace, which is equipped with a pressure relief system, is operated under a small overpressure. Due to a pressure rise in the furnace an alarm occurred. The furnace was immediately relieved. A small amount of phosphorus trichloride was released via the pressure relief system until the furnace was stopped. the pressure rise in the furnace was caused by the sudden evaporation of a small amount of carried along liquid chlorine in the chlorine gas. Most probably chlorine gas condensed in a tubular bridge because of low outside temperatures and low chlorine use (the main customer sustained a production stop). Upon restart of an evaporator the abovementioned condensation occurred that fast that condensed chlorine evaporated in a very short time. This caused a pressure rise in which liquid chlorine was carried along with the chlorine gas flow into the phosphorus furnace. A condensation of chlorine in a tubular bridge cannot be prevented, because of the system pressure falling below the dew point and therefore condensation is possible. Downstream consumers therefore use liquid chlorine separators with overload safety equipment or chlorine evaporators. Because of the proximity of the phosphorus trichloride plant to a chlorine factory and a company heating line such a safety measure was not deemed necessary.</p>
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150.	1999	USA	RAILT	RAILW	PHOSPHORUS WHITE	-	-	<p>At about 1225 pm on a Sunday, 42 cars of a 97-98-car goods train carrying automobiles, pickup trucks, auto parts, sugar and some hazardous materials (yellow phosphorus) derailed, causing 2 rail cars with pickup trucks to catch fire and forcing police and fire officials to warn nearby residents and motorists to stay indoors and keep their windows closed due to possible toxic fumes. None of the cars containing hazardous materials derailed. Some nearby roads were closed for several hours. The derailment caused an estimated 6,000,000 USD in damage.</p> <p>The cause of the accident was a red warning light on the tracks as the train approached the township border. The light indicates a possible break in the tracks. Instead of slowing from 72.4 km/h to 24.1 km/h to visually monitor the tracks, the engineer applied the emergency brakes.</p>
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151.	2000	CDN	PROC	CHEMF	<p style="text-align: center;">AMMONIA NITRATES N.O.S.. PHOSPHORUS N.O.S.. SULPHURIC ACID NITRIC ACID HYDROCHLORIC ACID</p>	-	4	<p>About 0930 pm a blaze erupted in an acid-transformation plant believed to contain up to 49 m³ of toxic materials, including ammonia, phosphorus, nitrate, sulphuric, nitric and hydrochloric acid. It sent a cloud of toxic smoke into the air. The plant was closed when the fire began. Though the blaze raged into the morning after the day before, measurements detected no serious environmental contamination and most residents were told they could return home shortly before 0500 am. Only a few hundred people in one particular neighbourhood are being told to stay away. About 5000-7000 people had been evacuated from a nearby community, which was hit hardest by the smoke. Firefighters arrived an hour later. About 100 firefighters battled the blaze, but a lack of water made the task difficult. Four firefighters were hospitalised with symptoms such as throat and eye irritation. They were listed in satisfactory condition. Firefighters also held back from dousing the fire with water for fear flooding the special containment area on the plant site (toxic fumes such as sulphuric, nitric and hydrochloric acid) and contaminating nearby creeks and the sewer system. As the thick cloud moved westward, shelters were set up to accommodate those who chose to leave their homes. Authorities and Emergency personnel also planned to use truckloads of lime to neutralise any spilled acid. Firefighters used lime to neutralise chemical runoff in ditches and advised all residents to wash fruits and vegetables in their gardens next day. The accident may have been triggered by faulty electrical systems. The Ministry for Environment monitored the surrounding area on a weekly basis.</p>
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152.	2000	USA	PROC	WAREH	PHOSPHORUS WHITE	-	1	A 16-year-old worker moving dangerous P ₄ from a storage tank at an army arsenal suffered serious burns on about a third of his body. He suffered 2nd and some 3rd degree burns and was in serious condition upon arrival of first responders. The arsenal holds 12% of the nation's chemical weapon stockpile. The worker and 2 other were transferring the phosphorus from the storage tank to another tank in preparation for a routine work procedure . An initial investigation showed possible mechanical failure.
153.	2001	USA	TRANSS	CHEMF	PHOSPHORUS WHITE	-	4	A 44-year-old worker was critically burned by P ₄ as he was unloading the material from a railroad car at a chemical plant. The man was taken to a burn unit at a medical centre. The worker was reported to have been wearing protective clothing at the time of the accident. An emergency medical technician and 2 paramedics, who took him to the medical centre, were treated when they showed signs of chemical exposure. They suffered skin irritation, sore throats and inflamed mucous membranes. A hazardous materials unit had to clean the ambulance.
154.	2001	USA	PROC	LAB	CLEANING AGENTS PHOSPHORUS WHITE	-	--	About 100 employees of a company that makes coatings for computer chips were evacuated briefly when a chemical reaction caused a small explosion in a laboratory. Employees at the company were evacuated as a precaution after phosphorus cleaning agent combusted, releasing a small amount of phosphine gas. Employees were evacuated for about 10 min while the air was tested to make sure all traces of gas were gone. The company's ventilation system cleared the air quickly and the employees returned. Workers were cleaning a machine when the explosion happened. During the manufacturing process a coating of phosphorus can develop on machinery, and the coating can ignite when exposed to air. The company produces coatings of gallium arsenide (GaAs) on computer wafers from which computer chips are made.

