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Review of Tier 1 Workplace Exposure Estimates for Petroleum Substances in REACH dossiers

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Review of Tier 1 Workplace Exposure Estimates for Petroleum Substances in REACH dossiers

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ABSTRACT

For the exposure assessment in the 2010 REACH dossiers of petroleum substances, Concawe has used the Tier 1 exposure model ECETOC TRA v.2. In order to account for the heavier, less volatile and more complex petroleum substances and the corresponding exposure situations, several modifications not originally within the scope of the ECETOC TRA were developed. These modifications include an approach to estimate liquid aerosol along with some risk management measures describing the use and handling of petroleum substances commonly in use in the European oil refining industry.

In this project, Chemical Safety Assessments (CSAs) on these petroleum substances were evaluated concerning relevant industry areas and included scenarios. Measured data were collated in order to evaluate the exposure estimates in general and the modifications made by Concawe.

Data were collected from the database built in the course of the Evaluation of Tier 1 Exposure Assessment Models (eteam) project (www.eteam-project.eu) undertaken by IOM and ITEM, from Concawe reports and via literature search. These include kerosines (mainly as jet fuel), heavy fuel oils (HFOs), two naphtha groups (0-1% and 1-5% benzene, essentially corresponding to gasoline after and before the year 2000), gas oils (vacuum, hydrocracked gas oils and distillate fuels; i.e. mainly diesel fuels) and other lubricant base oils (OLBOs). The quantity and quality of datasets, however, varies between the groups and there are still a number of substance groups and scenarios which could not be evaluated due to lack of suitable data (e.g. gas oils, foots oils, other naphthas). This was partly due to changes brought about by the REACH process in how exposures are assessed against a reference value. For instance, it was customary to assess inhalation exposure to diesel fuel as vapour, but the REACH process resulted in a Derived No Effect Level (DNEL) expressed as aerosol.

The comparison exercise showed some discrepancies depending on substance group and the specific scenarios. These discrepancies may be partly attributed to new modifiers or other changes of the ECETOC standard algorithm (e.g. concentration modifier in case of naphthas). In general, for most measures such as draining of equipment or training of operatives, both under- and overestimations can be found; therefore, it is difficult to reach a final conclusion concerning their applicability.. Other possible reasons for the observed underestimations were variations within an exposure scenario (e.g. Research and Development laboratory activity vs. production laboratory activity, bottom loading vs. top loading) or the age of datasets (e.g. in case of naphthas).

Concerning aerosol exposure, measured data for OLBOs and HFOs could be identified. No significant underestimations were found for the evaluated scenario in case of OLBOs while in the case of HFOs results were inconclusive (partly underestimations but only few data points). Overall it is recognised that available sampling methods for liquid aerosol often tend to give biased or at least variable exposure results and this has to be taken into account for future investigations concerning risk assessment of petroleum substances or validation of the existing CSAs. Measurements made for HFOs show higher overall and vapour concentrations compared to the aerosol values which may suggest that either vapour may be more relevant than previously assumed for high boiling petroleum substances or the corresponding aerosol measurements may not be suitable for a comparison with DNELs or model estimates. Comparable difficulties will probably exist for other semi- or low volatile substances which tend to form aerosols.

Although some underestimations have been observed, there are also cases where clear overestimations were observed and thus, a further refinement with higher Tier tools may be possible. Two possible tools, STOFFENMANAGER© and ART were discussed and illustrated with an example scenario. Petroleum substances and the resulting exposure types (vapour and aerosols) are within the scope of both models; however, the new modifiers introduced by Concawe are only implemented to a limited extent (vapour recovery in the case of ART).

A qualitative evaluation of the updates made when changing from ECETOC TRA v.2 to v.3 suggested that inhalation exposure estimates will probably be lower if the more recent version is used. This is partly due to newly introduced or changed measures or operational conditions and partly due to modified initial exposure estimates.

Overall, there are a number of situations where the comparison of measurements and estimates suggests reasonable results and a controlled risk. There are other situations, however, where, due to different reasons, the contrary is observed. A particular problem seems to be the lack of high quality aerosol data.

KEYWORDS

Occupational exposure, REACH, exposure assessment, chemical safety assessment, exposure scenario, exposure estimate, risk management measures

INTERNET

This report and supplementary material is available as an Adobe pdf file on the Concawe website (www.Concawe.eu).

Concawe H/STF-29 response to the findings

May 2018

General

This report commissioned by Concawe was prepared by two independent entities (Fraunhofer ITEM and IOM) and contains a number of important findings. These will be used to guide further work by Concawe to improve the Exposure Assessments. The report was reviewed by the Concawe Exposure Assessment Task Force (H/STF-29) and the following comments were captured:

1. Efficiency: The sheer effort and time required to collect and collate the available exposure data into the estimates needed for chemical safety assessment would have been prohibitive in the run-up to the first REACH registration deadline in 2010: this took several years but still left important data gaps. Hence the decision to adopt the simplified approach put forward by ECETOC, adapted by Concawe (as documented in report 11/12), to produce nearly all necessary exposure estimates proved to be right one under the circumstances.
2. DNELs: The Derived No Effect Levels which emerged in the preparation of the REACH dossiers following the newly issued ECHA guidance resulted in some cases in a misalignment with available occupational exposure data. Notably for gas oils a considerable effort was made by Concawe in anticipation of REACH with field measurements (report 1/06) for a number of scenarios. The measured exposures were focused on the vapour phase, believed at the time to be the most relevant exposure entity for inhalation, yet the inhalation DNEL was set later in the form of aerosol and for which no data were available. An exposure monitoring method has now been developed and published (report 8/15), but to-date no new data have been reported.
3. Data gaps: For several categories of substances there were no measured exposure data – either inhalation or dermal, for example for Residual and Distillate Aromatic Extracts. In some of these cases the level of the DNELs does not drive immediate concerns and the work in the years ahead in Concawe on the maintenance and further development of the exposure scenarios will eventually address this. For others, action is required in the shorter term. In fact, for Heavy Fuel Oils (HFOs) with their very low DNELs, action has already been taken in the form of a Concawe-funded project in several member companies of new measured exposure data in one of the main scenarios in the HFO lifecycle, i.e. bulk transfer into barges and trucks; the results will be reported later in 2018.
4. Exposure underestimates:
    - Naphtha's with 0-1% benzene (assessment entity benzene, see Table 4.9):
        - Bulk closed loading, the modelled estimate of 0.48 mg/m^3 will be replaced by the measurement based 75th percentile value of 0.50 mg/m^3;
        - Bulk closed unloading, the modelled estimate of 0.80 mg/m^3 will be replaced by the measurement based 75th percentile value of 1.60 mg/m^3 until such time that more data become available which would suggest this value is too high;
        - Laboratory activities: there is a notable discrepancy between the measurement based 75th and 90th percentiles (0.73 and 4.80 mg/m^3) suggesting this data set contains some outliers. Concawe has recently launched a member company data call to address this issue and replace the modelled estimate of 0.16 mg/m^3.
5. Exposure overestimates: For several groups of substances (kerosine, other lubricant base oils) some considerable overestimates of the modelled exposure, though still indicating safe use, were found when compared with the percentiles of the distributions of measured exposure concentrations. Depending on feedback from registrants and downstream users on the feasibility of implementing the Operational Conditions and Risk Management Measures in the relevant Exposure Scenarios, these overestimates may be refined in future with higher tier modelling tools, as recommended by the authors of the report. Otherwise the overestimates will be retained in the REACH registration dossiers, but readers should note that these do not reflect 'real world' conditions.

CONTENTS

1. INTRODUCTION

Petroleum products are complex hydrocarbon substances which are characterised by the refining process, the range of boiling point and range of carbon chain length, or according to their general chemical composition such as aliphatic, alicyclic or aromatic hydrocarbons.

Under REACH, Chemical Safety Assessments (CSAs) for chemicals have to be provided including hazard and exposure assessments. Exposure assessments may be based on measured data or on modelling approaches.

Easy-to-use exposure tools with a comparably small number of input parameters and whose aim is to provide conservative modelled exposure estimates are usually referred to as Tier 1 tools, while more complicated tools are often referred to as Tier 2 tools.

An example of a Tier 1 tool is the ECETOC Targeted Risk Assessment (TRA), whose version 2 (v.2) has been used to estimate occupational exposure for petroleum products in the course of the REACH registration. However, when applying the tool it was observed that this model did not cover all possibilities for the heavier, less volatile and more complex petroleum substances. Therefore, some modifications where developed which have been documented in a compendium and include details concerning the use of gloves, operating instructions on draining equipment and vapour recovery [1]. In addition, an approach has been developed to deal with exposure to liquid aerosols, which is not officially covered by ECETOC TRA but is of high relevance in the area of semi-volatile petroleum products.

In order to validate the resulting exposure estimates in this project, the CSAs developed by Concawe are evaluated, and measured data are investigated, collected and assigned to the corresponding scenarios.

Scenarios or situations with clear over- or underestimations are identified and the extent to which refinements with other models (Tier 2) may be an alternative is discussed.

In addition, the extent to which the modifications made for v.3 of ECETOC TRA may have an influence on the outcome of the estimate and the corresponding validation exercise is discussed in a qualitative way.

2. EVALUATION OF CHEMICAL SAFETY REPORTS

In this project, the Tier 1 estimates of occupational exposure to petroleum substances for different identified uses generated using the modified ECETOC TRA v.2 as applied in the Concawe CSAs were evaluated by comparison with available recent measurement data. The impact of using a modified version of the TRA v.2 to estimate exposure to (probably mainly semi-volatile and/or heavier) petroleum substances was also evaluated. Another objective was to identify and describe the impact of using the ECETOC TRA v.3 model in place of the original or modified versions of the TRA v.2.
In this section, the existing CSAs for a selection of petroleum substances prepared by Concawe were evaluated and described. The aim of this evaluation process was to set a basis which could be used to search and select relevant measured data (see section 3).

2.1. SUBSTANCE GROUPS AND INDUSTRY AREAS

Petroleum substances are grouped in categories based on similarities in terms of manufacturing processes, physical/chemical descriptors (including refining history, boiling point and carbon number ranges) and limited analytical chemical properties (such as hydrocarbon classes).
The single substances within each category are summarised with the relevant Chemical Abstracts Service (CAS) Number in an inventory list published in the REACH section of the Concawe website[1]. These different CAS numbers that make up a Concawe petroleum category are a reflection of the manufacturing process (mostly the last refining step). It is important to note that CAS numbers are not necessarily leading to different substances, but are merely slightly different ways of making the same substance which can be grouped together.

CSAs for occupational exposure and the following substance groups were provided by Concawe to Fraunhofer ITEM / IOM for the evaluation process:

- Gas oils:
  - Straight run gas oils (not used outside refinery) – [SRGOs]
  - Cracked gas oils (not used outside refinery) – [CGOs]
  - Vacuum gas oils / hydrocracked gas oils / distillate fuels (diesel fuel) – [VHGOs]
  - Other gas oils – [OGOs]
- Low boiling point naphthas – [LBPN]
  - Low boiling point naphthas (< 0.1% benzene)
  - Low boiling point naphthas (< 1% benzene)
  - Low boiling point naphthas (1-5% benzene)
  - Low boiling point naphthas (5-20% benzene)
  - Low boiling point naphthas (79% benzene)
- Highly refined base oils (only for special applications, e.g. sewing machines) – [HRBOs]
- Other lubricant base oils (most lubricants are based on this group) – [OLBOs]
- Heavy fuel oils – [HFOs]
- Foots oils
- Treated distillate aromatic extracts – [TDAE]
- Severely oxidised bitumen
- Kerosine (usually jet fuel, sometimes blended into winter diesel)
- MK1 diesel fuel (Swedish diesel fuel)
- Crude petrolatum
- Unrefined acid treated oils – [UATOs].

[1] https://www.concawe.eu/reach/

In these CSAs, the following general identified uses were included:

- Manufacture of substance
- Use of substance as intermediate
- Distribution of substance
- Formulation & (re)packing of substances and mixtures
- Uses in coatings
- Use as fuel
- Use as lubricant
- Metal working fluids / rolling oils
- Use as release agents or binders
- Oil and gas field chemicals
- Use in cleaning agents
- Functional fluids
- Rubber manufacture and processing
- Water treatment applications
- Use as mould release & binder
- Use in road and construction applications
- Use in explosive manufacture and use
- Polymer processing
- Use in laboratories
- Mining chemicals
- Agrochemicals
- Manufacture of articles

Not all of these identified uses are present in each of the CSAs. However, there are several overlaps which are summarised in Table A1.1 -Table A1.3 in Appendix 1. It must be noted that some uses have since been removed (in 2016) due to further clarification of the distinction between petroleum substances and hydrocarbon solvents. Typical solvent uses such as use in coatings are no longer supported for several petroleum substances.

2.2. LIMIT VALUES AND CONSIDERATIONS FOR EXPOSURE ASSESSMENT

The majority of the petroleum substances are of complex and variable composition. The main reference values for the assessment of occupational inhalation exposure prior to REACH were Occupational Exposure Limits (OELs), including the Threshold Limit Values (TLVs) of American Conference of Governmental Industrial Hygienists (ACGIH). For some petroleum substances there were OELs and TLVs, e.g. gasoline, kerosine, diesel fuel and mineral oil mist.

Furthermore, where workplace exposure measurements were reported, it was common to include measurements of certain well-known chemical components with OELs present in the petroleum substance, e.g. toluene in gasoline - in some cases even without some overall measure (e.g. 'total hydrocarbons') of the petroleum substance.

Concawe conducted a series of exposure studies in support of its commitment to product risk assessment prior to REACH in the period 2000 – 2007, which used commonly applied OELs at the time. With the advent of the REACH technical guidance and the Derived No Effect Levels (DNELs) that were set on the basis of available hazard studies, some references values emerged that did not align with previous OELs or TLVs. For example, many hazard studies conducted for heavier petroleum substances have been done using dermal or oral dosing of experimental animals and the inhalation DNELs based on this are expressed as aerosol. However, very few aerosol measurements have been reported for petroleum substances other than base oils (from lubricants) and bitumen fume (in paving operations). On the other hand, Concawe report 1/06 includes extensive measurements on inhalation exposures to vapour from diesel fuel, but no DNEL was set for this fraction.

Finally, the assessment entity selected for the CSA under REACH for low-boiling point naphthas is benzene which is widely measured in gasoline handling operations, but for which both the allowable content in gasoline and OEL were lowered in the year 2000, rendering exposure studies from the period prior to 2000 of limited use. The current European OEL for benzene has been adopted by Concawe as the Derived Minimal Effect Level (DMEL) for naphthas.

Amongst the different petroleum substance groups some mainly generate vapour exposure (e.g. naphthas), while others can lead to both vapour and aerosol inhalation exposure (e.g. gas oils) or only aerosol exposure (e.g. aromatic extracts) (see Appendix 1 and Ref. [1]). As the distribution of aerosols into the lung differs from that of vapour, effects of aerosols and vapour should be assessed separately and as a consequence, different limit values have been used for the different petroleum substances.

In case of the naphtha groups, benzene has been used as the marker substance (‘Assessment Entity’) concerning measurements and limit values.

An overview of limit values (DNELs and other occupational exposure limits) used for the assessment of petroleum substances has been provided by Concawe and is presented in Appendix 2. Values used in the Concawe CSAs are highlighted.

In general, the relevance of aerosol exposure depends on several aspects such as the temperature of the atmosphere, the boiling point distribution of the substance group, the aerosol size distribution and the concentration level. Scenarios leading to aerosol exposure are often associated with significant amounts of kinetic or thermal energy applied to the product.

Overall, Concawe developed criteria based on volatility and process category in order to determine the appropriate exposure assessment approach [1] for each product/scenario combination:

- For light products (FBP<200 ºC): only vapour exposures assessed
- For products with lower boiling points (IBP<200 ºC, FBP<340 ºC): vapour exposure assessed except where potential for aerosol generation identified
- For products with moderate boiling products (IBP>150 ºC, FBP>340 ºC): aerosol exposure assessed except where potential for significant vapour release and co-exposure identified
- For heavier products (IBP>200 ºC, FBP>340 ºC): only aerosol exposures assessed.

Aerosol predictions were usually based on ECETOC TRA predictions for solids of medium dustiness. However, ART estimates have also been used for risk assessment purposes partly, i.e. for HFOs.

2.3. RISK MANAGEMENT MEASURES

The algorithm of ECETOC TRA v.2, which has been used for the chemical safety assessments of petroleum substances, already offers a basic set of modifiers for operational conditions and protective measures. However, these were not always considered to be sufficient for the description of typical situations during the handling and application of petroleum products.

Therefore, Concawe has developed a set of new measures / modifiers that can be applied if necessary. A summary of risk management measures implemented in the Concawe exposure assessments used under REACH is given in Ref. [1]. These include the provision of drum pumps, location of operator to minimise exposures, operating instructions on draining of equipment, operating instructions on draining and flushing of equipment, specific operator training to reduce exposure, vapour recovery on road tankers or railcar loading operations and a selection of glove applications for dermal exposure.

As a consequence, the CSAs have been screened for these measures and other measures not implemented in ECETOC TRA v.2, which were used in the exposure estimations. A detailed list of the phrases, influenced exposure routes and associated exposure reduction efficiencies can be found in Table 2.1.

Apart from the measures documented in Concawe report 11/12, some additional refinements (e.g. concerning the exposure modifier based on benzene concentrations for naphtha) were undertaken as follows (and as detailed in Table 2.1):

- For naphtha/modern EU gasoline with <1% gasoline: modifier 0.01;
- For naphtha with 1-5% (mainly within the refinery): modifier 0.02;
- No exposure data were retrieved for >5%, although other modifiers are available for these.

Some introduced modifiers are anticipations of parameters later implemented in ECETOC TRA v.3 (e.g. enhanced general ventilation, see Table 2.2).

Table 2.1 Risk management measures used for exposure assessments of petroleum substances under REACH; not implemented in ECETOC TRA v.2.

Non-ECETOC TRA v.2 modifiers found in CSAs	Phrase number[1]	Efficiency	Applicable routes
From Concawe report 11/12: completely new			
Use drum pumps	E53	80 %	inhalation
Use drum pumps or carefully pour from container	E64	80 %	inhalation
Location of operator to minimise exposure[2]	E77	80 %	inhalation + dermal
Drain down system prior to equipment break-in or maintenance.	E65	80 % or 90 %	inhalation
Drain or remove substance from equipment prior to break-in or maintenance	E81	80 %	inhalation
Drain down system prior to equipment break-in or maintenance	E55	90 %	inhalation
Ensure operatives are trained to minimise exposures	EI19	15 %	inhalation + dermal
Ensure operatives are trained to minimise exposures	C&H17	15 %	inhalation + dermal
Application of gloves	PPE18	98 %	dermal
Vapour recovery on road tanker or railcar loading operations*	A7	80 %	inhalation
Completely new - not reported in [1]			
Carefully pour from containers	E62	80 %	inhalation
Closed loop sampling system	E8	95 %	inhalation
Closed system	E84	95 %	inhalation
Containment or extract ventilation	E66	e.g. 90 %, 80% (according to LEV efficiency in TR107 [2])	inhalation
Air mover	E40	70%	inhalation
Apply from within a vented cab supplied with filtered air under positive pressure and with a protection factor of >20.	E70	95 %	inhalation
From CSAs: anticipation of TRA v.3 modifiers or parameters			
General ventilation (good and enhanced)	E11 and E40	30 % and 70 %	inhalation
Application of gloves (also in report 11/12 [1])	PPE15, 16, 17, 18	80, 90, 95 %	dermal
In some cases: Implementation of duration for dermal exposure, concentration for dermal exposure	*n.a.*	*80, 90, 95 %*	*dermal*
For benzene/naphtha: refined modifiers for inhalation concentration for mixtures, at least partly on basis of measurements of vapour pressure, used only for high volatility naphthas/benzene		*< 1 %: modifying factor 0.01 instead of 0.1* *< 5 %: modifying factor 0.02 instead of 0.2* *< 20 %: modifying factor 0.2 instead of 0.6* *< 80 %: modifying factor 1, in line with ECETOC TRA suggestions*	*inhalation*

[1] The code refers to a phrase library originally developed in CEFIC, but now included in the ESCOM library with different codes

[2] Reported in Ref. [1] but not applied in CSAs

Table 2.2 ECETOC TRA v.3: Implemented parameters *(available since 2011; parameters not in v.2 are marked in italics)*

	Categories	***Exposure reduction***
Molecular weight	free number	linear dependence (ideal gas law)
Dustiness	high / medium / low	included in initial exposure estimate
Vapour pressure	high / medium / low / very low	included in initial exposure estimate
Process description (PROC no)	PROC 1-25 according to the descriptor system	included in initial exposure estimate
Process temperature (PROC 22-25)	process temperature relative to melting point	included in initial exposure estimate via fugacity
Process temperature (PROCs 1-21)	*vapour pressure at process temperature is entered* *high / medium / low / very low*	*included in initial exposure estimate*
Type of setting	industrial / professional	included in initial exposure estimate and LEV efficiency
Ventilation	indoor without LEV indoor with LEV	0% PROC specific
	good general ventilation *enhanced general ventilation* *good general ventilation + LEV* *enhanced general ventilation + LEV*	*30%* *70%* *PROC specific* *PROC specific*
	outdoor	30%
Respiratory protection equipment (RPE)	90 % efficiency 95 % efficiency	90 % 95 %
Gloves	*Any gloves / gauntlet without permeation data and without employee training*	*0 %*
	Gloves with available permeation data indicating that the material of construction offers good protection for the substance	*80 %*
	Chemically resistance gloves with basic employee training	*90 %*
	Chemically resistant gloves in combination with specific activity training (e.g. procedures for gloves removal and disposal) for tasks where dermal exposure can be expected to occur	*95 %*
Concentration (w/w)	< 1% 1-5% 5-25% > 25%	90 % 80 % 40 % 0 %
Duration	< 15 min 15-60 min 1-4 h > 4 h	90 % 80 % 40 % 0 %
	Short term 15 min	*400 % (exposure peaks)*

3. EVALUATION OF AVAILABLE MEASURED DATA

For the validation of the Concawe CSAs, measured data from different sources were searched. For data to be suitable for the present purpose, they should be documented with a sufficiently high level of detail and contain information about relevant scenario details such as the evaluated process and risk management measures present.

Details of the evaluation process were summarised in an interim report and led to the datasets later used for the validation process (see Supplementary material 1A and 1B). The following potential sources of measured exposure data were evaluated and the data owners were contacted, if necessary:

HSE reports (Health and Safety Executive) (UK):

Available measured data did not contain a sufficient amount of contextual information and were therefore excluded from the further validation process. One study report funded by the UK HSE on aerosol exposures in metal-working applications was retrieved. However, it was not evaluated separately as the data are included in a publication which is used in the present study, see aggregated data below [3, 4].

NIOSH (National Institute for Occupational Safety and Health) (USA):

Some downstream exposure data to oil mists, naphtha (kerosine) and gasoline were identified and NIOSH gave permission to use them for the validation process.

MEGA database (Germany):

The MEGA database ("Measurement data relating to workplace exposure to hazardous substances" (Messdaten zur Exposition gegenüber Gefahrstoffen am Arbeitsplatz" in German)) contains air measurements of a number of workplaces (overall 2.83 million measurements end of 2014[2]). The data are gathered within the framework of the Measurement system for exposure assessment of the German Social Accident Insurance Institutions. However, after several discussions, a final formal response was received indicating that they were not able to provide data for the project.

SECO (Secretariat for Economic Affairs) (Switzerland):

A request was made to SECO, concerning the use of their exposure data for the validation of Concawe CSAs. However, following additional interim discussions regarding preferred data types, a response was received indicating that they were not able to participate in the project.