155.	2003	F	TRANSS	CHEMF	AIR WATER PHOSPHORUS WHITE PHOSPHORUS PENTOXIDE	-	46	<p>An explosion followed by a phosphorous fire occurred in the transport depot of a plant, producing much smoke. Nearby roads and railways were closed for about 90 min. A shelter-in-place was ordered for residents of nearby villages. Firefighters extinguished the fire within 11 min. The plant employed about 31 workers and was specialised in phosphorus compounds. The fire occurred during unloading procedures of a wagon carrying P₄ at a phosphorus pentoxide factory. The operator stopped the pumps, pushed the emergency stop button and triggered the sprinkler system, which did not work. The emergency response plan was started immediately and the fire was extinguished after 11 min, but a white cloud of smoke of 4000 m length, 200 m width and 50 m height, with a concentration of 2 mg/m³ P₄O₁₀, was formed in the valley, where chemical plant was located. The road and train traffic was stopped for 2 hrs. The pupils of a nearby school were confined for the same time. 46 people were examined in a medical centre. The cloud was dispersing while moving towards 2 villages, which were closed until the next morning. At the time of the discharge, the P₄ was heated up to 60 °C by vapour injected into the double shell. It was then pumped through the top of the tank car by hot water (p max = 3.8 bar). Liquid phosphorus was then extracted with a diving tube connected in a transfer line (p = 100 kPa). 63 kg of P₄ escaped from a joint. The released P₄ ignited upon contact to air, emitting thick smoke. The discharge started 2 days earlier and had been stopped following detection of the first leakage under the heat insulator. This accident led to downstream immediate replacement of junction equipment located at the flexible section of the junction. The discharge then began again without check ups after the intervention. Supposing the cause of the accident, human error regarding handling valves and variations in the temperature, led to damage of the sealing of the accused joint.</p>
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156.	2004	USA	PROC	REFIN	SILICATE CATALYST ALUMINIUM OXIDE MAGNESIUM OXIDE PHOSPHORUS N.O.S.	-	-	At 0400 am, silica catalyst escaped for 20 min when a fluid catalytic cracker (FCC) was being shut down. The 20 minute release covered boats, cars and about 150 homes in a the nearby neighbourhood with dust. The FCC had been closed a the night earlier but had undergone repairs and had been running for several days when concerns about the instrumentation had led to the shutdown. The FCC was reset and was running at full capacity the next day. Residents found their yards, boats and vehicles dusted with white powder and called the police. A lack of communication from the refinery following the accident was one of the main complaints raised by residents and elected officials were attending a meeting of residents later on. The processed clay catalyst, which contains silica, aluminium oxide, magnesium oxide, rare earth oxide and a phosphorus compound, was said to be not hazardous.
157.	2005	USA	HIGHW		PHOSPHORUS WHITE, IN WATER	-	-	Costs: 10,900 USD
158.	2006	USA	REP	WWTP	PHOSPHORUS N.O.S. METHANOL	2	1	An explosion and fire occurred at a Wastewater Treatment Plant (WWTP), killing two employees and severely burning a third that stayed 4 months in hospital. The WWTP additional process to remove nitrogen and phosphorus compounds requires the addition of methanol (highly flammable), which is stored in an aboveground storage tank. The methanol was stored in one 38 m ³ steel tank, with plastic piping. An aluminium flame arrester had been installed on the vent of the tank, but had not been changed or maintained since and was heavily corroded by the methanol vapours. A metal roof, 9 m above ground, and shading the tank, was damaged by hurricanes in 2005 and required repair. At 1115 am., maintenance workers were using an oxy-acetylene cutting torch just above the methanol storage tank and, sparks accidentally ignited vapours coming from the tank. The ignition created a fireball on top of the tank which flashed back into the storage tank, causing an explosion inside the tank that damaged multiple methanol PVC-piping and a large fire (11.35 m ³ of methanol) that engulfed the tank and workers.

159.	2006	B	STOR	WAREH	PHOSPHORUS WHITE	-	-	At around 1100 am, a short-lived fire in a harbour area occurred. The fire broke out in a container with P ₄ in a warehouse due to spontaneous ignition. The fire department quickly brought the fire under control with sand. Because toxic fumes were released during the smouldering fire in the warehouse, the fire brigade ventilated the warehouse and, nearby inhabitants were advised to keep their doors and windows closed for a while.
160.	2006	NL	USE/APP	SCHO	PHOSPHORUS WHITE	-	-	At about 1230 a., P ₄ ignited spontaneously in a chemistry class when a chemistry teacher cut a small piece of the material for a chemical experiment. The piece of phosphorus fell onto the ground causing a small fire and smoke. The floor was slightly damaged. Subsequently the secondary school was evacuated and staff, teachers and 600 students were assembled at the assembly point across the street on a sports field. When the fire brigade arrived the whole school was evacuated. Around 1400 hours everybody was allowed to enter the school. The surroundings of the school were blocked by the police for about 1 hr.

161.	2006	CW	USE/APP	OTHER	AMMUNITION EXPLOSIVES PHOSPHORUS WHITE	-	3	<p>A military exercise was held under responsibility of the Commander of the Navy in the Caribbean Area (CZMCARIB) and the regional Commander of the Command Naval Forces (CZSK). The exercise was focussing on the training of Antillean conscripts. Among the ammunition used during the exercise were smoke hand grenades to obscure military operations. On the third day of the exercise, smoke hand grenades were used. In the course of the afternoon, the standard smoke hand grenades 7C2 were out of stock and as a replacement, the smoke hand grenade WP (P₄), no.23 was issued. The two sergeant-instructors never handled the WP smoke hand grenade before. The second sergeant-instructor advised to throw the grenade away. The first sergeant-instructor threw the grenade against the wind direction. They expected a hissing noise and immediate smoke development, but not only until a few seconds an explosion followed, releasing burning phosphorus. Both instructors were within the deployment range and suffered first- and second-degree burns. One of the conscripts suffered burns as well. The injured were transported to the hospital. The instructor who threw the grenade had to be transported to a special burn unit within The Netherlands.</p>
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162.	2007	UA	RAILT	RAILW	PHOSPHORUS YELLOW	-	<200	<p>15 railroad tanker cars of a 58-car goods train carrying toxic substances derailed in Ukraine on 16 July in the Lviv area. 8 railroad tanker cars caught fire including the tank wagons with yellow phosphorus. The freight train carrying 700 tons of liquefied yellow phosphorus derailed near a town and the fire formed a smoke cloud covering about 86 km² area including nearby villages. This event prompted the evacuation of 815-900 people. Initially authorities advised the residents to maintain shelter-in-place procedures. After 9 hrs, the blaze was under control. However, the threat posed by the huge toxic cloud remained. Ten residents, six persons from emergency personnel and two railroad workers were transported to a nearby hospital after showing signs of intoxication. Authorities issued warnings to 14 villages in danger of being affected by the cloud. The number of people exposed to the irritant cloud tripled two days later from 20 to 70. About half of the people affected, including 19 children, were hospitalised. Authorities have checked 16000 people for symptoms of chemical poisoning. More than 180 people, who were intoxicated, remained hospitalised 4 days later, including 34 children and 14 emergency responders. Two days after the accident, the government announced that the accident site was no longer polluted. The railway was repaired, tank leaks plugged, railroad tank cars placed upright, and the convoy was sent back to Kazakhstan at low speed, passing big cities and accompanied by 2 fire-protection trains. The polluted parcels were cleaned and dikes built adjacent to the site in order to protect a village and to collect polluted water. Approximately 900 kg of crystallised phosphorus were recovered at the accident site. Two weeks later phosphorus residue left onsite spontaneously ignited. According to the regional branch of the Ministry of Emergency Situations, measurements of the air, soil and water both at the accident site and in the vicinity revealed a rise in the phosphorus rate "two to three times higher than the standard" in the area the epicentre, i.e. covering an area "roughly 1 km. The costs incurred to farms were estimated 109,000 USD.</p>