Concawe reports:

Several Concawe reports are available including measured data on petroleum substances for various processes. The following reports were evaluated and the datasets included into the validation exercise:

- Report no. 6/07: Human exposure information for EU substance risk assessment of kerosine (primarily relating to jet fuel handling operations) [5]
- Report no. 1/06: Human exposure information for EU substance risk assessment of gas oils (primarily relating to diesel fuel and heating oil handling operations) [6]
- Report no. 4/87: A survey of exposure to gasoline vapour [7]
- Report no. 97/52: Exposure profile: gasoline [8]
- Report no. 2/00: A review of European gasoline exposure data for the period 1993-1998 [9]
- Report no. 9/02: A survey of European gasoline exposures for the period 1999-2001[10]
- Report no. 5/09: Additional human exposure information for gasoline substance risk assessment (period 2002-2007) [11]
- Report no. 1/15R: Risk assessment for emissions from hot heavy fuel oil during barge loading [12]

[2] http://www.dguv.de/ifa/Gefahrstoffdatenbanken/Expositionsdatenbank-MEGA/index-2.jsp

Further data on gasoline and metalworking fluids were identified via literature research [3, 4, 13-18].

Auffarth et al. reported inhalation exposure to hydrocarbons, gasoline and benzene released during draining and disassembly of cars are reported. Measurements were done before and after 2000, i.e. naphtha groups with benzene contents between 1-5% and below 1% were included [13].

Saarinen et al. reported the exposure to C3±C11 aliphatic hydrocarbons, MTBE, benzene, toluene and xylene at service stations before and after installation of vapour recovery systems. The samples could be used for a direct comparison with CSA estimations as well as the derivation of an efficiency concerning vapour recovery, resulting in an efficiency range of 42-87% (reduction of total concentration 86%) [14].

Gasoline exposure was also evaluated by Periago et al. The study includes benzene exposures measured between 1995 and 2003, thereby including situations with 1-5% benzene content in the evaluated naphtha and situations with lower benzene concentrations (<1%) [15].

Simpson et al. evaluated exposure to metalworking fluid mist and sump fluid contaminants during machining operations. The study evaluated exposure at 24 sites but also includes previous measurements from pilot studies and routine measurements, resulting in overall 31 sites visited. No selection was made concerning company size or occupational hygiene practices [4].

Data containing information about metalworking fluid exposure has also been published by Breuer et al. and Piacitelli et al. [16-18].

The data identified and collated reflect a range of substances and activity types in both industrial and professional settings. There are evident limitations regarding the quality of some of the contextual information; however, in general, there was enough detail given to allow a comparison of the situations with the input parameter assumptions / choices made in modelling of the exposures.

Further details on the handling of data and individual scenarios / situations are described in the Supplementary material (1A and 1B).

3.1. FITTING OF MEASURED DATA TO CSA SCENARIOS

The available data include a selection of datasets related to scenarios where non-ECETOC TRA v.2 (new) risk management measures have been applied.

No scenarios using the phrases [A7] (Vapour recovery on road tanker or railcar loading operations), [C&H17] (Ensure operatives are trained to minimise exposures) or [E77] (Location of operator to minimise exposure) were identified in the CSAs. Regarding phrase [A7], however, it was noted that the CSAs used an analogous but more generic phrase to indicate the presence of vapour capture and return, i.e. [E66] (Ensure material transfers are under containment or extract ventilation).

No measured data were assigned for scenarios implementing use of drum pumps ([E53] / [E64]) and no suitable dermal data were identified, therefore no datasets could be assigned to usage of gloves ([PPE18]).

As mentioned earlier, there are certain petroleum substances for which the formation of aerosols is likely. Corresponding substance groups and general availability of data are summarised in Table 3.1.

Table 3.1 Petroleum substance classes with a high tendency of aerosol formation vs. available measured datasets.

Petroleum substance class	Measured data available (in general)
Gas oils	yes (inhalation)- vapours only
Other lubricant base oils	yes (inhalation- metal working fluids measured as total inhalable particulate)
Highly refined base oils	no
Heavy fuel oils	yes (inhalation only: vapours and aerosol measurements; dermal measurements incorporated currently in CSA)
Foots oils	no
Treated distillate aromatic extracts	no
Severely oxidise bitumen	no
Crude petrolatum	no

In addition, a number of inhalation and dermal measurements for exposure to vapours and aerosols containing Polycyclic Aromatic Hydrocarbons (PAHs) during asphalt paving activities were identified. As no relevant CSA was developed, these were excluded from the validation.

A summary of the available data (individual and aggregated data) is given in Table 3.2 (for further details on phrases for communication for corresponding scenarios see Table S2.1 in the Supplementary material.

In general, the identified measured data were entered in a Microsoft (MS) Access database. This also included the assignment of model input parameters by IOM representatives in order to allow for a comparison with scenarios from the CSAs. Model estimates and corresponding contextual information were stored in this database as well. In both cases, the data transfer into the database was done via MS Excel templates that were prepared for each relevant substance and scenario, including all relevant information. Subsequent descriptive and statistical analyses were done using Statistical Analysis Software (SAS) v.9.4.

It can be summarised that a number of datasets were identified that could be used to evaluate the specific modifications of ECETOC TRA v.2 used for the assessment of petroleum substances. However, since the number of aerosol measurements is limited, a detailed discussion of the dustiness-based approach used for the estimation of the corresponding exposure could not be performed.

Table 3.2 Available measured data and corresponding scenarios in the Chemical Safety Assessments (individual and aggregated data)

Substance	PROC	Situation	General description of situation	Conditions used for exposure assessment	RMM use for exposure assessment	n	measurements
Kerosine	PROC 8a Transfer of substance or preparation (charging/discharging) from/to vessels/large containers at non-dedicated facilities.	CS39 Equipment cleaning and maintenance	Manufacture of substance	>4 hours, ambient temp.	Drain down system prior to equipment break-in or maintenance. E65. (80%)	11	vapour
Kerosine	PROC 8b Transfer of a substance or preparation (charging /discharging) from/to vessels/large containers at dedicated facilities	CS14 Bulk transfers	use as fuel / professional	>4 hours, ambient temp. outdoors (30%)	Ensure operatives are trained to minimise exposures. EI19. (15%).	175	vapour
Kerosine	PROC 8a Transfer of substance or preparation (charging/discharging) from/to vessels/large containers at non-dedicated facilities.	CS39 Equipment cleaning and maintenance. Equipment maintenance e.g. Vehicle, boiler, pump maintenance, pump calibration.	use as fuel / professional	>4 hours, ambient temp.	Drain down system prior to equipment break-in or maintenance. E65. (80%)	32	vapour
Kerosine	PROC 13 Treatment of articles by dipping and pouring	CS4 Dipping, immersion and pouring	use in road and construction applications/ professional	1-4 hours (*0.6), ambient temp. outdoors (30%)	Ensure operatives are trained to minimise exposures. EI19. (15%)	8	vapour
Heavy fuel oil	PROC8b Transfer of substance or preparation (charging /discharging) from/to vessels/large containers at dedicated facilities.	CS_new Marine vessel/barge (un)loading	ES2 - Distribution of substance - industrial	<4 hours, moderately elevated temp.		5	aerosol+vapour (only aerosol used)
Naphtha 0-1% benzene	PROC 8a Transfer of substance or preparation (charging/discharging) from/to vessels/large containers at non-dedicated facilities.	CS39 Equipment cleaning and maintenance	Manufacture of substance - Industrial	>4 hours; ambient temp. , concentration modifier 0.01.	Drain down and flush system prior to equipment break-in or maintenance. E55. (90%)	11	vapour

Substance	PROC	Situation	General description of situation	Conditions used for exposure assessment	RMM use for exposure assessment	n	measurements
Naphtha 0-1% benzene	PROC 8b Transfer of a substance or preparation (charging /discharging) from/to vessels/large containers at dedicated facilities	CS500 Bulk closed loading. Bulk closed loading and unloading (e.g. road/rail car bottom loading/ unloading; marine vessel/barge loading/unloading)	Distribution of substance - Industrial	>4 hours, ambient temp. concentration modifier 0.01.	LEV or containment E66 (90%)	237	vapour
Naphtha 0-1% benzene	PROC 8b Transfer of a substance or preparation (charging /discharging) from/to vessels/large containers at dedicated facilities	CS501 Bulk closed loading and unloading. Bulk closed loading (e.g. road/rail car bottom loading; marine vessel/barge loading)	Distribution of substance - Industrial	>4 hours, ambient temp. concentration modifier 0.01.	LEV or containment E66 (90%)	4	vapour
Naphtha 0-1% benzene	PROC 8a Transfer of substance or preparation (charging/discharging) from/to vessels/large containers at non-dedicated facilities.	CS5 Equipment maintenance. Equipment maintenance e.g. Vehicle, boiler, pump maintenance, pump calibration	Use as a fuel - Professional	> 4 hours daily; ambient temp. concentration modifier 0.01. Intended to cover usual incidental exposures plus injector strip down and work on fuel tank.	Drain down system prior to equipment break-in or maintenance. E65. (80%) Ensure operatives are trained to minimise exposures. EI19. (15%).	58	vapour
Naphtha 0-1% benzene	PROC 15 Use as laboratory reagent	CS36 Laboratory activities	manufacture of substance - industrial	>4 hours, ambient temp. concentration modifier 0.01.	With LEV (90%)	26	vapour
Naphtha 0-1% benzene	PROC 8b Transfer of a substance or preparation (charging /discharging) from/to vessels/large containers at dedicated facilities	CS502 Bulk closed unloading. Bulk delivery (closed) (e.g. heating oil, diesel, bunker fuel deliveries)	Use as a fuel - Professional	>4 hours, ambient temp. concentration modifier 0.01.	No LEV but Extract Ventilation (90%)	35	vapour
Naphtha 0-1% benzene	PROC 8b Transfer of a substance or preparation (charging/ discharging) from/to vessels/large containers at dedicated facilities	CS507 Refuelling. Refueling vehicles, light aircraft or marine	Use as a fuel - Professional	daily; ambient temp. No lev. but Extract Ventilation (90%), concentration modifier 0.01.		73	vapour

Substance	PROC	Situation	General description of situation	Conditions used for exposure assessment	RMM use for exposure assessment	n	measurements
Naphtha 1-5% benzene	PROC 2 Use in closed, continuous process with occasional controlled exposure (e.g. sampling)	CS15 General exposures (closed systems). + CS56 With sample collection.	Manufacture of substance – Industrial	>4 hours, ambient temp., concentration modifier 0.02.	Sample via a closed loop system. E8. (95%)	1665	vapour
Naphtha 1-5% benzene	PROC 8a Transfer of substance or preparation (charging/discharging) from/to vessels/large containers at non-dedicated facilities.	CS39 Equipment cleaning and maintenance	Manufacture of substance – Industrial	>4 hours, ambient temp., concentration modifier 0.02.	Drain down and flush system prior to equipment break-in or maintenance. E55. (90%)	157	vapour
Naphtha 1-5% benzene	PROC 2 Use in closed, continuous process with occasional controlled exposure (e.g. sampling)	CS67 Storage	Manufacture of substance - Industrial	>4 hours, ambient temp., concentration modifier 0.02.	Store substance within a closed system. E84. (95%)	27	vapour
Naphtha 1-5% benzene	PROC 15 Use as laboratory reagent	CS36 Laboratory activities	Manufacture of substance - Industrial	>4 hours, ambient temp. concentration modifier 0.02.	With LEV (90%)	628	vapour
Naphtha 1-5% benzene	PROC 8a Transfer of substance or preparation (charging/discharging) from/to vessels/large containers at non-dedicated facilities.	CS39 Equipment cleaning and maintenance	Distribution of substance - Industrial	daily; ambient temp. concentration modifier 0.02.	Drain down and flush system prior to equipment break-in or maintenance. E55. (90%)	64	vapour
Naphtha 1-5% benzene	PROC 8a Transfer of substance or preparation (charging/discharging) from/to vessels/large containers at non-dedicated facilities.	CS39 Equipment cleaning and maintenance	Formulation & (re)packing of substances and mixtures - Industrial	daily; ambient temp. temp. concentration modifier 0.02.	Drain down and flush system prior to equipment break-in or maintenance. E55. (90%)	2	vapour
Naphtha 1-5% benzene	PROC 8b Transfer of a substance or preparation (charging/discharging) from/to vessels/large containers at dedicated facilities	CS501 Bulk closed loading and unloading. Bulk closed loading (e.g. road/rail car bottom loading; marine vessel/barge loading)	Distribution of substance - Industrial	>4 hours, ambient temp. concentration modifier 0.02.	No LEV but Extract Ventilation (90%)	2223	(vapour)
Other lubricant base oils - aerosol	PROC 17 Lubrication at high energy conditions and in partly open process	CS79 Metal machining operations	Metal working fluids / rolling oils professional	1-4 hrs, ambient temp. < 4hrs duration (0.6x);	Ensure operatives trained to minimise exposures EI19 (15%) + Enhanced general ventilation (0.3x);	860	aerosol

Substance	PROC	Situation	General description of situation	Conditions used for exposure assessment	RMM use for exposure assessment	n	measurements
					<25% conc (0.6x); resulting in overall 91% reduction.		
Other lubricant base oils - vapour	PROC 17 Lubrication at high energy conditions and in partly open process	CS79 Metal machining operations	Metal working fluids / rolling oils professional	1-4 hrs, ambient temp. < 4hrs duration (0.6x);	Ensure operatives trained to minimise exposures EI19 (15%) + Enhanced general ventilation (0.3x); <25% conc (0.6x); resulting in overall 91% reduction.	6601	vapour

4. COMPARISON OF CHEMICAL SAFETY ASSESSMENTS WITH MEASURED DATA

A detailed discussion of the comparison process and involved methods is provided in the Appendix 3. This section presents a summary overview of the findings.

Two types of measurement data were retrieved: single measurement results with sufficient contextual information for each measurement, called 'individual measurements' in the present report; and combined data sets, for example a mean, minimum and maximum, with contextual information primarily at the level of the data set, and called 'aggregate measurement data sets' in this report.

In the report restricted and full data-sets are referred to in relation to naphtha 0-1% and 1-5% benzene concentrations respectively. Restricted datasets comprise only of relevant measurement data collected after the year 2000 concerning naphtha with 0-1% benzene concentration and before the year 2000 for naphtha with 1-5% benzene concentrations. Full datasets combine all the pre-and post-2000 measurements suitable for the CAS descriptions of each of the naphtha types concerned in an analysis aiming for increased statistical power. Details in relation to the handling and assumptions behind these analyses as well as for the composition of each of the involved datasets is provided within the Appendix 3 and the Supplementary material.

Tables 4.1 and 4.2 summarise the available measurement data points used during the comparison exercise across all substance types, for illustrative purposes only.

It should be noted that in chemical safety assessment it is common to use a value at the high end of the distribution of measured data (e.g. the 75th or the 90th percentile). Indeed, the exposure estimate as provided by ECETOC in the TRA is intended to represent approximately a 75th percentile. If the 75th percentile of a data set is lower than the modelled estimate, then the model estimate is considered to be conservative.

Thus, for the comparison of estimates with measured data the 75th and 90th percentiles were calculated for the different scenarios and compared with the corresponding model output in order to judge whether the modelled estimate was sufficiently conservative. In addition, the data were put into graphs in order to present the comparison (measurements vs. exposure estimate) in a visual way. In cases where not all statistical parameters were available, the calculations were based on equations as described in Appendix 3 (see also [19]).

If the duration modifier was applied in order to derive an exposure estimate, it was removed again before comparing the value with any measurements.

Table 4.1 Summary of individual measurements available for comparisons with the exposure estimates from CSAs (by substance)

Substance	s	n	AM (mg/m^3)	GM (mg/m^3)	GSD	Min (mg/m^3)	Max (mg/m^3)
Kerosine – vapour		209	5.63	1.04	7.26	0.02	290.00
Heavy fuel oil – aerosol		5	0.13	0.10	1.97	0.06	0.31
Naphtha – vapour (0-1% benzene)		189	0.41	0.14	4.77	<0.01	9.20
Naphtha – vapour (1-5% benzene)		39	0.88	0.59	2.31	0.20	5.40
Other lubricant base oils – aerosol		4	1.15	0.91	2.31	0.30	2.30

s= number of exposure scenarios for which measurements were available; n=number of measurements; AM=arithmetic mean of the measurement results; GM=geometric mean of the measurement results; GSD=geometric standard deviation of the measurement results; min=lowest measurement result; max=highest measurement result.

Aggregated data are summarised in Table 4.2.

Table 4.2 Summary of aggregated measurement data sets available for comparison with the exposure estimates from CSAs

Substance	s	g	n	Mean AM (mg/m³)	GM AM (mg/m³)	GSD	Min AM (mg/m³)	Max AM (mg/m³)
Kerosine – vapour	2	4	17	128.00	119.35	3.29	27.00	240.00
Naphtha – vapour (0-1% benzene)	2	3	47	0.31	0.24	2.28	0.14	0.62
Naphtha – vapour (1-5% benzene)	7	59	4777	8.47	1.13	3.15	0.17	414.34
Other lubricant base oils – vapour	1	15	6601	7.79	7.08	1.54	2.79	20.83
Other lubricant base oils – aerosol	1	9	856	0.54	0.44	1.87	0.23	1.61

s= number of exposure scenarios for which data were available; g=number of aggregate data points; n=number of measurements; Mean AM=mean of the arithmetic means of the measurement results; GM=geometric mean of the means of the measurement results; GSD=geometric standard deviation of the means of the measurement results; min AM=lowest arithmetic mean value of the aggregated measurement results; max AM= highest arithmetic mean value of the aggregated measurement results.

In the following paragraphs further information about the single substances and comparison of their available measurements with exposure estimates is given in the form of selected Tables and figures (see Appendix 3 for full details).

4.1. KEROSINE

The vast majority (>87%) of the 219 measurements available for comparisons with model estimates were obtained from Concawe sources. A comparison of the available individual measurement data with the exposure estimates is tabulated in Table 4.3. The comparison results are presented as the ratio of the measurement result to the modelled estimate contained in the CSA. The estimates are generally observed to be highly conservative (i.e. the ratio is far below 1), with only a single measurement out of more than 200 above the estimated value.

Table 4.3 Summary of the ratios of the individual measurement results over the exposure estimate and percentage of measurements exceeding the exposure estimate (%M>T) for kerosine (by exposure scenario description)

Exposure scenario description	n	AM	GM	GSD	Min	Max	%M>T
Bulk transfers (CS14)	175	0.02	0.01	6.86	<0.01	0.45	0
Equipment cleaning and maintenance (CS39), Use as a Fuel (Prof)	32	0.16	0.03	5.96	<0.01	2.77	3
Dipping, immersion and pouring (CS4), (use in road construction)	2	0.07	0.07	1.18	0.06	0.07	0

n=number of measurements; AM=arithmetic mean of the ratio of the measurement result over the exposure estimates; GM=geometric mean of the ratio of the measurement result over the exposure estimates; GSD=geometric standard deviation of the ratios; min=lowest measurement/ exposure estimate ratio; max=highest measurement/ exposure estimate ratio; %M>T=percentage of the measurements that exceed the relevant exposure estimate

A scatterplot of the measurement data vs. the corresponding exposure estimates from the CSA is also shown on a log scale in Figure 4.1, with the 1:1 line representing situations where the exposure estimate and measurement data were identical. Below the 1:1 line the exposure estimates are higher than the actual measurements, indicating that the exposure tool provided conservative estimates in these instances. The degree of conservatism also becomes apparent in Table 4.4, where the modelled exposure estimates were found to be higher than the 75th (and even the 90th) percentile(s) of the individual measurement sets for all of the exposure scenario descriptions.

For a good understanding of the figures presented in this report it must be noted that the ECETOC TRA is a Tier 1 tool which provides only a limited number of discrete exposure estimates for any given activity. This means that the available workplace measurement results can usually only be compared to between 1 and 4 different exposure estimates (in the present report), which leads to the vertical alignment of many data points in the figures (see e.g. Figure 4.1).

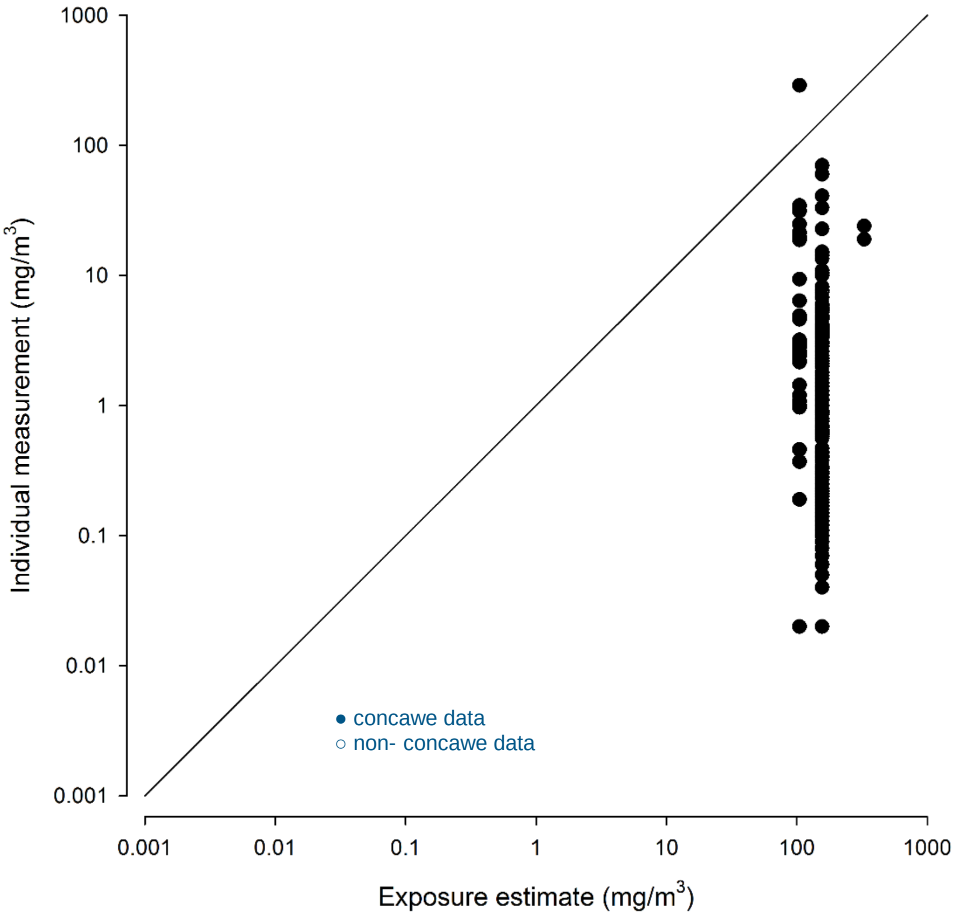

Figure 4.1 Measured data vs. exposure estimate for exposure to kerosine; both Concawe and non-Concawe data are available and included in the comparisons

Table 4.4 Comparison of the exposure estimates with the 75th and 90th percentile values of the distribution of the available individual measurements for kerosine (by exposure scenario description)

Exposure scenario description	n	T (mg/m³)	PCT (95% CI) measurements (mg/m³)		T>75th PCT	T>90th PCT
			75th %ile	90th %ile		
Bulk transfers (CS14)	175	155.75	3.70 (2.86-4.90)	6.84 (5.50-10.90)	Yes	Yes
Equipment cleaning and maintenance (CS39), Use as a Fuel (Prof)	32	104.70	14.08 (3.20-31.20)	24.80 (19.00-290.00)	Yes	Yes
Dipping, immersion and pouring (CS4) (use in road construction)	2	327.85	24.00*	24.00*	Yes	Yes

n=number of measurements; T= exposure estimate; PCT=percentile of the measurement results; T>75th PCT=exposure estimate exceeds 75th percentile of the measurement results; T>90th PCT=exposure estimate exceeds 90th percentile of the measurement results; *= Confidence intervals not estimated due to small number of observations.

The results for aggregated data are shown in Table 4.5 and Table 4.6 for equipment cleaning and maintenance and dipping activities and seem to indicate conservative results (estimates are above the 75th and 90th percentile of measurements). These percentiles though should not be confused with those of the individual measurements comprising each of the included aggregates. The predicted proportion of actual measurements above the tool estimates is shown in Table 4.5.