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163.	2008	NL	TRANSS	CHEMF	PHOSPHORUS WHITE WATER WASTE WATER	-	1	At about 0100 pm, a worker, who had just finished unloading a railroad car with P ₄ , was injured and taken to hospital by ambulance. A spray release of water and P ₄ from a gap between the flexible discharge hose and a blind flange, reached the platform above the railroad tanker car, on which he was standing. There was only one escape route. Therefore, the worker had to jump and broke his ankle. Moreover, the worker put off his fireproof clothing, exposing him to the heat of the flames.
164.	2009	GB	PROC	CHEMF	PHOSPHORUS YELLOW PHOSPHORUS RED CHEMICAL N.O.S. PHOSPHINE	-	4-6	Thousands of people were advised to stay indoors after a fire at a chemical plant released a large cloud of toxic gas. 115 kg of phosphorus vapour and about 37 kg of phosphine were accidentally discharged from the plant, which produces phosphorus-based chemical intermediates. On contact with air, the mixture auto-ignited to produce about 390 kg of phosphorus pentoxide which reacted with moist in the atmosphere to produce about 538 kg of phosphoric acid in the form of a mist over a period of approximately 114 min. The gas ignited on contact with the air, producing a dense mist of phosphorus pentoxide and phosphoric acid. The thick, low hanging cloud of phosphorus pentoxide was reported to be heading south over houses and towns after the fire ignited. Police said the cloud, which measured about 15 m by 122 m, was blown south towards the highway. The chemicals reacted badly upon contact with water and was likely to cause skin irritation and breathing difficulties. Residents were told to keep windows and doors closed until the cloud dispersed after four hrs. A cordon was placed around the factory. The accident was caused by a 30 mm orifice from which P ₄ leaked, causing a small fire as phosphorus gas reacts with air forming phosphoric acid. The phosphorus feed was switched off and emergency cooling was applied to the affected converter. The flame at the orifice continued for about 114 min until the installation was recovered. Two police officers were taken to hospital after becoming nauseous and two local residents were also affected.

165.	2010	F	PROC	CHEMF	PHOSPHORUS WHITE	-	-	A 25 mm diameter pipe broke in a chemical installation. 60 kg of P ₄ ignited in contact with air releasing an extensive white smoke plume. The internal emergency plan was activated at 1205 pm, and 2 nozzles were deployed by the plants' fire brigade. The fire brigade stopped the leak and extinguished the fire by 1225 pm. Arriving on the scene at 1237 pm, local firefighters completed the spraying operation to eliminate any remaining flashpoints. Sand dams were set up at 1300 hours to prevent water pollution. The phosphorus transfer pipe leading from the burners was broken at the level of a sectional valve. The day before, an intense wave of cold weather (-10 °C) had caused a drainage problem on a compressor, leading to a full shutdown of installations. Downstream events led to the breakage of the pipe.
166.	2012	USA	RAILT		PHOSPHORUS WHITE, DRY	-	-	Weight of spillage: 0.1250 solid lb. Costs: 800 USD

Legend

CHEMF: Chemical Factory, CLEAN: Cleaning, FACT: Factory, HIGHW: Highway, LAB: Laboratory, LEVELCR: Levelcrossing, PROC: Processing, RAILT: Railtransport, RAILW: Railway, RAILY: Railyard, REFIN: Refinery, REP: REPAIR, SCHO: School, STOR: Storage, TRANSS: Transshipment, USE/APP: Use/Application, WWTP: Wastewater treatment plant, WAREH: Warehouse/Depot