Table 4.5 Summary of the ratios of the arithmetic mean of the aggregated measurement results over the exposure estimates and predicted percentage of measurements exceeding the exposure estimates (%M>T) for kerosine (by exposure scenario description)

Exposure scenario description	n	AM	GM	GSD	Min	Max	%M>T
Equipment cleaning and maintenance (CS39), manufacture	11	0.53	-	-	0.53	0.53	9
Dipping, immersion and pouring (CS4)	6	0.49	0.34	3.43	0.08	0.73	17

n=number of measurements; AM=arithmetic mean of the ratio of the measurement result over the exposure estimate; GM=geometric mean of the ratio of the measurement result over the exposure estimate; GSD=geometric standard deviation of the ratios; min=lowest measurement/ exposure estimate ratio; max=highest measurement/ exposure estimate ratio; %M>T=percentage of the measurements that exceed the relevant exposure estimate.

Table 4.6 Comparison by exposure scenario description of the exposure estimates with the 75th and 90th percentile values of the distribution of the available aggregated measurement data for kerosine (by exposure scenario description)

Exposure scenario description	**g**	**T (mg/m^3)**	**PCT (95% CI) measurements (mg/m^3)**		**T>75th PCT**	**T>90th PCT**
			75th %ile	**90th %ile**		
Equipment cleaning and maintenance (CS39), manufacture	1	52.35	28.00*	28.00*	Yes	Yes
Dipping, immersion and pouring (CS4)	3	327.85	240.00*	240.00*	Yes	Yes

g=number of aggregates; T= exposure estimate; PCT=percentile of the arithmetic means of the measurement results; CI=Confidence intervals; T>75th PCT=exposure estimate exceeds 75th percentile of the arithmetic means of the measurement results; T>90th PCT=exposure estimate exceeds 90th percentile of the arithmetic means of the measurement results; *= Confidence intervals not estimated due to small number of observations.

4.2. HEAVY FUEL OILS

Very limited measured data, all from Concawe own sources, are available for HFOs. Model estimates have been done with ART in this case. A comparison of this data with estimates from the CSAs can be found in Table 4.7 and Figure 4.2. Some values above the estimate were identified. However, several measured values were below or close to the limit of detection, making a valid comparison difficult.

Table 4.7 Summary of the ratios of the individual measurement results over the exposure estimate and percentage of measurements exceeding the exposure estimate (%M>T) for heavy fuel oil (aerosol)

Exposure scenario description	**n**	**AM**	**GM**	**GSD**	**Min**	**Max**	**%M>T**
Marine vessel/barge (un)loading	5	1.79	1.45	1.97	0.83	4.36	60

n=number of measurements, AM=arithmetic mean of the ratio of the measurement result over the exposure estimates, GM=geometric mean of the ratio of the measurement result over the exposure estimates, GSD=geometric standard deviation of the ratios, min=lowest measurement/ exposure estimated ratio, max=highest measurement/ exposure estimate ratio, %M>T=percentage of the measurements that exceed the relevant exposure estimate.

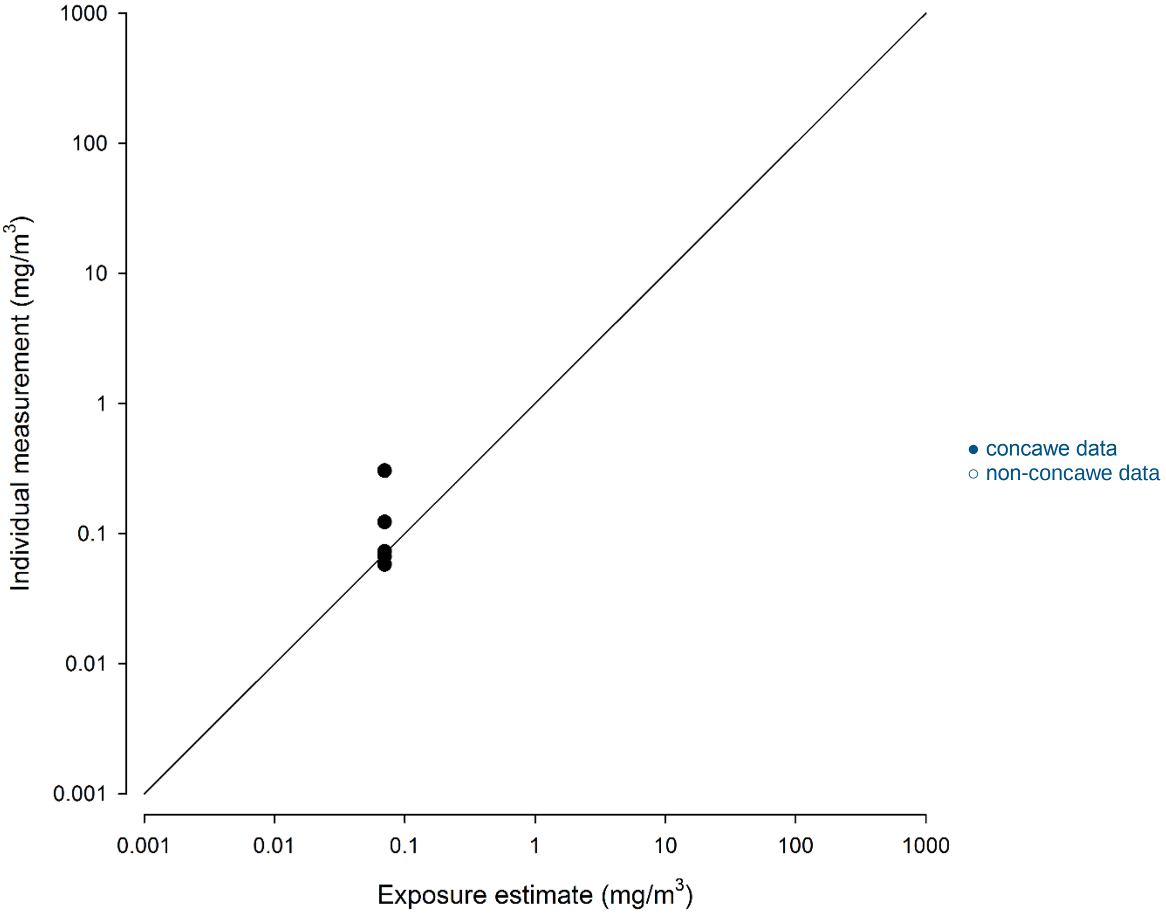

Figure 4.2 Measured data vs. exposure estimate for exposure to heavy fuel oil

4.3. NAPHTHAS

In the year 2000 the EU specification for the maximum amount of benzene in gasoline was set at 1% v/v and since then naphthas with benzene content above 1% are not widely used. Consequently, the scenarios of main relevance for which the results are presented and discussed below are those related to naphthas with 0-1% benzene content. Further analysis for naphthas with 1-5% benzene content as well as analysis utilising measurements collected outside the relevant specification periods for each naphtha type (i.e. pre- and post- to the year 2000 for naphtha 0-1% and 1-5%, respectively also referred above as the analysis of the full datasets) is provided in Appendix 3.

Results of the comparison with individual data are summarised in Figure 4.3, Table 4.8 and Table 4.9. Further comparisons with aggregated data are given in the appendix. It should be noted that for some scenarios only a small number of measurements are available for comparison.

A further comparison with aggregated measured data for bulk unloading and refuelling is described in the Appendix 3 and indicates conservative results (estimates are above 75th and 90th percentile of measurements).

Table 4.8 Summary of the ratios of the individual measurement results (restricted dataset) over the exposure estimates and percentage of measurements exceeding the exposure estimate (%M>T) for naphtha [0-1% benzene concentration] (by exposure scenario description)

Exposure scenario description	n	AM	GM	GSD	Min	Max	%M>T
Equipment cleaning and maintenance (CS39)	11	0.19	0.09	4.56	0.01	0.75	0
Equipment maintenance (CS5)	57	0.09	0.03	6.20	<0.01	1.07	2
Laboratory activities (CS36)	26	7.37	1.31	6.89	0.04	57.50	46
Bulk closed loading (CS500)	30	0.74	0.56	2.13	0.21	3.33	30
Bulk closed unloading (CS502)	7	1.59	0.77	4.16	0.13	5.75	43
Bulk closed loading and unloading (CS501)	4	0.09	0.07	2.18	0.04	0.20	0
Refuelling (CS507)	54	0.29	0.20	2.66	0.03	0.75	0

n=number of measurements; AM=arithmetic mean of the ratio of the measurement result over the exposure estimate; GM=geometric mean of the ratio of the measurement result over the exposure estimate; GSD=geometric standard deviation of the ratios, min=lowest measurement/ exposure estimate ratio; max=highest measurement/ exposure estimate ratio, %M>T=percentage of the measurements that exceed the relevant exposure estimate.

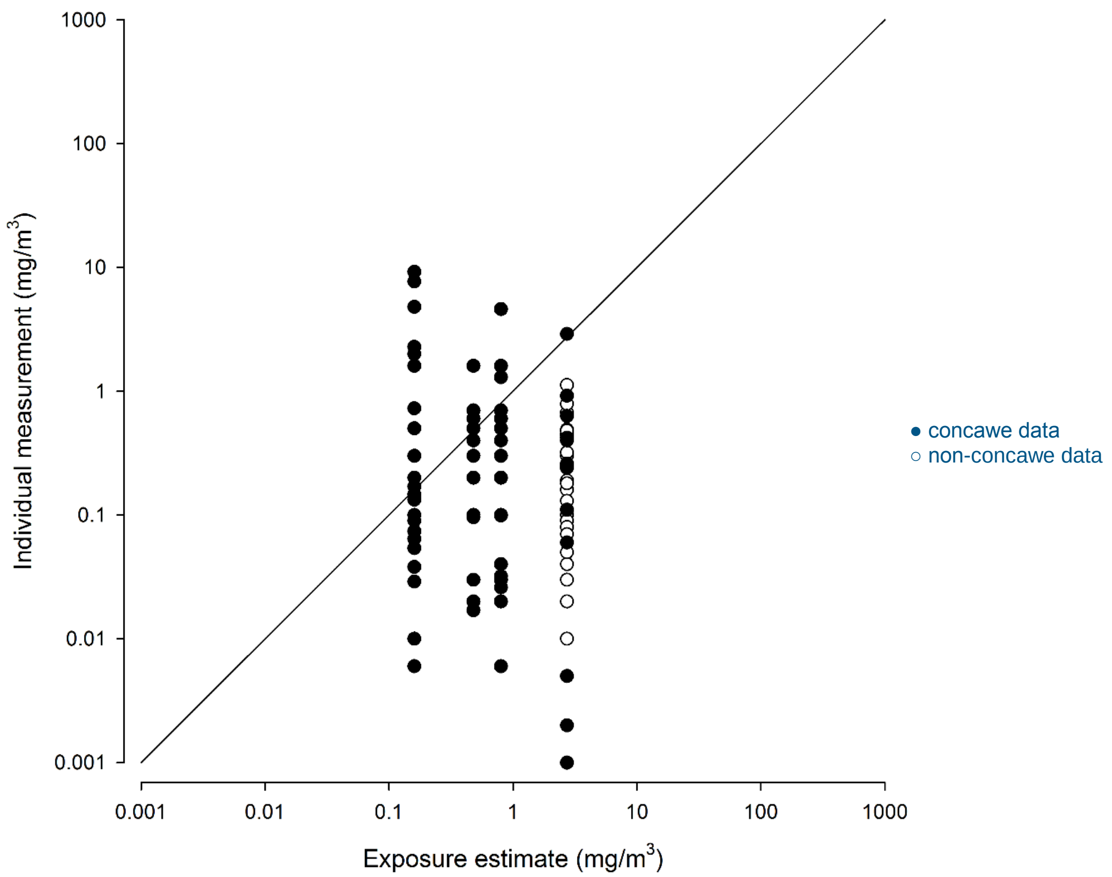

Figure 4.3 Measured data vs. exposure estimate for naphtha (0-1% benzene concentration)

Table 4.9 Comparison by exposure scenario description of the exposure estimates with the 75th and 90th percentile values of the distribution of the available individual measurements (restricted dataset) for naphtha [0-1% benzene concentration] (by exposure scenario description)

Exposure scenario description	**n**	**T (mg/m³)**	**PCT (95% CI) measurements (mg/m³)**		**T>75th PCT**	**T>90th PCT**
			75th %ile	**90th %ile**		
Equipment cleaning and maintenance (CS39)	11	0.80	0.30 (0.10-0.60)	0.30 (0.30-0.60)	Yes	Yes
Equipment maintenance (CS5)	57	2.72	0.26 (0.18-0.48)	0.63 (0.42-1.12)	Yes	Yes
Laboratory activities (CS36)	26	0.16	0.73 (0.20-7.70)	4.80 (0.73-9.20)	No	No
Bulk closed loading (CS500)	30	0.48	0.50 (0.30-0.70)	0.70 (0.60-1.60)	No	No
Bulk closed unloading (CS502)	7	0.80	1.60*	4.60*	No	No
Bulk closed loading and unloading (CS501)	4	0.48	0.06*	0.10*	Yes	Yes
Refuelling (CS507)	54	0.80	0.40 (0.30-0.40)	0.40 (0.40-0.60)	Yes	Yes

n=number of measurements; T= exposure estimate; PCT=percentile of the measurement results; T>75th PCT=exposure estimate exceeds 75th percentile of the measurement results; T>90th PCT=exposure estimate exceeds 90th percentile of the measurement results; *= Confidence intervals not estimated due to small number of observations.

4.4. OTHER LUBRICANT BASE OILS

A comparison of individual aerosol data with model estimates is given in Table 4.10, Table 4.11 and Figure 4.4. No measured values above the estimated exposure were identified. All relevant measurement data available were obtained from non-Concawe sources.

Further comparison with vapour measurements and aggregated data is given in the Appendix 3 and Table 4.12 and indicate conservative results.

Table 4.10 Summary of the ratios of the individual measurement results over the exposure estimates and percentage of measurements exceeding the exposure estimate (%M>T) for other lubricant base oils (as metal working fluids)

Exposure scenario description	**n**	**AM**	**GM**	**GSD**	**Min**	**Max**	**%M>T**
Metal machining operations (CS79) - aerosol	4	0.15	0.12	2.31	0.04	0.31	0

n=number of measurements; AM=arithmetic mean of the ratio of the measurement result over the exposure estimates; GM=geometric mean of the ratio of the measurement result over the exposure estimates; GSD=geometric standard deviation of the ratios; min=lowest measurement/ exposure estimate ratio; max=highest measurement/ exposure estimate ratio; %M>T=percentage of the measurements that exceed the relevant exposure estimate.

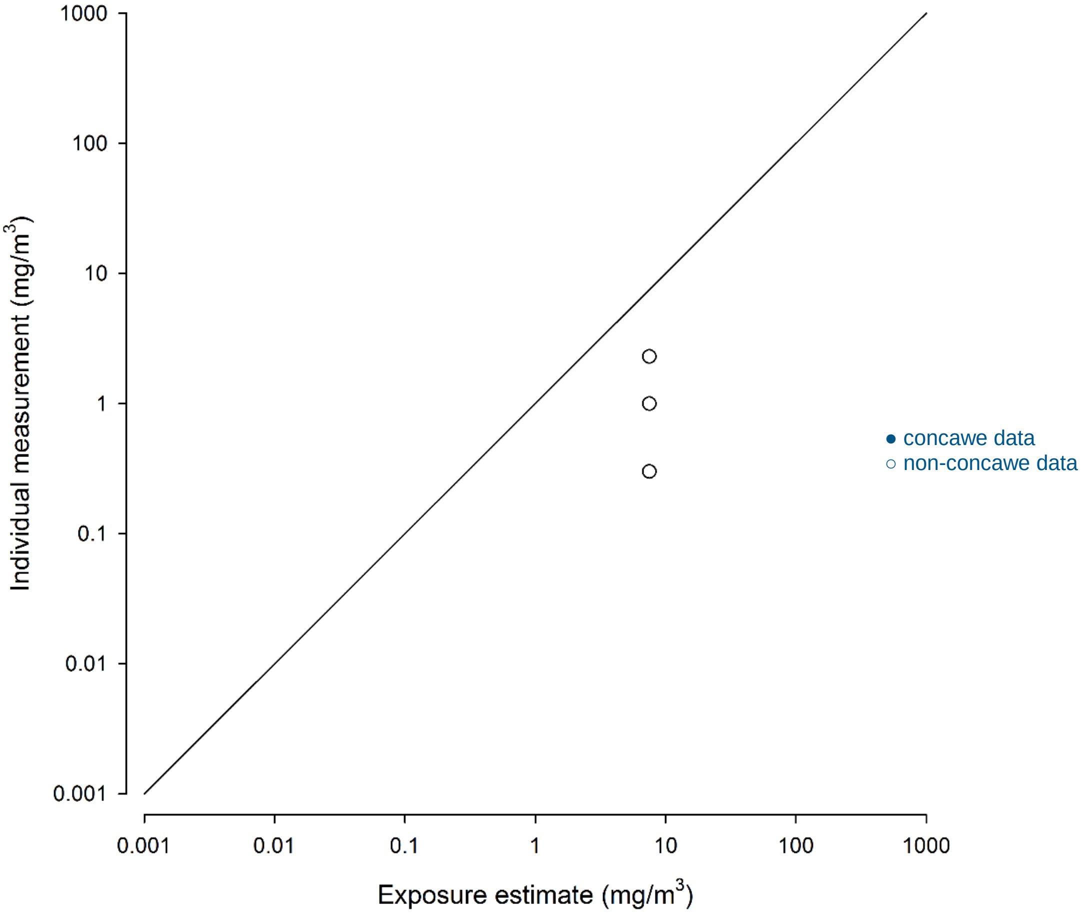

Figure 4.4 Measured individual data vs. exposure estimate for other lubricant base oils (as metal working fluids) - aerosol

Table 4.11 Comparison by exposure scenario description of the tool estimates with the 75th and 90th percentile values of the distribution of the available individual measurements for other lubricant base oils (as metal working fluids)

Exposure scenario description	**n**	**T (mg/m^3)**	**PCT (95% CI) measurements (mg/m^3)**		**T>75th PCT**	**T>90th PCT**
			75th %ile	**90th %ile**		
Metal machining operations (CS79)- aerosol	4	7.50	1.65*	2.30*	Yes	Yes

n=number of measurements; T= exposure estimate; PCT=percentile of the measurement results; T>75th PCT=exposure estimate exceeds 75th percentile of the measurement results; T>90th PCT=exposure estimate exceeds 90th percentile of the measurement results; *= Confidence intervals not estimated due to small number of observations.

Table 4.12 Summary of the ratios of the AM of the aggregated measurement results over the exposure estimates and predicted percentage of measurements exceeding the exposure estimates (%M>T) for other lubricant base oils (as metal working fluids)

Exposure scenario description	n	AM	GM	GSD	Min	Max	%M>T
Metal machining operations (CS79) - aerosol	856	0.07	0.06	1.87	0.03	0.21	0

n=number of measurements; AM=arithmetic mean of the ratio of the measurement result over the exposure estimate; GM=geometric mean of the ratio of the measurement result over the exposure estimate; GSD=geometric standard deviation of the ratios; min=lowest measurement/ exposure estimate ratio; max=highest measurement/ exposure estimate ratio; %M>T=percentage of the measurements that exceed the relevant exposure estimate.

4.5. SUMMARY

From the available scenarios and measured data the results summarised in Table 4.13 can be drawn via descriptive statistics as described in Appendix 3.

It can be seen that there is some variation in the percentage of measurements exceeding the exposure estimates for the different petroleum substances, with relatively higher percentages of underestimation for naphtha 1-5% benzene concentration (most of these data, however, pre-date the year 2000 when allowable exposure was higher than the present OEL), and for heavy fuel oil albeit based on a very small data set. However, within the single substance group results are more variable and differ between the scenarios and groups of datasets (individual vs. aggregated).

For gas oils / diesel fuels, it was decided not to include any comparison into the final discussion as the Concawe CSA mainly evaluates aerosol exposure while only measured data for vapour exposure were identified.

For naphthas, the Concawe CSAs estimate benzene concentrations corresponding to the different content in the liquid fractions (0-1% vs. 1-5% benzene). To increase the available database for both Naphtha groups, an approach was made to correct the measured values for the benzene concentration by using a factor of 0.5 for datasets before 2000 (1-5%), to be used together with lower benzene content, and a factor of 2 for datasets after 2000 (0-1%), to be used together with higher benzene content ("unrestricted datasets"; see Appendix 3 for details). However, results of the comparison were deemed to be very variable and less reliable than the restricted dataset, i.e. due to the different age of the datasets, and include the inherent additional level of uncertainty caused by the use of concentration modifier whose influence is hard to evaluate. Details of the analyses are described in Appendix 3; however, comparisons were not included in the final discussions.

In addition, following initial analysis, a group of aggregated estimates (n=11) on CS501 (Bulk closed loading and unloading) appeared to have an unreasonably high estimated AM value (207.17 mg/m^3). This was a direct consequence of an unrealistically high GSD value (54.4) provided in the report, most likely as a result of a typographical error. This estimate was excluded from the analysis (see Appendix 3 for details), resulting in 4766 instead of 4777 aggregated data and 4805 datasets overall (Table 4.13).

Concerning the measured exposure ranges (see Table 4.1 and Table 4.2), for each substance group some values are identified above the corresponding inhalation DNEL values (see section 2.2 and Appendix 2). These indicate a possible risk for the exposed worker and further suggest that a more detailed evaluation of the corresponding scenarios is warranted. It must be noted that the measurement results do not account for any respiratory protective equipment that may have been in use.

Table 4.13 Overall proportion of measurements exceeding the exposure estimates across all substances (individual and aggregated data combined)

Substance	**s**	**n**	**nM>T**	**%M>T**
Kerosine	4	226	3	1
Heavy fuel oil	1	5	3	60
Naphtha (0-1% benzene)	7	236	28	12
*(Naphtha (1-5% benzene)**	*7*	*4805*	*2705*	*56*
Other lubricant base oils-vapour	1	6601	44	1
Other lubricant base oils-aerosol	1	860	2	0

s= number of exposure scenarios; n=number of measurements; nM>T=number of measurements that exceed the relevant exposure estimate; %M>T=percentage of the measurements that exceed the relevant exposure estimate.

**mostly historical value*

5. DISCUSSION OF DISCREPANCIES BETWEEN MEASURED DATASETS AND ESTIMATES

In general, the origin of a discrepancy may be within the modelled estimate or within uncertainties related to the measured value. Within the model estimate uncertainties come from the initial estimate, from the default ECETOC TRA v.2 modifiers (LEV, concentration etc.) or from the refined approach such as a new modifier (e.g. use of drum pumps) or the estimation of liquid aerosols. Within the collated measurements there can be statistical errors or a multitude of reasons related to sampling and analytical methods which can cause biases leading to over- or underestimations of exposure. The assignment of a measurement to a modelled scenario is also a source of uncertainty in itself.

In this section, mainly underestimations within the CSAs are discussed. According to TR114 ECETOC TRA, 8-h estimate is intended to reflect the 75th percentile of an exposure distribution [20]. Therefore, as long as the 75th percentile of all measurements is below the estimate, the aim of the model is fulfilled. Nevertheless, on a case-by-case basis these scenarios may be discussed in the following subsections in case a comparably high number of scenarios showed values above the estimate.

Details on the comparison with measured data can be seen in Appendix 3.

5.1. KEROSINE

The scenarios evaluated for kerosine were the following:

- Bulk transfers (CS14)
- Equipment cleaning and maintenance (use as a fuel and manufacture) (CS39)
- Dipping, immersion and pouring (CS4).

All exposure estimates for the corresponding scenarios were vapour-based.

The comparison of the individual measurements with the corresponding scenarios from the CSAs showed minor underestimations of exposure. If the aggregated measurements and the overall database are considered, all scenarios still show 75th and 90th percentiles below the modelled estimate for aggregated and individual measurements and a maximum percentage of measurements above the estimate of 13% for “Dipping, immersion and pouring” (PROC 13). Only small numbers of measurements are available for “Dipping, immersion and pouring” (n=8) and equally for “Equipment cleaning and maintenance (use as a fuel and manufacture)” (n=11, from 1988-89).

Thus, it can be summarised that, although in some cases a larger number of datasets would be desirable, no significant underestimations were observed.

5.2. HEAVY FUEL OILS

For HFOs, one scenario was evaluated:

- marine vessel/ barge (un)loading.

The corresponding model estimate had to be aerosol-based in order to match the inhalation DNEL.

Only a small number (n=5) of recent individual inhalation individual measurements is available against which the scenario was compared. As a result it can be seen that 60 % of the measured data are above the estimate with the AM of the measurements (0.13 mg/m^3) being a factor of 2 higher than the estimate (0.07 mg/m^3).

The estimate has in this case been developed with ART and in addition been modified using a duration modifier of 0.6 (<4 h duration), which was, however, removed from the estimate for validation purposes (final estimate 0.04, without duration modifier 0.064 mg/m^3). Further details of the exposure assessment are not documented within the CSA.

The measurements used for the validation exercise represent aerosol measurements [12] which were done using the Berufsgenossenschaftliches Institut für Arbeitssicherheit (BIA) method[3]. Depending on the exact vapour pressure of the sampled substance, this method tends to shift exposure results with longer sampling durations in a way that will result in higher vapour and lower aerosol concentrations [21] due to evaporation of the aerosol. The sampling durations used during the corresponding study vary and partly correspond to the measured aerosol concentrations[4,] i.e. lower aerosol concentrations correspond to longer sampling durations. This does not explain the difference between measured value and estimate since this bias would only mean a smaller exposure value and less underestimation. Further repeat measurements are clearly advisable.

Vapour concentrations and overall concentrations are often significantly higher than aerosol concentrations and their inclusion in the comparison would not improve the result of the validation. Overall, vapour and mist concentrations range from 0.457 to 16.01 mg/m^3 (on-board) and <0.284 - <0.357 mg/m^3 (on-shore).

Liquid aerosols are within the scope of ART [22] and the corresponding background report [23] states aerosol as the predominant type of exposure for liquids of low volatility.

The experiments confirmed that both phases exist in practice but should not be added up, because the composition and biological activity of the vapour is very different from the bulk product.

Another relevant source of uncertainty, mainly linked to the sampling of aerosols for on-board workers, is the fact that all measurements are below the limit of quantification. This limit is variable, due to the different sampling duration, which leads to the range that is reported and has been used for the validation. However, it means that actual measured aerosol concentrations may be lower and more consistent with the provided estimate, although it does not allow a conclusion about the possibility of vapour exposure or a possible bias of the sampling method.

5.3. NAPHTHAS (0-1% BENZENE)

The following scenarios were evaluated during this step:

- Equipment cleaning and maintenance (CS39), manufacture
- Bulk closed loading and unloading (CS501)
- Equipment maintenance (CS5)
- Laboratory activities (CS36)
- Bulk closed unloading (CS502)
- Refuelling (CS507)
- Bulk closed loading (CS500).

All exposure estimates for the corresponding scenarios are vapour-based and use benzene as the Assessment Entity.

Concerning the comparison with individual measurements, relevant underestimations have been identified for laboratory activities (CS501), bulk closed loading and bulk closed unloading (CS502 and 500), for which neither the 75th nor the 90th percentile of the measurements lie below the model estimates, although the difference for the 75th percentile of Closed Loading is minimal, and the data set for Closed Unloading is rather small. Aggregated measurements are available for CS507 and CS502 but they do not indicate severe underestimations and do not change the overall picture to a great extent. Percentages of measurements above the exposure estimates are 18, 30 and 46% for CS502, CS500 and CS36, respectively, in all combined datasets; for the other scenarios the percentages are below 10% and therefore not considered relevant.

[3] The standard BIA sampler consists of the GSP (Gesamtstaubprobenahmesystem) with a 37 mm filter holder and cartridge for 3 g adsorbent

[4] K. Blümlein, personal communication, July, 2015

The overall number of measurements is small for CS39 and CS501 (n=11 and 4), therefore a final conclusion may still be difficult for them as results may not be representative of actual exposure for these scenarios.

All model estimates apply a concentration modifier of 0.01 to estimate benzene inhalation exposure.

The full description of **CS500, Bulk closed loading**, according to the CSA is “Bulk closed loading and unloading (e.g. road/rail car bottom loading/unloading; marine vessel/barge loading/unloading)”. The model estimate of 0.48 mg/m^3 has been derived using modifiers for the concentration (0.01) and LEV or containment (E66, 90% reduction).

The measurements used for the validation exercise were taken from Concawe report 9/02 and are a mixture of peak and full (or part) shift samples of various durations [10]. It is, however, not possible to define the extent to which this combination of different types of measurements may have influenced the validation, since peak values may not necessarily be the highest values when different specific tasks are involved. The included specific tasks within one shift vary as well (e.g. railcar lid opening/closing included or not, time in loading area/control room) which obviously influences the exact exposure pattern. Most situations refer to railcar loading of which all use a vapour recovery system (exception: two values for marine jetty crew). This is relatively consistent with the scenario description used within the CSA. The exposure reduction of vapour recovery had usually assumed to be 80% instead of 90% by Concawe. However, a replacement of this modifier would not change the outcome of the comparison.

Most measured values lie in a range between 0.1 and 0.7 mg/m^3 with only one value being at 1.6 mg/m^3.

According to the Concawe report 2/09 [10], during some measurements, petroleum products other than gasolines, e.g. light virgin naphtha and jet fuel, were loaded as well; therefore, measured benzene concentrations may have been influenced by these activities..

Another source of deviation may be the assignment of the measured samples. While the definition of the scenario in the CSA calls for bottom loading, the Concawe report describes railcar top loading with vapour recovery, which can show higher exposures than bottom loading and hence may have led to underestimations of exposure by the tool. It may, however, be debatable to which extent a generic PROC code should be able to cover both varieties within the ECETOC TRA.

The full description of CS501 from the CSA is “**CS501 Bulk closed loading and unloading**”. Bulk closed loading (e.g. road/rail car bottom loading; marine vessel/barge loading)”. Measurement data for the comparison has been taken from Concawe report 5/09 [11] and includes filling of railcars via submerged top loading but also bottom loading and unloading. Although the dataset is very small and should be used with caution, it indicates that for bottom loading no or no severe underestimations may be anticipated.

Furthermore, it is noted that both scenarios (CS501 and 500) are very similar and lead to identical estimates within the CSA. Although only the contributing scenario reference of CS501 includes “loading and unloading” while CS500 only defines “loading”, both scenarios somehow entail the same steps if the complete description in the CSA is considered. Consequently, it may be possible to discuss and evaluate them together.

In contrast to this, **bulk closed unloading (CS502)** has a more unique definition within the CSA (“CS502 Bulk closed unloading. Bulk delivery (closed) (e.g. heating oil, diesel, bunker fuel deliveries)”). The modifiers used for the estimations process are the concentration modifier (0.01) and extract ventilation (90% reduction), leading to an estimate of 0.798 mg/m^3 (higher than previous loading scenarios due to professional surroundings).

The measured data used for the validation are mainly from Concawe report 9/02 [10] and relate to road tanker drivers. Three values out of seven have been identified to be above the tool estimate.

As mentioned in report 9/02, a possible reason for this is that at some service stations where deliveries were made there were no vapour recovery facilities, but that it was assumed that this would not influence the results of the exposure measurements.

Some remarks corresponding to the analytical evaluation of the measurements include detector overloads (however not for benzene) or not typical gasoline pattern.

For **laboratory activities (CS36)** LEV (90% reduction) has been used for the assessment, leading to an estimate of 0.16 mg/m^3.

Measurements for the comparison have been found in Concawe reports 9/02 and 5/09 [10, 11] and are again based on a mixture of peak and full shift values.

It has been recognised during the assignment of scenarios that, for laboratory activities, larger scale work than generally done in laboratory settings may have been included into the comparison (e.g. blending of volumes > 1000 l). However, the corresponding situations were labelled as laboratory activity in Concawe reports.

The highest values above 1 mg/m^3 mostly refer to blending activities.

Moreover, in the Concawe report 5/09 it is recognised that exposures in production laboratories are generally low, whereas in R&D facilities occasionally elevated exposures occur during gasoline handling. This is confirmed by an evaluation of the single values in Concawe report 5/09 which show a maximum of 0.726 (fuel dispensing) for R&D and a maximum of 0.052 for production. In the earlier report 2/09, which includes values from 1999-2001, no differentiation between R&D and production is possible for laboratory work. However, it is clear that much higher values are reached than in the more recent report 5/09, which includes measurements made between 2002 and 2007 (up to 9.2 mg/m^3, although corresponding benzene concentration below 1% for both reports).

These results indicate that for laboratory work in production, especially after 2002, the probability of an underestimation is much lower, while for R&D laboratory work another assessment approach may be needed.

Details of the exposure situation (movable hood, fume hood, outside etc.) also vary and correspondingly influence the exposure result.

Overall, it can be summarised that no new Risk Management Measures (RMMs) were implemented for the discussed scenarios.

However, extract ventilation / containment were used as a reduction measure which may only approximately describe the usually present vapour recovery systems in case of loading / unloading. The concentration modifier of 0.01 is less conservative than the ECETOC default and its influence on the validation outcome cannot be evaluated in detail. The fact that it is based on measurements by Concawe suggests, however, that deviations should not be overly large. Another possible reason for the underestimation is scenario variations (e.g. presence of vapour recovery, top loading vs. bottom loading).

In case of laboratory activities, clear tendencies concerning the age and location of datasets can be identified (R&D vs. production), therefore a further differentiation, potentially amended by up-to-date measurements may be an option for improvement.

5.4. NAPHTHAS (1-5% BENZENE)

The following scenarios were evaluated:

- General exposures with sample collection (CS15 + CS56).
- Equipment cleaning and maintenance (CS39)
    - Formulation of substance
    - Manufacture of substance
    - Distribution of substance
- Bulk closed loading and unloading (CS501)
- Laboratory activities (CS36)
- Storage (CS67).

All estimates discussed in this section are vapour-based. It must be noted that where these scenarios include handling of finished European gasolines, for example in distribution, the exposures must be considered as historic, because current legislation only allows up to 1% benzene in gasoline. On the other hand, low-boiling point naphthas with 1-5% benzene continue to exist in the manufacturing environment, e.g. as intermediates and blending stocks.

Concerning individual data, scenario CS501 has only been evaluated and while the 75th percentile of the measurements was still below the estimate, the 90th exceeded it (23% of measurements above estimate).

Concerning aggregated measurements, a main point of concern is the scenario “general exposures with sample collection”, which showed 93% of all measurements above the estimate and, obviously, both the 75th and 90th percentile above the model estimate.

Other scenarios where both estimated percentiles are above the modelled value for aggregated measurements are CS39 (equipment cleaning and maintenance, mainly manufacture of substance), CS501 (bulk loading) and CS67 (storage).

The numbers of measurements above the model estimates represent 22, 28, 39 and 50% for these scenarios (individual and aggregated data). Only for “Distribution of substance / equipment cleaning and maintenance and formulation of substance / equipment cleaning and maintenance” a fraction of measurements above the estimate below 10% has been derived. This finding generally suggests that for the substance group Naphthas with 1-5% benzene the CSAs do not correlate well with the available measurements.

For formulation of substance / equipment cleaning and maintenance, only a small dataset is available (n=2) which precludes a final conclusion at this point.

For **general exposures with sample collection (CS15 + CS56)** the model estimate has been derived using PROC2 and a concentration modifier of 0.02 in combination with the RMM “sample via a closed loop system (95% reduction)”.

This measure is not a standard ECETOC TRA RMM; however, the reduction efficiency is more conservative than the difference between PROC2 (closed, continuous process with occasional controlled exposure, e.g. via sampling) and PROC1 (closed process – high integrity including sampling through closed loop systems) estimates (e.g. 2.5 ppm (PROC2 + 95% reduction) vs. 0.01 ppm (PROC1) for high volatile liquids, initial estimate).

The datasets for the validation (refinery on-site and off-site workers) have been taken from Concawe report 97/52 [8], which indicates full containment and natural ventilation / partly LEV and should therefore be compatible with the chosen PROC. However, the significant number of underestimations suggests either discrepancies between the scenario definition within model and the real situation at the workplace or an inaccurate transformation of the scenario into a model estimate.

As an example, the estimate without the 95% reduction would lead to 3.19 mg/m^3, which is still below the maximum measured value but would probably lead to less severe underestimations. Nevertheless, it cannot be decided based on the available information whether the applied RMM, its assumed efficiency, a lack of its actual application or some other unknown factor is the reason for the discrepancy.

In case of **equipment cleaning and maintenance (CS39)** especially the sub-scenario for manufacture of substance seems to be prone to underestimations.

For the calculation, the concentration modifier of 0.02 and an additional RMM “Drain down and flush system prior to equipment break-in or maintenance. E55. (90% reduction)” have been used, leading to an estimate of 1.6 mg/m^3.

The measurements used for the comparison were taken from the same report as those for the previous scenarios (97/52) and represent refinery and maintenance workers and tank cleaners. The report indicates only natural ventilation and mechanically induced dilution ventilation as RMMs. It is considered to be reasonable to assume that tanks and other tubes or parts will be drained before maintenance and other activities. How exactly the cleaning procedure (or flushing procedure) may take place and if and how this will affect the overall exposure level is, however, not known. Since the maximum measured value is 2.5 mg/m^3, a removal of the RMM exposure reduction of 90% (→16 mg/m^3) would also have removed the underestimation completely.

It is worth noting that these data also originate from refineries, while other sub-scenarios of cleaning and maintenance for formulation or distribution seem to be less problematic.

For **CS501 (bulk loading)** the concentration modifier and extract ventilation (90%) have also been used for the estimation process, leading to 0.96 mg/m^3.

A large number of datasets could be identified for the validation from Concawe reports 9/02, 2/00 and 4/87 and 97/52 [7-10].

As previously discussed, a large influence seems to be the age of the datasets which most likely also reflects general handling and applied RMMs (e.g. no or only partial vapour recovery yet; more bottom loading instead of top loading for more recent measurements).

The ranges of measured value to estimate ratios (M/T) are as follows:

- Report 9/02 [10]: 0.2-5.6
- Report 2/00 [9]: 0.39-2.2
- Report 97/52 [8]: 0.23-6.6
- Report 4/87 [7]: 0.44-6.4 (M/T ratio 432 in the Supplementary material 1B, Table S1.20 removed from analyses).

Apart from a tendency towards higher values for older measurements, differences between sub-scenarios such as top loading and bottom loading can again be observed. Since the scenario includes the description “bottom loading”, it might lead to more fitting results to remove measurements for top loading from the validation database.

For **storage (CS67)** PROC2 has been combined with a concentration modifier of 0.02 and the RMM “Store substance within a closed system. E84.” (95% reduction), leading to an exposure estimate of 0.16 mg/m^3. Again it can be argued that PROC1 would have been a more reasonable choice when a completely closed system is assessed. However, as the reduction does not lead to values below the estimate for PROC1, this approach should not lead to less conservative results.

The measurements used for the comparison refers to a terminal operator (Concawe report 97/52 [8]), who may carry out ancillary operations, e.g. like laboratory technicians (quality control/research tests), tank farm activities (dipping/sampling), water effluent treatment or occasionally drum filling. Thus, although the job is listed under “Product storage tasks”, it involves a lot of tasks not related to storage which are not all carried out under full containment (comment within report “Natural ventilation”). It is therefore questionable if it is representative for a person whose only source of exposure is the presence of contained petroleum product.

For **laboratory activities (CS36)** the concentration modifier 0.02 with LEV (90%) has been used in order to reach a model estimate of 0.32 mg/m^3.

Measured values were taken from Concawe report 2/00 [9] and refer to refinery laboratory workers, who carry out gasoline analyses (for quality assurance purposes) plus research and octane rating tests. This report contains only aggregated data sets.

There is little contextual information available in the report, therefore no further discussion of possible reasons for the deviations is possible.

In general, it can be summarised that the concentration modifier used for all model estimates does not represent the ECETOC default. It is, however, based on Concawe measurements which suggest a relatively low level of uncertainty. In some scenarios where tool estimates appear to underestimate exposure, new RMMs (closed loop sampling, drain and flush system, store within closed system) have been used. It is, however, difficult to be conclusive concerning the influence of the use of new RMMs on the discrepancy since there could also be other factors within the measured datasets (e.g. that the workers have not applied the RMM correctly) that could lead to the discrepancy.

Like in the case of the 0-1% Naphtha analyses, older datasets tend to show more underestimations than more recent ones and certain factors, such as presence of vapour recovery for bulk loading or bottom vs. top loading, may play a role as well.

5.5. OTHER LUBRICANT BASE OILS

The following scenario was evaluated during this step:

- Metal machining operations (CS79).

Both the model estimate and the available measurements were aerosol-based in the case of individual measurements, while for aggregated measurements values for both aerosol and vapour values were available.

Modifiers for the duration (1-4 h, x 0.6), enhanced general ventilation (70% reduction), < 25% concentration (40% reduction) and “Ensure operatives are trained to minimise exposures EI19 (15% reduction)” were used, leading to an estimate of approximately 4.5 mg/m^3. For the purpose of the validation, the duration modifier was removed from the estimation, leading to an estimate of 7.5 mg/m^3.

Measurements have been identified among the NIOSH datasets, in BIA report 5/99 and some additional publications related to metalworking fluids [3,16-18] and cover several tasks such as grinding, machining and turning.

No underestimations have been identified for individual datasets and only minor underestimations for the aggregated and combined datasets. Both 75th and 90th percentile of the measurements are below the model estimate and the overall fraction of measurements above the estimate is very low (0 for aerosol, 1 for vapour).

Also in this case, evaporation of mist from the filter during sampling cannot be completely excluded. This issue has also been recognised by Simpson et al., [3]. Breuer et al. on the other hand concluded that aerosol concentrations are much smaller than vapour concentrations (4.7 vs. 0.25 mg/m^3 for all metalworking fluids). The BIA report 5/99 describes a technique that captures both physical states (GGP probe head of BIA sampling system) but does not define the nature of the values included into the summarising tables.

In summary, for the vapour scenario an underestimation probably can be excluded, while for the aerosol scenario, due to the known bias of the used sampling method some uncertainty exists. However, the available measurements do not suggest a tendency for underestimation.

6. REFINEMENTS

6.1. GENERAL CONSIDERATIONS

The aim of this section is to evaluate the discrepancies identified during the comparison of measured data and CSA scenarios and discuss possibilities for refinements.

In general, there are two types of discrepancies: 1. severe overestimates of the measured value and 2. underestimates.

The ideal case is considered to be a moderate overestimation of the exposure, i.e. a conservative exposure estimate. In these cases, further refinements are usually not considered necessary.

In case of underestimates, it is not advisable to develop refined model estimates on a higher tier level. The only modelling approach available in theory in this case would be to switch to lower tier models. Since ECETOC TRA is already a Tier 1 tool, there is no tool available to our knowledge which can be assumed to give more conservative and still reasonable estimates. Other Tier 1 tools either aim at a similar level of conservativeness and/or have a different applicability domain (e.g. EMKG-EXPO-TOOL, MEASE). Therefore, in case of scenarios where only default options have been used, a further switch to more conservative options is difficult. However, in cases where already additional modifications have been implemented (e.g. RMMs, concentration modifiers) it may be argued that an estimate without these would have been more advisable, although it is usually not known which specific reason can be found for an underestimation.

On the other hand, ECETOC TRA without additional modifiers would most likely have led to some Risk Characterisation Ratio (RCR) values above 1, i.e. some kind of refinement would have been necessary anyway which as a consequence may include the risk of underestimation. Additional exposure estimates provided by other, higher tier tools may be used for comparison with the modified ECETOC TRA results in these cases.

Another approach to deal with underestimated scenarios may be the planning of experimental studies in order to verify the results of the validation with up-to-date data, identify possible flaws in the comparison exercise and, if necessary, remove sources of high exposure from the workplaces in order to reduce the risk.

In case of a clear overestimation, a refinement of the estimates with the aim to produce lower, better suited results is a possibility.

To refine an exposure estimate several options are possible:

The easiest way to achieve lower exposure estimates may be a refinement within ECETOC TRA itself, e.g. by implementing measures or modifying factors which have been indicated within the CSA but not used for the exposure assessment. This procedure may be used to further evaluate the applicability of the ECETOC TRA model to petroleum substances and scenarios. However, it would also restrict the usability of the corresponding scenarios, since the implementation of additional measures and conditions (durations, concentrations etc.) would limit their applicability to real life situations.

The model would still have the same limitations concerning scope (e.g. no liquid aerosols) and parameters.

The other option is a refinement with other, higher tier exposure models which may be better suited to describe the situation and therefore give results closer to the measured value. The application of these tools may also allow a wider definition of the scenarios concerning the applied RMMs and modifiers.

This should, however, only be done in cases where the overestimation is high enough, in order to ensure a sufficient level of conservativeness. According to the ECETOC technical report TR114 [20], the TRA is intended to reflect the 75th percentile value of the 8 h value, i.e. if the estimate lies above the 75th percentile of the measured value this should be considered to be sufficient from the model point of view. However, this does not mean that the estimate should be even lower. Thus, the approach used in this section is as follows:

A refinement is only suggested for scenarios where the tool estimate lies above the 90th percentile of the measured values. This approach will, however, only be meaningful in cases where enough data points are available. If only small numbers of measurements are available (e.g. below ~10), no conclusion on the conservativeness of a certain scenario is possible and it cannot be decided if a refinement would be possible.

Apart from that it is noted that the possibility of a refinement and the desired level of conservativeness also depends on the owner of the CSAs, who has to make the final decision concerning their implementation.

If the criteria described above are used, the following scenarios can be selected for a possible refinement:

Kerosines

- Equipment cleaning and maintenance (use as a fuel) (CS39)
- Bulk transfers (CS14)

HFOs

- no refinement is recommended, since underestimations already present for the evaluated scenario and the assessment has been done with ART. However, in general it is suggested to obtain more data and to use a method with a low enough LOQ to match the estimates.

Naphthas (0-1% benzene)

- Refuelling (CS507)
- Equipment maintenance (CS5)
- (Equipment cleaning and maintenance (CS39), manufacture – only 11 datapoints)

Naphthas (1-5% benzene)

- no refinement is recommended

OLBOs

- Metal machining operations (CS79).

6.2. POSSIBLE TOOLS

In the following subsections two possible tools, ART and STOFFENMANAGER®, that can be used for refinements, will be shortly described.

Other options may be possible for some situations (e.g. ConsExpo (general exposure part) and SprayExpo); however, these will not be evaluated further since their applicability in this context is limited. While the general exposure part of ConsExpo offers a high number of options concerning ventilation rates, room sizes etc. it does not allow for other specific RMMs or a definition of specific, occupational tasks. SprayExpo, on the other hand, is specialised on spray applications. A validation of SprayExpo, where both tools were compared concerning spray applications showed that calculation of the aerosol concentration in ConsExpo tends to overestimate the measured concentration for room spraying, but within one order of magnitude. For the spraying onto a wall or floor surface, however, ConsExpo overestimates the actual concentration partly by a factor of 10 [24].

6.2.1. STOFFENMANAGER®

STOFFENMANAGER® is a web-based inhalation exposure tool, consisting of several distinct parts[5] The parts of interest in the context of this project are mainly the quantitative part and the REACh worker exposure module. The most recent model version is STOFFENMANAGER® v.6. STOFFENMANAGER® is often referred to as a Tier 1.5 tool [31] and, therefore, offers a higher level of

[5] https://stoffenmanager.nl/Public/Explanation.aspx

detail than ECETOC TRA, although it is still comparably easy to use and does not need a lot of information in order to provide reasonable exposure estimates.