Note: 1 lb ≈ 0.45 kg
1 USD ≈ 0.75 EUR
1 gal ≈ 3.79 litres

Appendix D

Table 15: Combustion and dispersion specific literature

Authors	Title	Year	Relevance
Berkowitz J. et al.	Occupational and environmental hazards associated with the formulation and use of P ₄ -felt and red phosphorus-butyl rubber screening smokes	1981	P ₄ combustion behaviour and atmospheric fate of P ₄ combustion products
Katz S. et al.	Physical and chemical characterisation of military screening smokes. Part III-WP/Felt Smokes Final Report	1981	
Yon R. et al.	Programmatic life cycle environmental assessment for smoke/obscurants, Volume 2 of 5 volumes, Red, white, and plasticized	1983	
Spanggord R. et al.	Environmental fate of WP/felt and red phosphorus-butyl rubber military screening smokes: Phase I – Literature review	1983	
Spanggord R. et al.	Environmental fate of WP/felt and red phosphorus-butyl rubber military screening smokes: Final report	1985	
Rivera Y. et al.	Summary and evaluation for white phosphorus remediation: A literature review	1996	
Witlox H. & Woodward J.	Modelling of phosphorus pool fires and subsequent dispersion of combustion products with hydrolysis in the plume	1997	
Witlox H. et al.	Modelling of phosphorus fires with hydrolysis in the plume	1998	
Kapias T. & Griffiths R.	Spill behaviour using REACTPOOL. Part III. Results for accidental releases of phosphorus trichloride (PCl ₃) and oxychloride (POCl ₃) and general discussion	2001	
DNV Software	POLF (Pool Fire) Theory manual	2005	
DNV Software	UDM (Unified Dispersion Model) Theory manual	2005	

Table 16: Thermodynamics and chemistry specific literature

Authors	Title	Year	Use
Melville H.	The oxidation of phosphorus vapour at low pressures	1932	P ₄ /P ₄ O ₁₀ /H ₃ PO ₄ /other compounds thermodynamics and chemistry
Fontana B.	The vapour pressure of water over phosphoric acids	1951	
LaViolette R & Benson M.	Structure and thermodynamics of phosphorus oxide caged clusters	2012	

Table 17: Accident specific literature

Authors	Title	Year	Use
Ross B. et al.	Aetiology of an impossible railway tank car explosion	1987	Accidents
Badyugin I.	Incendiary and toxic characteristics of phosphorus. Lessons learned from the accident in Lviv	2009	

Table 18: Toxicity specific literature

Authors	Title	Year	Use
Agency for Toxic Substances and Disease Registry (ATSDR)	Toxicological profile for P ₄	1997	Toxicity of P ₄ , P ₄ O ₁₀ and H ₃ PO ₄
Deutsche Forschungsgemeinschaft (DFG)	Diphosphorpentaoxid	2004	
Deutsche Forschungsgemeinschaft (DFG)	Phosphorsäure (ortho-Phosphorsäure)	2006	
Deutsche Forschungsgemeinschaft (DFG)	Phosphor	2006	

Table 19: Production process specific literature

Authors	Title	Year	Use
Schrödter K. et al.	Phosphoric Acid and Phosphates	2000	Production process
Bettermann G. et al.	Phosphorus Compounds, Inorganic	2000	
Diskowski H. & Hofmann, T.	Phosphorus	2005	
Wang, Z. et al.	Thermodynamic modelling and gaseous pollution prediction of the yellow phosphorus production	2011	

Table 20: Literature with additional thermodynamical information

Authors	Title	Year	Use
Melville H.	The oxidation of phosphorus vapour at low pressures	1932	O ₃ decreases minimum partial O ₂ pressure for P ₄ "explosion"
Fontana B.	The vapour pressure of water over phosphoric acids	1951	Over even very concentrated H ₃ PO ₄ very low vapour pressure, pyrophosphoric acid (H ₄ P ₂ O ₇) from H ₃ PO ₄ formation confirmed