Example Refinement: Bulk loading of kerosine (CS14)

A full refinement of the validated CSAs is not the aim of this project. However, to give a general idea of the model structure of the discussed alternatives and exposure ranges estimated by the suggested tools, one example scenario has been selected for illustration.

The ECETOC TRA v.2 estimate for this scenario is 155.75 mg/m^3 while measured values range from below the limit of detection to 70.1 mg/m^3 and include scenarios such as aircraft refuelling activities, loading and general depot activities. The 75th percentile of all measurements is at 3.70 while the 90th percentile is 6.84 mg/m^3.

According to the CSA description, all scenarios are supposed to happen outdoors and daily for 1 - 4 hours at ambient temperature. Enclosed transfers are to be used and lines should be cleared prior to decoupling.

A test calculation with STOFFENMANAGER© led to the following output (performed in September 2015 with STOFFENMANAGER© version 6.1.1):

Results exposure estimations	
Estimate (mg/m^3)	50th percentile : 9.86 75th percentile : 31.47 90th percentile : 89.03 95th percentile : 166.73
Vapour pressure component (Pa)	10000 (upper border of moderate volatility range within ECETOC TRA as used in CSA)
Concentration in initial product (%)	100
Working conditions	
Vapour pressure product (Pa)	10000 Pa 20° C
Activity	Handling of liquids where only small amounts of product may be released
Duration of the task	4 to 8 hours a day (not used for assessment)
Frequency of the task	4-5 days a week (not used for assessment)
Regular cleaning of work area	Yes
Regular inspection and maintenance	Yes
Activity in breathing zone	No
Multiple employees	No
Evaporation, drying or curing after activity	No
Volume of the working room	Handling outdoors
Ventilation working room	General ventilation (open windows and doors)
Control measures at the source	No control measures at the source
Segregation of employee	The employee does not work in a cabin.
Protection of the employee	No protection

The output is lower than the ECETOC TRA estimate; however, it is still conservative.

6.2.2. ART (Advanced REACH Tool)

The Advanced REACh Tool (ART) is a web-based tool which combines a mechanistic model and an empirical part with information from an exposure database [23]. It has partly been used for exposure assessments of Concawe CSAs in case of HFOs and is able to estimate inhalation to dust, mist and vapour. The most recent version of ART is v.1.5.

Example Refinement: Bulk loading of kerosine (CS14)

The same scenario as discussed above in section 6.2.1 has been selected for illustration.

A test calculation with the Advanced REACh Tool (version 1.5; performed in September 2015) led to the following output:

Duration (mins):	480
Far-field exposure	
Operational Conditions	
Substance emission potential	
Substance product type	Liquids
Process temperature	293 K
Vapour pressure	10000 Pa
Liquid mole fraction	1
Activity coefficient	1
Activity emission potential	
Activity class	Falling liquids
Situation	Transfer of liquid product with flow of > 1000 l/minute
Containment level	Open process
Loading type	Splash loading, where the liquid dispenser remains at the top of the reservoir and the liquid splashes freely
Surface contamination	
Process fully enclosed?	No
Effective housekeeping practices in place?	Yes
Dispersion	
Work area	Outdoors
Source located close to buildings?	Yes
Worker distance	< 4 m
Risk Management Measures	
Localised controls	
Primary	Medium level containment (99.00 % reduction)
Secondary	No localized controls (0.00 % reduction)
Segregation	No segregation (0.00 % reduction)
Personal enclosure	No personal enclosure (0.00 % reduction)
Mechanistic model results	
The predicted 75th percentile full-shift exposure is 3.3 mg/m^3. The inter-quartile confidence interval is 1.6 mg/m^3 to 6.8 mg/m^3. The predicted 90th percentile full-shift exposure is 7.9 mg/m^3. The inter-quartile confidence interval is 3.5 mg/m^3–19 mg/m^3.	

Both model estimates are approximately in line with the measured values. They are lower than ECETOC TRA estimates and STOFFENMANAGER® estimates, which is to be expected for a higher tier model.

Taking into account the different types of datasets contributing to this scenario (refuelling, tanker driving etc.) and the comparably high level of detail provided by the higher tier tool ART, also a further refinement of the scenario would be possible. As an example, a change of the situation to “Transfer of liquid product with flow of 100 - 1000 l/min”, corresponding e.g. to top wing refuelling of aircrafts would lead to 0.33 mg/m^3 (75^{th} percentile) and a further change to an activity class of “Bottom loading” (under wing refuelling) to a 75^{th} percentile of 0.11 mg/m^3. However, to evaluate the applicability of such a more detailed assessment, the validation database would need to be divided into several sub-sets corresponding to the different activities.

7. QUALITATIVE DISCUSSION OF THE IMPACT OF ECETOC TRA V.3

ECETOC TRA derives exposure estimates by assigning an initial estimate to each PROC / volatility (or dustiness) combination and then applying a range of modifying factors such as LEV, concentration modifiers or other RMMs or operational conditions. The majority of Concawe's CSAs was developed using the TRA v.2. In 2011 a new version, v.3, was published.

Modifications implemented during the change from TRA v.2 to v.3 include adaptations of the initial exposure estimates assigned to each process as well as the introduction of new organisational measures and modification of already implemented measures and RMMs (see Technical Report TR114 [20]).

The main changes concerning the update from v.2 to v.3 of ECETOC TRA have been summarised in Table 7.1.

They include, as an example, an additional volatility class for substances of very low vapour pressure, which can now be considered separately (vapour pressure < 0.01 Pa). However, this will probably be of minor relevance for petroleum substances. Although most of them are of "low volatility" according to ECETOC TRA categories (i.e. below 500 Pa), only single categories may have vapour pressures which are low enough to fit into this category (HFOs, aromatic extracts: petroleum products with highest boiling point ranges [1]). Another difficulty in this context is the sampling of very low vapour pressures [25]. As discussed in earlier sections, the possibly lower vapour exposure will probably be compensated by a higher tendency to form aerosols.

An influence of the duration on dermal exposure has been implemented in some cases (high and moderate volatility liquids and non-dusty solid substances). This may lead to lower exposure estimates for some scenarios, where the duration has been used (e.g. for naphthas). However, for the validation exercise, duration modifiers usually have not been taken into account, i.e. have been removed from the estimate before the comparison.

For inhalation exposure, short term values ("peak exposure") can be estimated with ECETOC TRA v.3, which can be used for a comparison with short term DNELs if available.

Other new modifiers include the implementation of gloves for dermal exposure and general ventilation for inhalation exposure, which have already been used for the estimation process for some scenarios[6].

To estimate the volatility, the vapour pressure at process temperature can now be entered directly into the tool. This will, however, not affect the CSA estimates or the validation outcomes, since process temperatures have already been taken into account in the course of the estimation process.

Concerning the initial inhalation exposure estimates of the following PROCs have been revised in the course of the change from TRA v.2 to TRA v.3:

- PROC2 (volatiles, high and moderate volatility, industrial), downward correction
- PROC3 (volatiles, high and moderate volatility, industrial), downward correction
- PROC8a (solids, moderate dustiness, professional), upward correction
- PROC8b (volatiles, moderate volatility, industrial) downward correction
- PROC8b (solids, moderate dustiness, industrial) downward correction

The following PROCs can be found in the scenarios used for the validation exercise:

- PROC 2 Use in closed, continuous process with occasional controlled exposure (e.g. sampling)
- PROC 3 Use in closed batch process (synthesis or formulation)
- PROC 8a Transfer of substance or preparation (charging/discharging) from/to vessels/large containers at non-dedicated facilities.

[6] Concerning validation exercise: Enhanced general ventilation used for scenario CS79: Metal machining operations.

- PROC 8b Transfer of a substance or preparation (charging /discharging) from/to vessels/large containers at dedicated facilities
- PROC 13 Treatment of articles by dipping and pouring
- PROC 15 Use as laboratory reagent
- PROC 17 Lubrication at high energy conditions and in partly open process

As can be seen, there is a large overlap between both groups. However, not always the type of setting and volatility of the substance group are consistent with the definition given by TR114 for a selected scenario.

The following scenarios included in the validation will be influenced by the updates of the initial exposure estimates (considering the restricted dataset validations and volatilities as summarised in Table A1.1, Table A1.2 and Table A1.3):

Naphthas (1-5%)

- CS15+CS56 General exposures with sample collection (PROC2)
- CS67 Storage (PROC2)

If in general the CSAs are compared with the updated initial estimates, the overlap is much larger, as each CSA covers a large number of possible scenarios and the different petroleum substance groups cover different volatility groups.

In addition, further revisions of the initial estimates and LEV efficiencies have been implemented for the dermal exposure estimates and will, therefore, influence the overall outcome. LEV efficiencies for inhalation and dermal exposure are now identical, leading to lower exposure reduction efficiencies for the dermal part.

Table 7.1 Summary of updates (ECETOC TRA v.2 → ECETOC TRA v.3)

		modifying factor	exposure route	physical state
process temperature (PROCs 1-21)	vapour pressure at process temperature is entered high / medium / low / very low	included in initial exposure estimate	inhalation/ (dermal)	liquid
ventilation	good general ventilation enhanced general ventilation good general ventilation + LEV enhanced general ventilation + LEV	0.3 0.7 PROC specific PROC specific	inhalation	liquid/solid
gloves	80 % efficiency 90 % efficiency 95 % efficiency	0.2 0.1 0.05	dermal	liquid/solid
duration	Short term 15 min	4	inhalation	liquid/solid

Most updates discussed above result in downward corrections of the estimate (downward corrections of the initial inhalation estimates, possible additional implemented measures and influences). Measures such as gloves and general ventilation have already been used for the exposure assessment and the duration modifier has rarely been used. Therefore, the main changing influences concerning the updates will probably be the updated initial estimates.

Concerning the validation exercise for naphthas (1-5% benzene), already significant underestimations have been identified using ECETOC TRA v.2, therefore a further shift to downward concentrations will worsen this result. However, since most of the scenarios are not relevant anymore and measured data used for validation are from the 1990s/80s the probable impact on the future REACH registration of naphthas is expected to be small.

For other scenarios in other substance groups, a downward shift due to the implementation of further measures might not lead to a negative impact or even give results closer to reality (see also section 6, "Possible refinements"). This depends, however, on the scenario as well as measurements used for the validation (e.g. age of samples).

8. DISCUSSION

In this report, measured exposure data for petroleum substances were collated and compared with the modelled estimates from chemical safety assessments provided by Concawe.

In addition, possible options for refinements were discussed and the impacts of the recent update of the algorithms in the ECETOC TRA (v.2 vs. v.3) were evaluated in a qualitative way.

In the following subsections the results are discussed and summarised.

Table 8.1 Overall proportion of measurements exceeding the exposure estimates across all substances (individual and aggregated data combined)

Substance	s	N	nM>T	%M>T
Kerosine	4	226	3	1
Heavy fuel oil	1	5	3	60
Naphtha (0-1% benzene)	7	236	28	12
*Naphtha (1-5% benzene)**	*7*	*4805*	*2705*	*56*
Other lubricant base oils-vapour	1	6601	44	1
Other lubricant base oils-aerosol	1	860	2	0

s= number of exposure scenarios; n=number of measurements; nM>T=number of measurements that exceed the relevant exposure estimate; %M>T=percentage of the measurements that exceed the relevant exposure estimate.

**mostly historical value*

8.1. DISCREPANCIES BETWEEN ESTIMATES AND MEASUREMENTS

The summary of results (comparison of measured values with CSA estimates) is given in Table 8.1. In general, for OLBOs, naphthas (0-1% benzene) and kerosine the average percentage of measurements above the modelled estimate is below 25%, hence the estimates included in the relevant REACH dossiers are suitably conservative.

For some substance-scenario combinations, underestimations have been identified. However, the availability of measured data for comparison with the estimates differs between substances and scenarios, with the majority of data being located for OLBOs and naphthas (1-5% benzene). There are many substances and use scenarios for which CSAs had to be developed, but no measured data could be identified. In addition, in the case of naphthas with 1-5% benzene, the high number of measurements is of little value, since most scenarios are not relevant anymore. Since the awareness concerning the dangers of benzene exposure has significantly increased over time, old scenarios may not be representative of today's safety standards [26].

Some discrepancies have been identified as an example for HFOs, scenario "marine vessel barge unloading", where 60% of all measurements and again both percentiles are above the estimate. However, the number of available measurements is still quite small in this case. Concerning naphthas, there is a clear difference between the 0-1% benzene content group and the 1-5% benzene content group with the lower benzene content giving less underestimations.

Occasionally, variability within one scenario, e.g. R&D laboratory work vs. production laboratory work, can be the cause of deviation as well. If such a scenario would be split up, a higher consistency between measurements and model may be possible.

In general, there is lack of data in cases where the substance in question tends to form aerosols (e.g. gas oils), as earlier works such as the Concawe reports mainly contain vapour data which should not be used without additional aerosol data for comparison. Available aerosol data may be biased - depending on the sampling technique – resulting in an overall lack of high quality measurement data. Even if the collection method for oil mist has been identical, large variability has been observed [27].

The sampling duration of the measurements within the database used for the comparison with the modelled estimates always varies, which may be an additional source of uncertainty potentially leading to under- or overestimations, depending on the specific tasks assessed and their distribution over the sampling time.

8.2. APPLICABILITY OF RISK MANAGEMENT MEASURES NOT IN THE ECETOC TRA

For several evaluated scenarios, RMMs not previously implemented in ECETOC TRA were used in the CSAs. However, it is difficult to judge to which extent this may have influenced the outcome of the validation exercise. For many situations, not enough information was documented in the corresponding literature to decide if the measure was applied in reality. However, the suggested RMMs which were implemented into CSAs were based on workplace situations in the petroleum industry, therefore it is likely that they were present for the majority of measurements. In addition, there are some scenarios for which it is considered to be unrealistic that the corresponding measures are not applied (e.g. cleaning of systems without prior draining).

Overall, there are scenarios where certain measures have successfully been applied without underestimations (kerosine, naphthas 0-1%, OLBOs), but also scenarios were underestimations have been identified (naphthas 0-1% /1-5%, kerosine) for the same RMMs. Therefore, a final conclusion concerning the applicability of the new RMMs described in section 2.3 based on this validation exercise is not possible.

8.3. APPLICABILITY OF AEROSOL APPROACH

For two situations, i.e. OLBOs: metal machining operations; and HFO: marine vessel / barge (un)loading), aerosol data were identified that could be compared with the CSA estimates. No underestimation could be identified for the metal machining scenario, while there has been evidence for underestimation for the marine vessel / barge (un)loading one (factor of 2). However, without further evaluation a general conclusion concerning the approach is not possible.

The available sampling techniques for liquid aerosols (e.g. BIA technique) often tend to give lower results with higher sampling durations and thus, may lead to biased concentrations values. These tendencies have to be taken into account when further measurement data are gathered and used for validation or risk assessment purposes.

8.4. IDENTIFIED DATA GAPS

The comparison of CSA results with measured data could not be carried out for all substance groups and all included scenarios. The following data gaps could be identified:

- Gas Oils:
  - some vapour data were available for vacuum, hydrocracked gas oils and distillate fuels, but no aerosol data were available for any gas oil substance group.
- LBPN:
  - LBPN (< 0.1% benzene): No data were available
  - LBPN (1-5% benzene): Old data were available
  - LBPN (5-20% benzene): No data were available
  - LBPN (79% benzene): No data were available
- HRBOs: No data were available
- OLBOs: Limited data were available (two scenarios)
- HFOs: Limited data were available (one scenario, small database)
- Foots Oils: No data were available
- TDAEs: No data were available
- Severely Oxidsed Bitumen: No data were available

- MK1 Diesel Fuel: No data were available
- Crude Petrolatum: No data were available
- UATOs: No data were available

In general, it can be summarised that for the majority of petroleum substance groups no adequate measured data for a validation exercise could be identified. In those cases where data could be gathered (e.g. Gas oils, kerosine, LBPN (<1% benzene)), not the entire CSA was covered but only a selection of the more widely occurring scenarios (e.g. loading, laboratory work).

A general issue is the lack of high quality aerosol measurements, especially if it is taken into account that commonly used sampling techniques may produce a biased result. One possibility to further evaluate this issue might be to sample vapour and aerosol concentrations in one experiment and compare them, separately and added up, with the ECETOC TRA estimates. In theory, the overall exposure measurement should show less bias and, thus, maybe a better consistency with modelled estimates for overall exposure (aerosol and vapour). Although usually only the aerosol exposure is used for the risk assessment, such an experiment may give additional insight into the options of modelling different forms of exposure with ECETOC TRA.

8.5. REFINEMENTS

Available higher tier tools have been discussed and illustrated via an example situation (bulk loading of kerosines). Both models, STOFFENMANAGER® and ART, are in general able to provide inhalation exposure estimates for petroleum substances. Both models are able to estimate aerosol exposure. However, new RMMs, as suggested by Concawe, are only implemented to a very limited extent (vapour recovery in ART). Partly, the higher level of detail offered by the models allows a splitting of scenarios into several sub-scenarios (e.g. bulk loading in ECETOC TRA vs. loading and two refuelling scenarios in ART). The example scenario presented in this report showed a good consistency between measurements and model estimates. However, other examples such as the ART estimates used for the HFO CSA, suggest that this may not always be the case and a careful evaluation of input parameters and the evaluated situation will be necessary in order to avoid an underestimation of the risk.

A recent comparison of ECETOC TRA v.3, STOFFENMANAGER® v.4.5 and ART v.1.5 published by Riedmann et al. [28] indicates that all three models put very different weight on the influence of the same aspect (e.g. the dilution compartment contributes approximately three times as much in ART as it does in ECETOC TRA v.3) which is a fact that should be taken into account during the selection process.

Results of available validation studies for STOFFENMANAGER® or ART vary and usually depend on the scenario and volatility of the use substance. To our knowledge no petroleum product specific validation was carried out so far for any of the discussed models.

In general, it may be debatable if refinements should be undertaken for scenarios other than the ones already validated as long as it is not known how conservative the assumptions made so far and the resulting exposure estimates in general are.

8.6. IMPACT OF ECETOC TRA V.3 UPDATES

A change from ECETOC TRA v.2 to v.3 tend to give lower exposure results for a number of scenarios and, therefore, lead to larger discrepancies between measured and modelled exposure values in cases where underestimations are already present, and, on the other hand, better estimates for those scenarios where exposure is currently overestimated [32]. However, this was only evaluated for a very limited number of scenarios in a qualitative way and applies to inhalation estimates. Depending on the scenario and implemented measures for dermal exposure other influences on the estimate are possible due to the revision of LEV efficiencies.

9. CONCLUSION

Overall, with the identified measurement data a limited validation of the inhalation part of the petroleum substance CSAs could be performed. A number of discrepancies between measured data and CSAs were identified and some possible reasons were discussed. However, with the available data, no conclusion concerning the applicability of the non-standard RMMs and the attempt to estimate liquid aerosols within ECETOC TRA can be made. In some situations where underestimations were identified, an update of the chemical safety assessment based on the information in this report is advisable.

Although some scenarios showed a tendency for underestimation, there are also situations were refinements with higher tier tools may be possible in order to give more realistic results and avoid unnecessary restrictions. Obviously, care must be taken in order to choose the correct input parameters and keep an appropriate level of conservatism. This especially applies after the update of all CSAs from ECETOC TRA v.2 to v.3, since a number of changes (e.g. additional modifiers and opportunities for refinement) may remove the need for further refinement.

Identified data gaps include some substance groups without any data and substance groups with limited data (e.g. due to a small number of covered scenarios or old experimental data). The most prominent data gap relates to aerosol data, which could only be identified for “other lubricant base oils” and HFOs. It can, therefore, be concluded that there is a clear need for high quality measurements, especially of aerosols, of several petroleum product substance groups.

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REFERENCES

1. Carter, M.D.W., P.; Maksimainen, K.; Margary, A.; Money, C.; Pizzella, G.; Svanehav, T.; Tsang, W.; Urbanus, J.; Rohde, A., *Developing human health exposure scenarios for petroleum substances under REACH*, 2012, CONCAWE: Brussels.
2. ECETOC, *TR 107 - Addendum to ECETOC Targeted Risk Assessment Technical Report No. 93*, 2009.
3. Simpson A, *Assessment of Exposure to Light Mineral Oil Based Metal Working Fluids*, 2000, Health and Safety Laboratory
4. Simpson, A.T., et al., *Occupational exposure to metalworking fluid mist and sump fluid contaminants.* Ann Occup Hyg, 2003. **47**(1): p. 17-30.
5. Sandt, P.v.d., et al., *Human exposure information for EU substance risk assessment of kerosine*, 2007, CONCAWE.
6. Carter, M., et al., *Human exposure information for EU substance risk assessment of gas oils*, 2006, CONCAWE.
7. Coker, D.T., et al., *A survey of exposures to gasoline vapour*, 1987, CONCAWE.
8. Cecil, R., et al., *Exposure profile: gasoline* 1997, CONCAWE.
9. Claydon, M.F., et al., *A review of european gasoline exposure data for the period 1993- 1998*, 2000, CONCAWE.
10. Carter, M., et al., *A survey of european gasoline exposures for the period 1999-2001*, 2002, CONCAWE.
11. Bomer, R., et al., *Additional human exposure information for gasoline substance risk assessment (period 2002-2007)* 2009, CONCAWE.
12. Bartelloni, A., et al., *Risk assessment for emissions from hot heavy fuel oil during barge loading* 2015, CONCAWE.
13. Auffarth, J., R. Hebisch, and A. Johnen, *Stoffbelastungen beim Kraftfahrzeugrecycling*, 2002, Bundesanstalt für Arbeitsschutz und Arbeitsmedizin (BAuA).
14. Saarinen, L., M. Hakkola, and J. Kangas, *Comparison of tanker drivers' occupational exposures before and after the installation of a vapour recovery system.* J. Environ. Monit. , 2000. **2**: p. 662-665.
15. Periago, J.F. and C. Prado, *Evolution of occupational exposure to environmental levels of aromatic hydrocarbons in service stations.* Ann Occup Hyg, 2005. **49**(3): p. 233-40.
16. Breuer D, et al., *BIA-Report 5/99 Messen, Beurteilen und Schutzmaßnahmen beim Umgang mit komplexen kohlenwasserstoffhaltigen Gemischen*, 1999.
17. Breuer, D., et al., *Kühlschmierstoffe und sonstige komplexe kohlenwasserstoffhaltige Gemische in Arbeitsbereichen. Ergebnisse eines Messprogramms zur Feststellung des Standes der Technik beim Einsatz kohlenwasserstoffhaltiger Gemische.* Gefahrst. Reinhalt. Luft, 2006. **66**(10): p. 399.
18. Piacitelli, G.M., et al., *Metalworking fluid exposures in small machine shops: an overview.* AIHAJ, 2001. **62**(3): p. 356-70.
19. Lavoué, J., et al., *Monte Carlo Simulations to Reconstruct Formaldehyde exposure levels from summary parameters reported in the literature.* Ann. Occup. Hyg., 2007. **51**(2): p. 161-172.
20. ECETOC, *TR 114: ECETOC TRAv3: Background and Rationale for the Improvements*, 2012.
21. Schuchhard, S. and A.M. Rhode, *Monitoring method for inhalation exposure to gas oil vapour and aerosol*, 2012, Fraunhofer ITEM; CONCAWE.
22. TNO, et al., *ART user guide*.
23. Fransman, W., et al., *Development of a mechanistic model for the Advanced REACH Tool (ART) - Version 1.5 – (Updates previous version 1.0, June 2010)*, 2013, TNO.
24. Koch, W., et al., *Validation of an EDP assisted model for assessing inhalation exposure and dermal exposure during spraying processes*, 2012.
25. US EPA, *Heavy Fuel Oils Category Analysis and Hazard Characterization*, 2011.
26. Infante, P.F., *Benzene: an historical perspective on the American and European occupational setting. Environmental issue report No 22/2001.*, in *Late lessons from early warnings: the precautionary principle 1896–2000*.

27. Galea, K.S., et al., *Oil mist and vapour concentrations from drilling fluids: inter- and intra-laboratory comparison of chemical analyses.* Ann Occup Hyg, 2012. **56**(1): p. 61-9.
28. Riedmann, R.A., B. Gasic, and D. Vernez, *Sensitivity analysis, dominant factors, and robustness of the ECETOC TRA v3, Stoffenmanager 4.5, and ART 1.5 occupational exposure models.* Risk Anal, 2015. **35**(2): p. 211-25.
29. Christopher, Y. and M.v. Tongeren, *Occupational Dermal Exposure to Heavy Fuel Oil Part II*, 2009, IOM.
30. Christopher, Y., et al., *Occupational Dermal Exposure to Heavy Fuel Oils*, 2007, IOM.
31. ECHA. Guidance on information requirements and chemical safety assessment. Chapter R.14: Occupational exposure estimation, Version 3.0 . 2016. Helsinki: ECHA. ISBN 978-92-9495-081-9.
32. van Tongeren M, Lamb J, Cherrie JW, MacCalman L, Basinas I, Hesse S. Validation of lower tier exposure tools used for REACH: comparison of tools estimates with available exposure measurements. Annals of work exposures and health. 2017 Jul 18;61(8):921-38.

APPENDIX 1: USE MAP FOR PETROLEUM SUBSTANCES REGISTERED UNDER REACH[7]

[7] It must be noted that some uses have since been removed (in 2016) due to further clarification of the distinction between petroleum substances and hydrocarbon solvents. Typical solvent uses such as use in coatings are no longer supported for several petroleum substances.

Table A1.1 Petroleum substances: Relevant industry areas (1)

	Vacuum Gas Oils, Hydrocracked, distillate fuels	Gas Oils (other)	Straight run gas oils	Gas oils (cracked)
	low volatility, aerosol and partly vapour	*low volatility, aerosol and partly vapour*	*low volatility, aerosol and partly vapour*	*low volatility, aerosol and partly vapour*
Manufacture of substance	industrial	industrial	industrial	industrial
Use of substance as intermediate	industrial	X	industrial	industrial
Distribution of substance	industrial	industrial	industrial	industrial
Formulation & (re)packing of substances and mixtures	industrial	industrial	industrial	industrial
Uses in coatings	industrial + professional	industrial + professional	industrial + professional	x
Use as a fuel	industrial + professional	industrial + professional	industrial + professional	industrial + professional
Use as a lubricant	industrial + professional	industrial + professional	industrial + professional	industrial
Metal working fluids / rolling oils	industrial	industrial + professional	industrial + professional	x
Use as release agents or binders	industrial	industrial	industrial + professional	industrial
Oil and gas field chemicals	industrial + professional	industrial + professional	industrial + professional	x
Use in cleaning agents	X	industrial + professional	industrial + professional	x
Functional fluids	industrial	industrial + professional	industrial + professional	x
Rubber manufacture and processing	industrial	industrial	industrial	x
Water treatment applications	industrial	industrial	x	x
Use as mould release & binder	X	professional	x	x
Use in road and construction applications	professional	professional	professional	x
Use in explosive manufacture and use	X	professional	professional	x

	Vacuum Gas Oils, Hydrocracked, distillate fuels	Gas Oils (other)	Straight run gas oils	Gas oils (cracked)
	low volatility, aerosol and partly vapour	*low volatility, aerosol and partly vapour*	*low volatility, aerosol and partly vapour*	*low volatility, aerosol and partly vapour*
Polymer processing	X	X	x	x
Use in laboratories	X	X	x	x
Mining chemicals	X	X	x	x
Agrochemicals	X	X	x	x
Manufacture of articles	X	X	x	x

Table A1.2 Petroleum substances: Relevant industry areas (2)

	Low boiling point naphthas (Gasoline) (<0.1% Benzene-containing Naphtha)	**Low boiling point naphthas (Gasoline) H340 and/or H350 and/or H361; (1 percent Benzene containing Naphtha)**	**Low boiling point naphthas (Gasoline) H340 and/or H350 and/or H361; (5 percent Benzene containing Naphtha)**	**Low boiling point naphthas (Gasoline) H340 and/or H350 and/or H361; (>5 <20 percent Benzene containing Naphtha)**	**Low boiling point naphthas (Gasoline) H340 and/or H350 and/or H361; (79 percent Benzene containing Naphtha)**	**Other lubricant base oil**	**Highly refined base oil**
	high volatility, vapour	*high volatility, vapour*	*high volatility, vapour*	*high volatility, vapour*	*high volatility, vapour*	*low volatility, aerosol and partly vapour*	*low volatility, aerosol and partly vapour*
Manufacture of substance	industrial	industrial	industrial	industrial	industrial	industrial	industrial
Use of substance as intermediate	industrial	industrial	industrial	industrial	industrial	industrial	industrial
Distribution of substance	industrial	industrial	industrial	industrial	industrial	industrial	industrial
Formulation & (re)packing of substances and mixtures	industrial	industrial	industrial	industrial	industrial	industrial	industrial
Uses in coatings	industrial + professional	industrial	X	x	x	industrial + professional	industrial + professional
Use as a fuel	industrial + professional	industrial + professional	X	x	x	industrial + professional	x
Use as a lubricant	x	X	X	x	x	industrial + professional	industrial + professional

	Low boiling point naphthas (Gasoline) (<0.1% Benzene-containing Naphtha)	Low boiling point naphthas (Gasoline) H340 and/or H350 and/or H361; (1 percent Benzene containing Naphtha)	Low boiling point naphthas (Gasoline) H340 and/or H350 and/or H361; (5 percent Benzene containing Naphtha)	Low boiling point naphthas (Gasoline) H340 and/or H350 and/or H361; (>5 <20 percent Benzene containing Naphtha)	Low boiling point naphthas (Gasoline) H340 and/or H350 and/or H361; (79 percent Benzene containing Naphtha)	Other lubricant base oil	Highly refined base oil
	high volatility, vapour	*high volatility, vapour*	*high volatility, vapour*	*high volatility, vapour*	*high volatility, vapour*	*low volatility, aerosol and partly vapour*	*low volatility, aerosol and partly vapour*
Metal working fluids / rolling oils	x	X	X	x	x	industrial + professional	industrial + professional
Use as release agents or binders	x	X	X	X	x	industrial + professional	industrial + professional
Oil and gas field chemicals	x	X	X	X	x	industrial + professional	x
Use in cleaning agents	industrial + professional	industrial	X	X	x	industrial + professional	industrial + professional
Functional fluids	x	X	X	X	x	industrial + professional	industrial + professional
Rubber manufacture and processing	industrial	X	X	X	x	industrial	industrial
Water treatment applications	x	X	X	X	x	industrial + professional	industrial + professional
Use as mould release & binder	x	X	X	X	x	x	x
Use in road and construction applications	x	X	X	X	x	professional	x

	Low boiling point naphthas (Gasoline) (<0.1% Benzene-containing Naphtha)	Low boiling point naphthas (Gasoline) H340 and/or H350 and/or H361; (1 percent Benzene containing Naphtha)	Low boiling point naphthas (Gasoline) H340 and/or H350 and/or H361; (5 percent Benzene containing Naphtha)	Low boiling point naphthas (Gasoline) H340 and/or H350 and/or H361; (>5 <20 percent Benzene containing Naphtha)	Low boiling point naphthas (Gasoline) H340 and/or H350 and/or H361; (79 percent Benzene containing Naphtha)	Other lubricant base oil	Highly refined base oil
	high volatility, vapour	*high volatility, vapour*	*high volatility, vapour*	*high volatility, vapour*	*high volatility, vapour*	*low volatility, aerosol and partly vapour*	*low volatility, aerosol and partly vapour*
Use in explosive manufacture and use	x	X	X	X	x	professional	professional
Polymer processing	x	X	X	X	x	industrial + professional	industrial
Use in laboratories	x	X	X	X	x	industrial + professional	industrial + professional
Mining chemicals	x	X	X	X	x	industrial	x
Agrochemicals	x	X	X	X	x	professional	professional
Manufacture of articles	x	X	X	X	x	x	x

Table A1.3 Petroleum substances: Relevant industry areas (3)

	Heavy fuel oils	**Foots oils**	**Treated distillate aromatic extracts**	**Severely oxidised Bitumen**	**Kerosine**	**Diesel fuel**	**Crude petrolatum**	**Unrefined acid treated oils**
	low volatility, aerosol	*low volatility, aerosol and partly vapour*	*low volatility, aerosol*	*Low volatility, aerosol and vapour (estimates based on measured data)*	*Medium volatility, vapour and partly aerosol*	*medium volatility, vapour*	*Low volatility, aerosol*	*Low volatility, aerosol*
Manufacture of substance	industrial	industrial	Industrial	industrial	industrial	industrial	industrial	industrial
Use of substance as intermediate	industrial	industrial	Industrial	industrial	industrial	industrial	industrial	industrial
Distribution of substance	industrial	industrial	Industrial	industrial	industrial	industrial	x	industrial
Formulation & (re)packing of substances and mixtures	industrial	industrial	Industrial	industrial	industrial	x	x	industrial
Uses in coatings	industrial + professional	industrial + professional	Industrial	X	industrial + professional	x	x	industrial
Use as a fuel	industrial + professional	industrial + professional	industrial + professional	X	industrial + professional	industrial + professional	x	industrial
Use as a lubricant	x	X	x	industrial	industrial + professional	x	x	industrial
Metal working fluids / rolling oils	x	X	X	X	industrial + professional	x	x	industrial
Use as release agents or binders	x	X	Industrial	X	industrial + professional	x	x	x

	Heavy fuel oils	Foots oils	Treated distillate aromatic extracts	Severely oxidised Bitumen	Kerosine	Diesel fuel	Crude petrolatum	Unrefined acid treated oils
	low volatility, aerosol	*low volatility, aerosol and partly vapour*	*low volatility, aerosol*	*Low volatility, aerosol and vapour (estimates based on measured data)*	*Medium volatility, vapour and partly aerosol*	*medium volatility, vapour*	*Low volatility, aerosol*	*Low volatility, aerosol*
Oil and gas field chemicals	x	X	X	X	x	x	x	x
Use in cleaning agents	x	X	X	X	industrial + professional	x	x	x
Functional fluids	x	industrial + professional	X	X	industrial + professional	x	x	industrial
Rubber manufacture and processing	x	industrial	Industrial	X	x	x	x	industrial
Water treatment applications	x	X	X	X	x	x	x	industrial
Use as mould release & binder	x	X	X	X	x	x	x	x
Use in road and construction applications	professional	X	X	professional	professional	x	x	x
Use in explosive manufacture and use	x	X	X	X	professional	professional	x	x
Polymer processing	x	X	Industrial	X	x	x	x	industrial
Use in laboratories	x	X	X	X	x	x	x	x
Mining chemicals	x	X	X	X	x	x	x	x
Agrochemicals	x	professional	X	X	professional	x	x	x

	Heavy fuel oils	**Foots oils**	**Treated distillate aromatic extracts**	**Severely oxidised Bitumen**	**Kerosine**	**Diesel fuel**	**Crude petrolatum**	**Unrefined acid treated oils**
	low volatility, aerosol	*low volatility, aerosol and partly vapour*	*low volatility, aerosol*	*Low volatility, aerosol and vapour (estimates based on measured data)*	*Medium volatility, vapour and partly aerosol*	*medium volatility, vapour*	*Low volatility, aerosol*	*Low volatility, aerosol*
Manufacture of articles	x	X	X	industrial	x	x	x	x

APPENDIX 2: LIMIT VALUES USED FOR ASSESSMENT OF PETROLEUM SUBSTANCES

Table A2.1 Derived-No-Effect Levels and occupational exposure limits of petroleum substances (in bold values used in Concawe quantitative CSAs)

	Worker							
	Acute				Long-term			
	Systemic		Local		Systemic		Local	
Petroleum Category	**Dermal**	**Inhalation**	**Dermal**	**Inhalation**	**Dermal**	**Inhalation**	**Dermal**	**Inhalation**
Oxidised Asphalt[8]	(a)	(a)	(a)	(a)	(a)	(a)	(a)	2.9 mg/m^3/8h
Bitumen[8]	(a)	(a)	(a)	(a)	(a)	(a)	(a)	2.9 mg/m^3/8h
Cracked Gas Oils	(a)	2230 mg/m^3/15 min (for lethality) (aerosol)	(b)	(a)	**2.4 mg/kg/8h**	**27.3 mg/m^3/8h (aerosol)**	(b)	(a)
Foots Oils (sufficiently refined, IP 346# < 3%)	(a)	(a)	(a)	(a)	(a)	(a)[9] **15 ppm limit (vapour, TLV-based)**	(a)	**5.4**[10] **mg/m^3/8h (aerosol)**
Foots Oils (insufficiently refined, IP 346 ≥ 3%)[11]	(a)	(a)	(a)	(a)	1.0 mg/kg/8h	2.7 mg/m^3/8h (aerosol)	(b)	5.4[10] mg/m^3/8h (aerosol)
Heavy Fuel Oil Components[12]	(a)	4700 mg/m^3/15 min (for lethality) (aerosol)	(a)	(a)	**0.06**[13] **mg/kg/8h**	**0.12 mg/m^3/8h (aerosol)**	(b)	(a)
Highly Refined Base Oils	(a)	(a)	(a)	(a)	**220 mg/kg/8h**	160 mg/m^3/8h **5.4 mg/m3/8h (aerosol)**[14] **15 ppm limit (vapour, TLV-based)[14]**	(a)	(a)
Kerosines	(a)	(a)	(b)	(a)	(a)	(a)[9] **200 mg/m3 = 40 ppm (vapour, OEL-based)**	(b)	(a)

IP (1993) Polycyclic aromatics in petroleum fractions by dimethyl sulphoxide - refractive index method, test method designation IP 346/80. In: IP Standards for Petroleum and its Products. Part I: Methods of Analysis and Testing. Volume 2. 53rd Annual Edition. London: Institute of Petroleum

Concawe (2016) Report no. 6/16: Critical review of the relationship between IP346 and dermal carcinogenic activity

[8] Category not classified according to CLP, thus no CSA carried out
[9] No hazard identified in the Chemical Safety Report (CSR) but limit value used in CSA
[10] 5.6 mg/m^3 reported in CSR
[11] No current substance registrations in this category, thus no CSA carried out
[12] Re-calculated inhalation DNEL in 2016: 0.18 mg aerosol/m^3, averaged across 8 hours
[13] 0.065 mg/kg reported in CSR
[14] Limit value used in CSA, not reported in CSR

Low Boiling Point Naphthas (Gasolines)	(a)	1300 mg/m^3/15min	(b)	1100 mg/m^3/15 min	(a)	(a)	(b)	**838[15] mg/m^3/8h**
Low Boiling Point Naphthas (Gasolines) (H340 and/or H350 and/or H361)	(a)	1300 mg/m^3/15 min	(b)	1100 mg/m^3/15 min	(a)[16] **0.234 mg/kg/8h (benzene, DMEL)**	(a)[16] **3.2 mg/m^3 = 1 ppm (benzene, DMEL)**	(b)	838[15] mg/m^3/8h
MK Diesel Fuel	(a)	(a)	(b)	(a)	(a)	(a)[16] **200 mg/m3 = 40 ppm (vapour, OEL-based)**	(b)	(a)
Other Gas Oils (non-carcinogenic)	(a)	5003 mg/m^3/15 min (for lethality (aerosol)	(b)	(a)	**2.9 mg/kg/8h**	**16.4 mg/m^3/8h (aerosol) 15 ppm limit (vapour, TLV-based)**[17]	(b)	(a)
Other Gas Oils (carcinogenic or unknown feed stock)	(a)	5003 mg/m^3/15 min (for lethality (aerosol)	(b)	(a)	**2.9 mg/kg/8h**	**16.4 mg/m^3/8h (aerosol)**	(b)	(a)
Other Lubricant Base Oils (sufficiently refined, IP 346 < 3%)	(a)	(a)	(a)	(a)	(a)	(a)[16] **15 ppm limit (vapour, TLV-based)**	(a)	**5.4[18] mg/m^3/8h (aerosol)**
Other Lubricant Base Oils (insufficiently refined, IP 346 ≥ 3%)	(a)	(a)	(a)	(a)	**1.0 mg/kg/8h**	**2.7 mg/m^3/8h (vapour)**	(b)	5.4[18] mg/m^3/8h (aerosol)
Paraffin and Hydrocarbon Waxes	(a)	(a)	(a)	(a)	(a)	(a)	(a)	(a)
Petrolatums (insufficiently refined, IP 346 ≥ 3%)	(a)	(a)	(a)	(a)	**5.8 mg/kg/8h**	**16.4 mg/m3/8h (aerosol)**[17] 2.7 mg/m^3/8h[19]	(b)	(a)
Petrolatums (sufficiently refined, IP 346 < 3%)	(a)	(a)	(a)	(a)	(a)	(a)	(a)	(a)
Residual Aromatic Extracts (MI< 0.4)	(a)	(a)	(a)	(a)	**48 mg/kg/8h**	**137 mg/m^3/8h**	(a)	(a)
Residual Aromatic Extracts (MI≥ 0.4)	(a)	(a)	(a)	(a)	**48 mg/kg/8h**	**137 mg/m^3/8h**	(b)	(a)
Slack Waxes (insufficiently refined, IP 346 ≥ 3%)[20]	(a)	(a)	(a)	(a)	5.8 mg/kg/8h	2.7 mg/m^3/8h (aerosol)	(b)	(a)

[15] 840 mg/m^3 reported in CSR
[16] No hazard identified in the CSR but limit value used in CSA
[17] Limit value used in CSA, not reported in CSR
[18] 5.6 mg/m^3 reported in CSR
[19] Limit value reported as DNEL in CSR, not used in CSA
[20] No current substance registrations in this category, thus no CSA carried out

Slack Waxes (sufficiently refined, IP 346 < 3%)	(a)	(a)	(a)	(a)	(a)	(a)	(a)	(a)
Straight-run Gas Oils	(a)	1500 mg/m^3/15 min	(a)	(a)	**2.9 mg/kg/8h**	**16.4 mg/m^3/8h (aerosol)** **15 ppm limit (vapour, TLV-based)**[21]	(a)	(a)
Sulfur	(a)	(a)	(b)	(a)	(a)	(a)	(a)	(a)
Treated Distillate Aromatic Extracts (sufficiently refined, IP 346 < 3%)	(a)	(a)	(a)	(a)	(a)	(a)	(a)	**5.4**[22] **mg/m^3/8h (aerosol)**
Treated Distillate Aromatic Extracts (insufficiently refined, IP 346 ≥ 3%)	(a)	(a)	(a)	(a)	**1.0 mg/kg/8h**	**2.7 mg/m^3/8h**	(b)	5.4[22] mg/m^3/8h (aerosol)
Unrefined Acid Treated Oils	(a)	(a)	(a)	(a)	**5.8 mg/kg/8h**[23] 32 mg/kg/8h[24]	**2.7 mg/m^3/8h**	(b)	5.4[25] mg/m^3/8h (aerosol)
Untreated Distillate Aromatic Extracts	(a)	(a)	(a)	(a)	**1.0 mg/kg/8h**	**2.7 mg/m^3/8h (aerosol)**	(b)	(a)

[21] Limit value used in CSA, not reported in CSR
[22] 5.6 mg/m^3 reported in CSR
[23] Limit value used in CSA, not reported in CSR
[24] Limit value reported as DNEL in CSR, not used in CSA
[25] 5.6 mg/m^3 reported in CSR

Vacuum Gas Oils, Hydrocracked Gas Oils and Distillate Fuels	(a)	4300 mg/m^3/15 min (for lethality) (aerosol)	(b)	(a)	**2.9 mg/kg/8h**	**68.3 mg aerosol/m^3/8h (aerosol)** **7 ppm limit (vapour, TLV-based)**[26]	(b)	(a)

(a) No hazard identified for this route (data available).

(b) No-threshold effect and/or no dose-response information available.

[26] Limit value used in CSA, not reported in CSR

APPENDIX 3A: VALIDATION OF CONCAWE OCCUPATIONAL EXPOSURE ESTIMATES FOR PETROLEUM SUBSTANCES: DRAFT FINAL REPORT ON THE COMPARISON EXERCISE (MAIN PART)

METHODS

This section describes the methods used for identification, collection, selection and comparison of workplace measurement data for occupational use of petroleum substances.

DATA COLLECTION AND SELECTION

A number of potential data sources were identified as being suitable for inclusion in the validation exercise. These were identified through searches of established literature databases and from in-house reports from ITEM and IOM. Additional risk assessment and summary reports for a number of substances were also provided by Concawe, together with the relevant CSAs. To maximise the amount of data collected, no restriction on the age of references was applied, however it is recognised that earlier work practices, substance composition and hence exposures may not be directly comparable with more recent exposure situations.

In addition, the data providers who had supplied information previously for the *eteam* project were also contacted to request permission to use the existing data and if possible to supply additional relevant measurements.

It has been previously observed that the sourcing and collation of detailed contextual information on workplace situations is difficult. In the context of tool validation, with its requirement to ensure that the relevant input parameters are addressed, this difficulty is further magnified (Maidment, 1998; Schinkel et al, 2010; Koppisch et al, 2012). A lack of detailed information on the type and efficiency of workplace exposure control measures is particularly evident in many datasets, with descriptions varying widely in terms of their level of detail, as noted by other researchers (Fransman, 2008).

To ensure that sufficient contextual detail could be gathered to allow matching to the exposure conditions described in the Concawe CSAs, inhalation and dermal exposure data entry Microsoft Excel templates were prepared by Fraunhofer ITEM (Appendix 1). These templates included the exposure scenario description and other relevant information from the substance CSA.

The selected data were used as input into the template, and then extracted into a Microsoft Access database, to facilitate subsequent descriptive and statistical analysis using Statistical Analysis Software (SAS) v.9.4.

Both individual measurement data (i.e. relating to a discrete work situation and worker) and aggregated data (relating to a group of workers) were collected and used in the exercise.

ANALYSIS

Descriptive statistics

The ranges, central tendencies and variability of the individual and aggregated data selected for inclusion in the exercise were described and the results tabulated, together with the exposure estimates with which they were compared. Exposure concentrations in occupational settings are known to be described best by a log-normal distribution (Rappaport et al, 1991). The data were therefore assumed to be log-normally distributed and all analyses were carried out on log-transformed values.

Whenever reasonable in terms of included number of measurements, the above assumption of log-normality was graphically inspected.

For the purpose of the statistical analyses, censored individual measurement data were assigned the values reported in the source material, with the exception of a small number of measurements where the actual limit of detection (LOD) was not provided. For those measurements, a value equal to half the lowest measured value for the specific substance included in the dataset was used, in the context of an expected censoring level of <50%, reduced numbers of observations for certain substances/scenarios and the need to estimate arithmetic means (AM) for the given distributions (Hornung and Reed, 1990; Hewett and Ganser, 2007)[27].

For the aggregated measurement data, descriptive statistical parameters (e.g. number of measurements; arithmetic or geometric means; medians; standard or geometric standard deviations; percentiles or ranges) were entered in a database on the basis of their availability in the literature sources identified. Subsequently, this information was used to calculate the values of statistical parameters required for the analyses but not provided in the report. For this, the equations provided by Lavoue et al (2007) were used, specifically:

For estimating the AM from the GM (Geometric Mean) and GSD (Geometric Standard Deviation):

$$\mathrm{AM} = \mathrm{GM} \times \exp\left(\frac{(\ln(\mathrm{GSD}))^2}{2}\right) \qquad \textbf{(Equation 2.1)}$$

For estimating the GM from the AM and GSD:

$$\mathrm{GM} = \frac{\mathrm{AM}}{\exp\left(\frac{(\ln(\mathrm{GSD}))^2}{2}\right)} \qquad \textbf{(Equation 2.2)}$$

For estimating the GSD from the minimum (α) and maximum (b) values of a measurement series:

$$\mathrm{GSD} = \exp\left(\frac{\ln(\mathrm{b}) - \ln(\alpha)}{\mathrm{W_{median}}}\right) \qquad \textbf{(Equation 2.3)}$$

where Wmedian is the theoretical median standardised range. Determination of Wmedian is performed as recommended by Lavoue et al (2007) using the tables of the cumulative probability of the sampling distribution for a certain sample size provided by Zwillinger and Kokoska (2000)[28].

For estimating the GSD from the x-th Percentile (PX) of the distribution of a measurement series:

$$\mathrm{GSD} = \exp\left(\frac{\ln(\mathrm{P_X}) - \ln(\mathrm{GM})}{\mathrm{Z_X}}\right) \qquad \textbf{(Equation 2.4)}$$

where Zx is the corresponding x-percentile/quantile of the standard normal distribution as extracted from a standard distribution table.

Where the median was reported instead of the AM or the GM, this value was considered to be equal to the GM for the log-transformed dataset. If both the GM and GSD values of a measurement series were provided, then the AM was estimated using Equation 2.1. When the GSD was not provided then it was estimated from Equations 2.3 and 2.4 on the basis of the information available. If only the range was provided, then Equation (2.3) was first used to estimate the GSD. The GM was then calculated as the exponentiation of the midpoint of the log-transformed minimum (a) and maximum (b) range (Equation 2.5):

$$\mathrm{GM} = \exp\left(\frac{\ln(\mathrm{a}) + \ln(\mathrm{b})}{2}\right) \qquad \textbf{(Equation 2.5)}$$

The result from Equations (2.5) and (2.3) were then used in Equation (2.1) in order to provide an estimate of the AM.

Prior to the estimations, aggregated measurements with a minimum below a certain value (e.g. < x mg/m3) were assigned the reported upper limit as the minimum value – e.g. for an aggregated set with values: AM = 54 mg/m^3, minimum (min) =<0.1 mg/m^3, maximum (max) =100 mg/m^3, the minimum is

[27] Hornung RW and Reed LD (1991) Estimation of Average Concentration in the Presence of Nondetectable Values. Appl Occ Hyg 5: 46-51 and Hewett P and Ganser GH (2007) A comparison of several methods for analyzing censored data. Ann Occup Hyg 51: 611-32.

[28] Zwillinger D and Kokoska S. (2000) CRC standard probability and statistics tables and formulae. Boca Raton: Chapman & Hall/CRC.

assumed to be equal to 0.1. Likewise, for aggregated measurements with a minimum equal to zero, a value of half of the lowest measured value in the individual measurement database for the specific substance was used. All measurements data for which central values (i.e. AM or GM) were provided without any information on the underlying distributions (e.g. GSD or range) were excluded from the comparison exercise.

Comparison of measurement data with exposure estimates

A number of methods were used to compare the exposure estimates from the CSAs with the corresponding measurement data. The methods used are detailed below.

Ratio of exposure estimate to the measurement value.

The ratio of the exposure estimate over the corresponding measurement value was determined, with a value of <1 suggesting that the estimate was conservative, i.e. exposure was overestimated in the CSA.

For individual measurements, the measurement value given was divided by the exposure estimate.

To ensure that any impact of higher measurement values was not reduced, the AMs of the aggregated data were used in preference to the GMs to calculate the ratio. Where available, the AM from the data source was used, otherwise it was estimated as described in Section 2.2.1.

Calculation of percentage of measurements exceeding the exposure estimate

The number of cases in which the exposure estimate was exceeded was calculated directly from the ratio for individual measurements and expressed as a percentage of the total number of cases.

For the aggregated data, the proportion of measurements within a series (i.e. an individual aggregate) predicted to exceed the exposure estimate was estimated by assuming that the measurement data followed a log-normal distribution and using the provided or estimated GM and GSD values describing their distribution (Equation 2.6):

$$P(x_i > T) = 1 - \Phi\left\{Ln(T.GM^{-1}) \times \left(ln(GSD)\right)^{-1}\right\} \qquad \textbf{(Equation 2.6)}$$

Where x_i is the result from an individual measurement series; T is the estimate obtained from the tool; Φ(t) denotes the probability that a standard normal variate falls below T; and GM and GSD are the geometric mean and standard deviation from the measurements respectively.

Graphical representation of comparison

Scatterplots of the exposure estimates vs the measured data (either the individual data point or AM for individual and aggregated data, respectively) were produced to provide a visual representation of the comparison exercise.

Comparison of the 75th and 90th percentiles of the measurement data with the exposure estimates

To further characterise the nature of any differences between the measurement data and the exposure estimates, a comparison was also made with the 75th and 90th percentiles of the distribution of the individual and aggregated measurement datasets. For all scenarios with >10 measurements confidence intervals for the percentiles were also estimated using the “cipctldf” option of the UNIVARIATE procedure in SAS. This specific option provides distribution free confidence limits for the estimated percentiles calculated on the basis of order statistics (ranks) as described by Hahn and Meeker (1991)[29].

[29] Hahn GJ and Meeker WQ (1991) Statistical Intervals: A Guide for Practitioners, New York: John Wiley & Sons.

RESULTS

Data collection exercise

As noted above, approaches were made to several providers that had supplied workplace measurement data for previous exposure assessment model validation exercises. Of these providers, only the National Institute of Occupational Safety and Health (NIOSH) was able to supply data, with resourcing and data protection restrictions preventing collaboration with the remaining organisations.

During interim discussions with the potential providers, it was suggested by Concawe that the numbers of available measurement data for comparison with less common identified uses of petroleum substances were likely to be limited. An example of such situations would be the professional use of kerosine as a diluent for pesticides. The data collection exercise therefore focussed on measurements relating to more common uses of petroleum substances, for example retail gasoline and aviation-related activities.

A number of publications from peer-reviewed journals were also identified as being of relevance to the study and contained sufficient contextual detail to allow their allocation to a specific exposure scenario description.

Although data were sought for all of the petroleum substances noted in Section 1 above, measurements could only be gathered for the following categories:

- Kerosine
- Heavy fuel oil
- Naphtha (0-1% benzene)
- Naphtha (1-5% benzene)
- Other lubricant base oils

No suitable data for comparison with exposure estimates were identified for the following categories.

- Cracked gas oils
- Crude petrolatum
- Foots oils
- Highly Refined Base Oil, Liquid, vapour pressure 0.5 kPa at STP
- MK1 diesel fuel (vapour pressure 0.5 -10 kPa at STP)
- Naphtha (0-0.1% benzene)
- Naphtha (5-20% benzene)
- Naphtha (20-79% benzene)
- Other gas oils
- Treated Distillate Aromatic Extracts Sufficiently Refined (3% DMSO extractables)
- Unrefined Acid Treated Oils

For vacuum cracked gas oils, vapour measurements (n=73) by CSA were identified. However, the vacuum cracked gas oils are considered 'semi-volatiles' and hence any airborne exposure to these oils will be a mix of aerosols and vapours (CONCAWE, 2012). These data were not suitable for comparison with the tools as they would provide estimates of aerosol exposure for low-volatile agents, and hence were not included in the analyses and not further considered.

Comparison of measurement data with estimates by substance

Kerosine

Both individual and aggregated measurement data were collected for kerosine.

The exposure estimates from the kerosine CSA have been converted from ppm to mg/m^3 to allow comparison with the measured data, using an average molecular weight of 128 g/mol (nonane), (as given in the CSA). In addition, for the exposure scenario description "Dipping, immersion and pouring (CS4)", the exposure duration modifier (a multiplier of 0.6) applied in the CSA exposure estimation process was removed following consultation with Concawe, to better reflect the work activities undertaken.

The individual and aggregated data collected, corresponding exposure estimates and comparisons undertaken are described below.

Kerosine: individual measurement data

There were individual measurement data available for a limited number of scenarios for kerosine, mainly relating to bulk transfers of the material, for example during refuelling of aircraft (Table A3.1).

The exposure estimates extracted from the CSAs for the relevant scenarios are also shown in Table A3.1.

Table A3.1 Overview of individual measurements and corresponding exposure estimates from the CSA available for comparison for kerosine (by exposure scenario description)

Exposure scenario description	**s**	**n**	**Measurements**					**Exposure estimates (T)**				
			AM (mg/m3)	**GM (mg/m3)**	**GSD**	**Min (mg/m3)**	**Max (mg/m3)**	**AM* (mg/m3)**	**GM* (mg/m3)**	**GSD***	**Min (mg/m3)**	**Max (mg/m3)**
Bulk transfers (CS14)	1	175	3.51	0.81	6.86	0.02	70.10	155.75	-	-	155.75	155.75
Equipment cleaning and maintenance (CS39), Use as a Fuel (Prof)	1	32	16.26	3.36	5.96	0.02	290.00	104.70	-	-	104.70	104.70
Dipping, immersion and pouring (CS4) (use in road construction)	1	2	21.50	21.35	1.18	19.00	24.00	327.85	-	-	327.85	327.85
Overall	*3*	*209*	5.63	1.04	7.26	0.02	290.00	149.58	147.61	1.18	104.70	327.85

s= number of exposure scenarios for which data were available; n=number of measurements; AM=arithmetic mean; GM=geometric mean; GSD=geometric standard deviation; min=lowest value; max=highest value; *estimate weighted across the number of measurements included.

The individual measurement data were compared with the exposure estimates, with the results tabulated in Table 4.3 (main report part). Additional detail on each of the comparisons is given in the Supplementary material, Table S1.17 to assist in identifying possible reasons for the observed exceedances. As can be seen from Table 4.3, the exposure estimates from the CSA are generally higher than the measured data as shown by the AMs and GMs of the ratios all being <1. In one case, i.e. CS39: Equipment, cleaning and maintenance during professional use of kerosine as a fuel, one measurement exceeded the estimate (equivalent to 3% of the total of 32 measurements for the scenario), with a corresponding maximum ratio of 2.77. This measurement was associated with a worker dismantling a valve in a garage, where exposures may not be well controlled, and therefore not fully representative of the risk management measures specified in the CSA.

A scatterplot of the measurement data vs the corresponding exposure estimates from the CSA is also shown on a log scale in Figure 4.1 (main report part), with the 1:1 line representing situations where the exposure estimate and measurement data were identical.

The degree of conservatism is further detailed in Table 4.4 (main report part), where the exposure estimate is higher than the 75th and 90th percentiles of the individual measurements for all of the exposure scenario descriptions.

Kerosine: aggregated measurement data

A number of aggregated data were also collected for exposure to kerosine, as described in Table A3.2 together with the corresponding exposure estimates from the CSAs.

Table A3.2 Overview of aggregated measurement data and corresponding exposure estimates from the CSA available for comparison for kerosine (by exposure scenario description)

Exposure scenario description	s	g	n	Measurements			Exposure estimates		
				Mean AM (mg/m3)	Min AM (mg/m3)	Max AM (mg/m3)	AM T (mg/m3)	Min T (mg/m3)	Max T (mg/m3)
Equipment cleaning and maintenance (CS39), manufacture	1	1	11	28.00	28.00	28.00	52.35	52.35	52.35
Dipping, immersion and pouring (CS4)	1	3	6	161.00	27.00	240.00	327.85	327.85	327.85
Overall	*2*	*4*	*17*	*128.00*	*27.00*	*240.00*	*258.98*	*52.35*	*327.85*

s= number of exposure scenarios for which data were available; g=number of aggregates (arithmetic mean estimates); n=number of measurements; Mean AM=mean of the arithmetic means of the measurement results; Min AM=lowest arithmetic mean value of the aggregated measurement results; Max AM= highest arithmetic mean value of the aggregated measurement results; AM T=arithmetic mean of the exposure estimates weighted across the number of aggregates included; Min T=lowest exposure estimate; Max T=highest exposure estimate.

The ratios of the AM of the aggregated measurement results over the relevant exposure estimates were calculated. These ratios are described in Table 4.5 (main report part), along with the estimated percentage of measurements exceeding the estimate (%M>T). As can be seen from the table, all of the AMs and GMs of the ratio for the exposure scenario involved were <1. For each of exposure scenario description, there was a very small number of measurements which exceed the estimate. However, there were limited numbers of comparator data for the exposure scenarios "Equipment cleaning and maintenance (CS39), manufacture" and "Dipping, immersion and pouring (CS4)", thus firm conclusions cannot be drawn regarding the match between the estimate and the measured data. A visual representation of the comparison of the exposure estimates with the measurements is also given on a log scale in Figure A3.1.

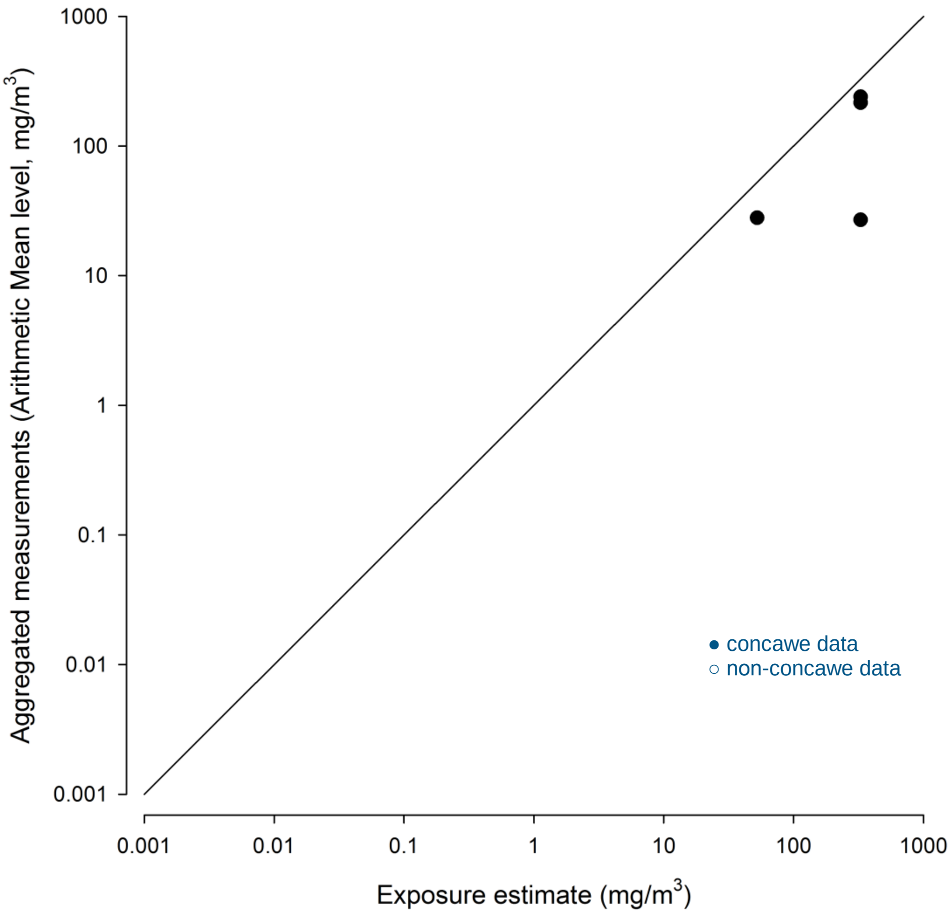

Figure A3.1 Comparison of the arithmetic means of the aggregated data with the exposure estimates for kerosine

Information on the comparison between the distribution of the measurement data and the exposure estimates is shown in Table 4.6 (main report part), where it can be seen that the exposure estimates for the scenarios "Equipment cleaning and maintenance (CS39), manufacture" and "Dipping, immersion and pouring (CS4)" are higher than the 90^{th} percentile of the aggregated datasets used.

Kerosine individual and aggregated (combined)

The individual and aggregated datasets were then combined and used to give an overall percentage of measurements exceeding the exposure estimate (Table A3.3). From the combined results it becomes clear that the overall level of conservatism of the exposure estimate is relatively high in the context of the validation dataset, i.e. <2%.

Table A3.3 Overall percentage of measurements of kerosine exceeding the exposure estimates across by exposure scenario description (individual and aggregated data combined)

Exposure scenario description	s	n	nM>T	%M>T
Bulk transfers (CS14)	1	175	0	0
Equipment cleaning and maintenance (CS39)				
Overall	*2*	*43*	*2*	*5*
Manufacture of substance	1	11	1	9
Use as a Fuel (Professional)	1	32	1	3
Dipping, immersion and pouring (CS4)	1	8	1	13
Overall	*4*	*226*	*3*	*1*

s= number of exposure scenarios for which data were available; n=number of measurements; nM>T=number of measurements that exceed the relevant exposure estimate; %M>T=percentage of the measurements that exceed the relevant exposure estimate.

Heavy fuel oil

Overall, the numbers of inhalation data available for comparison with the exposure estimates for use of heavy fuel oil were very limited. Although some dermal data were identified, its prior use in the determination of the CSA exposure estimate precluded its inclusion in the current validation exercise. Guidance from Concawe indicated that only measurement data for aerosols that related to a single scenario description (“Marine vessel/barge (un)loading”) were suitable for the comparison exercise. These data, relating to workers on-board the vessel, are shown with the relevant estimate in Table A3.4. The Advanced REACH Tool (ART) had been used to generate the exposure estimate for this scenario rather than the standard ECETOC TRA tool. In the heavy fuel oil CSA, an exposure modifier for task duration was subsequently applied to indicate that exposure time should be restricted. This modifier (a multiplying factor of 0.6) was removed from the estimate prior to its comparison with the measurements. In addition to being restricted in number and scope, the limits of detection for some of the data (n=4) were higher than or similar to the exposure estimate, making a valid comparison difficult.

The comparison of the data with the estimate is shown in Table 4.7 and Figure 4.2 (main report part).

Table A3.4 Overview of individual measurements and corresponding exposure estimate from the CSA available for comparison for heavy fuel oil (aerosol)

Exposure scenario description	s	n	Measurements					Exposure estimates (T)				
			AM (mg/m3)	GM (mg/m3)	GSD	Min (mg/m3)	Max (mg/m3)	AM (mg/m3)*	GM (mg/m3)*	GSD*	Min (mg/m3)	Max (mg/m3)
Marine vessel/barge (un)loading	1	5	0.13	0.10	1.97	0.06	0.31	0.07	-	-	0.07	0.07

s= number of exposure scenarios for which data were available; n=number of measurements; AM=arithmetic mean of the measurement results; GM=geometric mean of the measurement results; GSD=geometric standard deviation of the measurement results; min=lowest measurement result; max=highest measurement result; *estimate weighted across the number of measurements included.

The 75th and 90th percentiles of the distribution of the small comparator dataset were calculated and compared with the estimate. The results of this comparison are shown in Table A3.5, where it can be seen that the exposure estimate was lower than the 75th percentile of the measurements.

Table A3.5 Comparison of the tool estimates with the 75th and 90th percentile values of the distribution of the available individual measurements for heavy fuel oil (aerosol)

Exposure scenario description	s	n	AM T (mg/m3)	PCT (95% CI) measurements (mg/m3)		T>75th PCT	T>90th PCT
				75th %ile	90th %ile		
Marine vessel/barge (un)loading	1	5	0.07	0.12*	0.31*	No	No

s= number of exposure scenarios for which data were available; n=number of measurements; AM T= arithmetic mean of the exposure estimates weighted across the number of measurements included; PCT=percentile of the measurement results; T>75th PCT=exposure estimate exceeds 75th percentile of the measurement results; T>90th PCT=exposure estimate exceeds 90th percentile of the measurement results; *= Confidence intervals not estimated due to small number of observations.

Taking into consideration the very small dataset available for validation of the heavy fuel oil CSA exposure estimates, it is difficult to draw any firm conclusions regarding the level of conservatism. In particular, as the limits of detection for some of the measurements were higher than the given exposure estimate, it would be beneficial to collect additional specific aerosol measurements for a wider variety of tasks, to allow a more comprehensive validation to be carried out.

Naphtha

In this section, the establishment of a dataset for comparisons with the tool estimates for naphtha containing 0-1% benzene and 1-5% benzene concentrations is described alongside the applied approach for validation analyses. The results from the comparisons carried out are shown in the sections that follow, sorted by type of naphtha.

During the data mining process, measurement data for naphtha's to be used in comparisons were selected on the basis of the underlying activities and their match with the descriptions of the activities given in the CSAs for the various naphtha. From direct communications with Concawe during the project, the benzene concentration of naphtha (as gasoline) was generally higher prior to the year 2000, with concentrations of a maximum of 5% commonplace. This implied that measurements collected prior to 2000 could be considered as more suitable for direct comparisons with the exposure estimates for naphtha 1-5% benzene concentration. It also implied that these measurements were less representative of modern work practices, compared to those collected after 2000, and thereby less suitable for comparisons with the naphtha 0-1% benzene concentration tool estimates. In addition, the lack of detail in the task descriptions increased the amount of associated uncertainty regarding applicability to the CSAs, with similar uncertainty about the actual benzene concentration which also varied by refinery/site.

Discussions with Concawe following issue of the first draft report on the comparison exercise suggested that, for comparisons with the tool estimates for naphtha 0-1% benzene concentration, only measurement data collected after the year 2000 should be used. Similarly, comparisons for naphtha with 1-5% benzene content should most adequately be performed using data from measurement series performed prior to the year 2000. However, activity descriptions for several measurement data collected before 2000 were deemed suitable for CSA descriptions for naphtha (0-1% benzene concentration) and the case was similar for data collected after 2000 and the CSA descriptions for naphtha (1-5% benzene concentration). To increase analytical power, and despite the previously described limitations, it was decided that these measurements should not a priori be excluded from the naphtha type-specific analysis. Instead, following discussions with Concawe, these measurements had their measured concentrations corrected for the content of benzene by applying date-related modifiers and a two-step analytical strategy was applied.

Specifically, for naphtha 0-1% benzene concentration comparisons were made:

a) At first step by using a dataset comprising only of relevant measurement data collected post-2000 (hereafter called the “restricted dataset”) and

b) At a second step, all pre- 2000 measurements that fit the relevant CAS descriptions were included and the analysis was repeated using the combined pre- and post-2000 measurement dataset (hereafter called the “full dataset).

Likewise, for naphtha 1-5% benzene content comparisons were made:

a) First against only the relevant measurement data collected before 2000 (i.e. restricted dataset) and

b) At a second step, all relevant measurements collected after the year 2000 were also added and the analysis was repeated in a way similar to that of the naphtha 0-1% benzene concentration (i.e. full dataset).

An overview of the available measurements for comparisons across the different datasets is shown in Table A3.6, by measurement year and type of data concerned. A summary of the applied correction factors is also provided. As it can be seen from the table, the final dataset comprised of 258 individual and 98 aggregated measurements representing a total of 7330 measurements.

The vast majority (97%) came from the period prior to 2000, whereas only 236 measurements, mostly individual ones, were collected after that year. Exposure estimates for some CSAs where not available for both naphthas (e.g. estimates for CS507 were available only for naphtha 0-1% benzene) and measurement situations could not always be matched to the conditions described in the available CSAs. As a result, all data could not be used in comparisons with both the 0-1% benzene and the 1-5% benzene concentrations and the number of actual measurements included in the final databases is not identical between the two types of naphtha. This was true for 39 individual and 9 aggregated measurements (representing a total of 399 measurements) in concern to naphtha 0-1% benzene, and for 182 individual and 25 aggregated measurements (representing a total of 1723 measurements) for naphtha 1-5% benzene. A detailed list of the actual data comprising the restricted dataset and including their sources is provided in the Supplementary material 1B, Table S1.19 for naphtha (0-1% benzene) and in Table S1.20 for naphtha (1-5% benzene). All additional measurements included in the full-dataset and used in comparisons for naphtha (0-1% benzene) and for naphtha (1-5% benzene) are detailed together with their sources in Table S1.22 and S1.23, respectively.

The outcomes of all comparisons performed are presented below, sorted by naphtha content (i.e. naphtha 0-1% benzene concentration and naphtha 1-5% benzene concentration), starting always from those using the restricted dataset. Results from the analysis using all the measurements available (i.e. full dataset) should be considered, for both naphtha 0-1% benzene and 1-5% benzene concentration, as being less reliable that those using the restricted datasets and their interpretation should be made with caution.

Table A3.6 Overview of measurement data available for comparisons for naphtha by dataset, measurement period, and type of data together with the applied correction factors for benzene content.

Dataset	Before 2000				After 2000				All periods		
	CF	n (g) Individual data	n (g) Aggregated data	n (g) Total	CF	n (g) Individual data	n (g) Aggregated data	n (g) Total	n (g) Individual data	n (g) Aggregated data	n (g) Total
0-1% benzene											
Restricted	-	-	-	-	1.0	189 (0)	47 (3)	236 (3)	189 (0)	47 (3)	236 (3)
Additional	0.5	30 (0)	5911 (72)	5941 (72)	-	-	-	-	30 (0)	5911 (72)	5941 (72)
Full	0.5	30 (0)	5911 (72)	5941 (72)	1.0	189 (0)	47 (3)	236 (3)	219 (0)	5958 (75)	6177 (75)
Excluded	-	39 (0)	360 (9)	399 (9)	-	0 (0)	0 (0)	0 (0)	39 (0)	360 (9)	399 (9)
1-5% benzene											
Restricted	1.0	39 (0)	4777 (59)	4816 (59)	-	-	-	-	39 (0)	4777 (59)	4816 (59)
Additional	-	-	-	-	2.0	37 (0)	0 (0)	37 (0)	37 (0)	0 (0)	37 (0)
Full	1.0	39 (0)	4777 (59)	4816 (59)	2.0	37 (0)	0 (0)	37 (0)	76 (0)	4777 (59)	4853 (59)
Excluded	-	30 (0)	1494 (22)	1524 (22)	-	152 (0)	47 (3)	199 (3)	182 (0)	1541 (25)	1723 (25)
All naphtha											
Full	-	69 (0)	6271 (81)	6340 (81)	-	189 (0)	47 (3)	236 (3)	258 (0)	6318 (84)	6576 (84)

CF=Correction factor applied, n= number of measurements, g=number of aggregates

Naphtha (0-1% benzene concentration)

A two-step data gathering and analytical approach was applied in comparisons for the naphtha. In the following sub-section, two different sets of validation analyses for naphtha (0-1% benzene concentration) are described, together with the results from the comparisons carried out.

The outcomes of the analysis using the restricted dataset comprising only of measurements collected after the year 2000, i.e. with benzene content generally <1%, are first summarised. Then the results from the analysis using all measurements available (i.e. full dataset) are presented. This latter dataset includes measurements collected prior to the year 2000 when benzene concentration of naphtha (as gasoline) was generally higher with a maximum concentration of 5% commonplace. For the purpose of analysis, all relevant pre-2000 measurements were considered to represent naphtha with a benzene content of 1-5%, and (as recommended earlier in the project by Concawe) had their concentrations reduced by 50% (correction factor of 0.5) to represent measurements with a benzene content of 0-1%. Discussions with Concawe following issue of the first draft report on the comparison exercise suggested that these pre-2000 data may not be fully representative of more modern work practices. Therefore, results from the analysis using all the measurements available (i.e. full dataset) should be considered less reliable and interpretations should be made with caution.

Naphtha (0-1% benzene concentration): individual measurement data (restricted dataset)

The following individual measurements (Table A3.7) were collected and used in comparisons with the given exposure estimates for naphtha with a concentration of (0-1% benzene). As noted above, these comparator data include only measurements taken after 2000, i.e. comprise the restricted dataset.

Table A3.7 Overview of individual measurements (restricted dataset) and corresponding exposure estimates from the CSA available for comparison for naphtha [0-1% benzene concentration] (by exposure scenario description)

Exposure scenario description	s	n	Measurements					Exposure estimates (T)				
			AM (mg/m3)	GM (mg/m3)	GSD	Min (mg/m3)	Max (mg/m3)	AM* (mg/m3)	GM* (mg/m3)	GSD*	Min (mg/m3)	Max (mg/m3)
Equipment cleaning and maintenance (CS39)	1	11	0.15	0.07	4.56	0.01	0.60	0.80	-	-	0.80	0.80
Equipment maintenance (CS5)	1	57	0.24	0.07	6.20	<0.01	2.90	2.72	-	-	2.72	2.72
Laboratory activities (CS36)	1	26	1.18	0.21	6.89	0.01	9.20	0.16	-	-	0.16	0.16
Bulk closed loading (CS500)	1	30	0.36	0.27	2.13	0.10	1.60	0.48	-	-	0.48	0.48
Bulk closed unloading (CS502)	1	7	1.27	0.62	4.16	0.10	4.60	0.80	-	-	0.80	0.80
Bulk closed loading and unloading (CS501)	1	4	0.04	0.03	2.18	0.02	0.10	0.48	-	-	0.48	0.48
Refuelling (CS507)	1	54	0.23	0.16	2.66	0.02	0.60	0.80	-	-	0.80	0.80
Overall	*7*	*189*	*0.41*	*0.14*	*4.77*	0.01	*9.20*	*1.23*	*0.85*	*2.53*	*0.16*	*2.72*

s= number of exposure scenarios for which data were available; n=number of measurements; AM=arithmetic mean; GM=geometric mean; GSD=geometric standard deviation; min=lowest value; max=highest value; *estimate weighted across the number of measurements included.

The results of the comparison of the measurements with the exposure estimates are shown in Table 4.8 (main report part), where it can be seen that for some scenario descriptions, a number of measurements are higher than the estimate for the activity.

Additional detail on these comparisons is given in the Supplementary material, Table S1.19 to assist in evaluating the assumptions and exposure modifiers used during generation of the CSA exposure estimate. The measurement data were then plotted against the corresponding exposure estimate, (Figure 4.3, main report part), from where it can be seen that a number of points lie above the 1:1 line. This suggests that for this dataset, the exposure estimates may not always be conservative, in particular for laboratory activities (for example in fuel testing facilities) and bulk closed unloading activities where around half of the measurements were higher than the estimates.

To assist in identifying the cases where the exposure estimate was less than the measurement value, the estimates were also compared with the 75^{th} and 90^{th} percentiles of the individual measurement dataset distribution (Table 4.9, main report part). From this, it can also be seen that the exposure estimate is lower than the 75^{th} percentile of the measurements allocated to scenario descriptions “Laboratory activities (CS36)”; “Bulk closed loading (CS500)” and “Bulk closed unloading (CS502)”. However; it should also be noted that the numbers of data for the latter of these scenarios (“Bulk closed unloading (CS502)” are very limited (n=7), thus increasing the uncertainty of this comparison. Also, although care has been taken in matching measurement data to the correct exposure scenario description, there is a degree of uncertainty in the allocation of the measurement data for fuel testing activities and other similar tasks to the ““Laboratory activities (CS36)”. It is therefore possible that the measurement data used in the comparison relate to larger scale work than generally done in laboratory settings.

Naphtha (0-1% benzene concentration): aggregated data (restricted dataset)

A relatively small number of aggregated measurement data (n=47) were also collected in the restricted dataset for comparison with the exposure estimates for naphtha (0-1% benzene concentration). These data are shown in Table A3.8 by exposure scenario description, together with the corresponding exposure estimate. The comparisons are also shown visually as a scatterplot of the arithmetic means of the aggregated measurement data versus the relevant exposure estimate in Figure A3.2.

Table A3.8 Overview of aggregated measurement data (restricted dataset) and corresponding exposure estimates from the CSA available for comparison for naphtha [0-1% benzene concentration] (by exposure scenario description)

Exposure scenario description	**s**	**G**	**n**	**Measurements**			**Exposure Estimates (T)**		
				Mean AM (mg/m3)	**Min AM (mg/m3)**	**Max AM (mg/m3)**	**AM T (mg/m3)**	**Min T (mg/m3)**	**Max T (mg/m3)**
Bulk closed unloading (CS502)	1	2	28	0.38	0.14	0.62	0.80	0.80	0.80
Refuelling (CS507)	1	1	19	0.16	0.16	0.16	0.80	0.80	0.80
Overall	*2*	*3*	*47*	*0.31*	*0.14*	*0.62*	*0.80*	*0.80*	*0.80*

s= number of exposure scenarios for which data were available; g=number of aggregates (arithmetic mean estimates); n=number of measurements; Mean AM=mean of the arithmetic means of the measurement results; Min AM=lowest arithmetic mean value of the aggregated measurement results; Max AM= highest arithmetic mean value of the aggregated measurement results; AM T=arithmetic mean of the exposure estimates weighted across the number of aggregates included; Min T=lowest exposure estimate; Max T=highest exposure estimate.

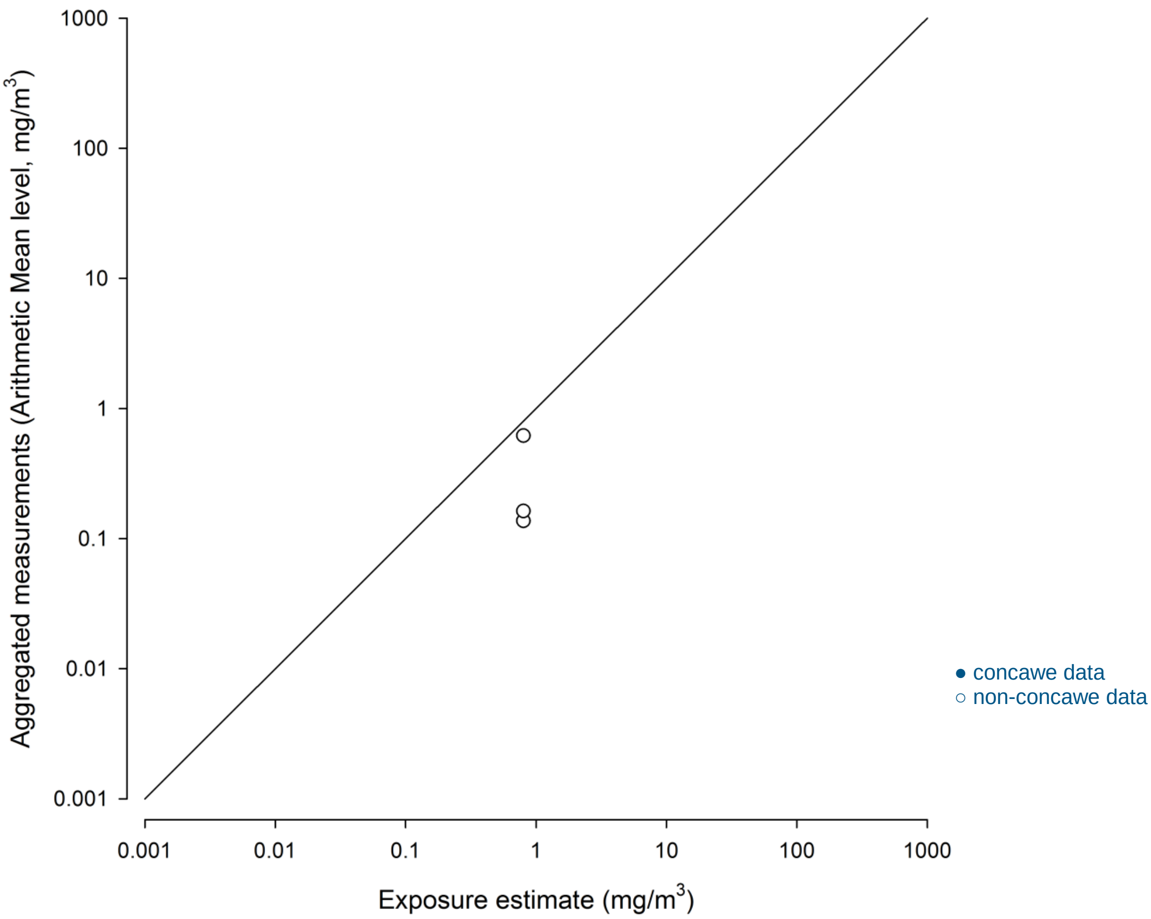

Figure A3.2 Comparison of the arithmetic means of the aggregated data with the exposure estimates for exposure to naphtha (0-1% benzene concentration)

From Table A3.9 and Figure A3.2, it can be seen that, whilst there were no cases where the AM or GM of the ratio of the AM of the aggregated data to the exposure estimate was >1, a small number of data points for "Bulk closed unloading (CS502)" activities were higher than the estimate value. These relate to non-Concawe data for benzene exposure during tanker loading and unloading [14]. As for the individual data set for naphtha, additional detail on the specific datasets where the estimate was exceeded and the relevant number of data points are given in the Supplementary material, Table S1.19, which may be of use in reviewing the assumptions made in the CSA.

Table A3.9 Summary of the ratios of the arithmetic mean of the aggregated measurement results (restricted dataset) over the exposure estimate and predicted percentage of measurements exceeding the exposure estimate (%M>T) for naphtha (0-1% benzene concentration)

Exposure scenario description	s	n	AM	GM	GSD	Min	Max	%M>T
Bulk closed unloading (CS502)	1	28	0.47	0.36	2.91	0.17	0.78	11
Refuelling (CS507)	1	19	0.20			0.20	0.20	0
Overall	*2*	*47*	*0.38*	*0.30*	*2.28*	*0.17*	*0.78*	*6*

s= number of exposure scenarios for which data were available, n=number of measurements; AM=arithmetic mean of the ratio of the measurement result over the exposure estimates; GM=geometric mean of the ratio of the measurement result over the exposure estimates; GSD=geometric standard deviation of the ratios; min=lowest measurement/ exposure estimate ratio; max=highest measurement/ exposure estimate ratio; %M>T=percentage of the measurements that exceed the relevant exposure estimate.

Comparisons between the 75th and 90th percentiles of the distribution of the aggregated data (restricted dataset) and the exposure estimates (Table A3.10) were also carried out. The results of these comparisons suggest that the exposure estimate is higher than the 75th and 90th percentiles, i.e. is representative for the activities and can be considered to be satisfactory.

Table A3.10 Comparison by exposure scenario description of the exposure estimates with the 75th and 90th percentile values of the distribution of the available aggregated measurement data (restricted dataset) for naphtha (0-1% benzene concentration)

Exposure scenario description	s	g	AM T (mg/m3)	PCT (95% CI) measurements (mg/m3)		T>75th PCT	T>90th PCT
				75th %ile	*90th %ile*		
Bulk closed unloading (CS502)	1	2	0.80	0.62*	0.62*	Yes	Yes
Refuelling (CS507)	1	1	0.80	0.16*	0.16*	Yes	Yes
Overall	*2*	*3*	*0.80*	*0.62**	*0.62**	*Yes*	*Yes*

s= number of exposure scenarios for which data were available; g=number of aggregates; AM T= arithmetic mean of the exposure estimates weighted across the number of measurements included; PCT=percentile of the arithmetic means of the measurement results; T>75th PCT=exposure estimate exceeds 75th percentile of the arithmetic means of the measurement results; T>90th PCT=exposure estimate exceeds 90th percentile of the arithmetic means of the measurement results; *= Confidence intervals not estimated due to small number of observations.

Naphtha (0-1% benzene concentration): individual and aggregated data combined (restricted dataset)

Combining and using all of the selected data into one dataset for the comparison gave rise to similar overall results as for the individual and aggregated datasets when considered in isolation, i.e. around 12% of the 236 measurements exceeding their corresponding exposure estimates (Table A3.12).

Table A3.12 Overall percentage of measurements of naphtha (0-1% benzene concentration) exceeding the exposure estimates by exposure scenario (individual and aggregated data combined - restricted dataset)

Exposure scenario description	s	n	nM>T	%M>T
Equipment cleaning and maintenance (CS39), manufacture	1	11	0	0
Bulk closed loading and unloading (CS501)	1	4	0	0
Equipment maintenance (CS5)	1	57	1	2
Laboratory activities (CS36)	1	26	12	46
Bulk closed unloading (CS502)	1	35	6	18
Refuelling (CS507)	1	73	0	0
Bulk closed loading (CS500)	1	30	9	30
Overall	*7*	*236*	*28*	*12*

s= number of exposure scenarios for which data were available; n=number of measurements; nM>T=number of measurements that exceed the relevant exposure estimate; %M>T=percentage of the measurements that exceed the relevant exposure estimate.

As noted above, duplicate analyses were also carried out for a dataset which incorporated individual and aggregated data to which a measurement date-related concentration factor of 0.5 had been applied to adjust for higher pre-2000 benzene levels in gasoline. The following sections describe these analyses where all data were included.

Naphtha (0-1% benzene concentration): individual measurement data (all data included)

Table A3.13 shows the individual measurement dataset with all values included, i.e. with those data where a date-concentration modifier has been applied to reduce the benzene concentration to 0-1%. From comparison with Table A3.6, it is apparent that inclusion of the modified data increased numbers of data for only one exposure situation description: Equipment maintenance (CS5).

Table A3.13 Overview of individual measurements (all data included) and corresponding exposure estimates from the CSA available for comparison for naphtha (0-1% benzene concentration) by exposure scenario description

Exposure scenario description	s	n	Measurements					Exposure estimates (T)				
			AM (mg/m3)	GM (mg/m3)	GSD	Min (mg/m3)	Max (mg/m3)	AM* (mg/m3)	GM* (mg/m3)	GSD*	Min (mg/m3)	Max (mg/m3)
Equipment cleaning and maintenance (CS39)	1	11	0.15	0.07	4.56	0.01	0.60	0.80	-	-	0.80	0.80
Equipment maintenance (CS5)	1	87	0.28	0.11	5.35	<0.01	2.90	2.72	-	-	2.72	2.72
Laboratory activities (CS36)	1	26	1.18	0.21	6.89	0.01	9.20	0.16	-	-	0.16	0.16
Bulk closed loading (CS500)	1	30	0.36	0.27	2.13	0.10	1.60	0.48	-	-	0.48	0.48
Bulk closed unloading (CS502)	1	7	1.27	0.62	4.16	0.10	4.60	0.80	-	-	0.80	0.80
Bulk closed loading and unloading (CS501)	1	4	0.04	0.03	2.18	0.02	0.10	0.48	-	-	0.48	0.48
Refuelling (CS507)	1	54	0.23	0.16	2.66	0.02	0.60	0.80	-	-	0.80	0.80
Overall	*7*	*219*	*0.40*	*0.15*	*4.50*	*<0.01*	*9.20*	*1.44*	*0.99*	*2.58*	*0.16*	*2.72*

s= number of exposure scenarios for which data were available; n=number of measurements; AM=arithmetic mean; GM=geometric mean; GSD=geometric standard deviation; min=lowest value; max=highest value; *estimate weighted across the number of measurements included.

As previously, the ratios of the measured data to the relevant exposure estimates were calculated and are described in Table A3.14. The comparisons between the measured data and exposure estimates are also shown on a scatterplot in Figure A3.3.

Table A3.14 Summary of the ratios of the individual measurement results (all data included) over the exposure estimates and percentage of measurements exceeding the exposure estimate (%M>T) for naphtha (0-1% benzene concentration)

Exposure scenario description	s	n	AM	GM	GSD	Min	Max	%M>T
Equipment cleaning and maintenance (CS39)	1	11	0.19	0.09	4.56	0.01	0.75	0
Equipment maintenance (CS5)	1	87	0.10	0.04	5.35	<0.01	1.07	1.1
Laboratory activities (CS36)	1	26	7.37	1.31	6.89	0.04	57.50	46
Bulk closed loading (CS500)	1	30	0.74	0.56	2.13	0.21	3.33	30
Bulk closed unloading (CS502)	1	7	1.59	0.77	4.16	0.13	5.75	43
Bulk closed loading and unloading CS501)	1	4	0.09	0.07	2.18	0.04	0.20	0
Refuelling (CS507)	1	54	0.29	0.20	2.66	0.03	0.75	0
Overall	*7*	*219*	*1.15*	*0.15*	*6.75*	*<0.01*	*57.50*	*11*

n=number of measurements; AM=arithmetic mean of the ratio of the measurement result over the exposure estimate; GM=geometric mean of the ratio of the measurement result over the exposure estimate; GSD=geometric standard deviation of the ratios, min=lowest measurement/ exposure estimate ratio; max=highest measurement/ exposure estimate ratio, %M>T=percentage of the measurements that exceed the relevant exposure estimate.

Inclusion of the additional data for the exposure scenario description appeared to have little impact on the overall findings, with a slight decrease in the percentage of measurements in excess of the estimate for this situation. This is related to the increase in the total number of data. The scatterplot in Figure A3.3, whilst more densely populated, is thus very similar to Figure A3.1 in its illustration of the number and distribution of measurements exceeding the corresponding estimate.

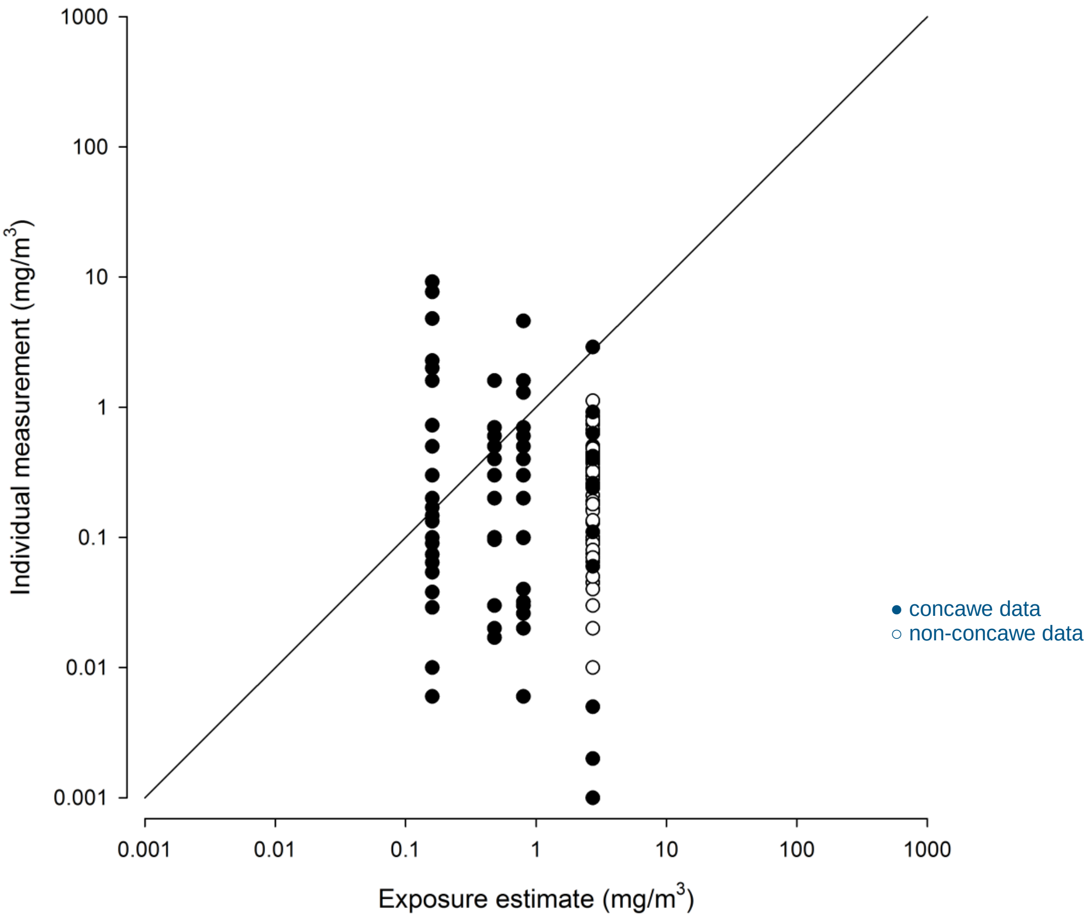

Figure A3.3 Measured data (all values included) vs. exposure estimate for exposure to naphtha (0-1% benzene concentration) (mg/m3)

The 75th and 90th percentiles of the distribution for the individual dataset (with all data included) were determined and compared with the relevant exposure estimates (Table A3.15).

Table A3.15 Comparison by exposure scenario description of the exposure estimates with the 75th and 90th percentile values of the distribution of the available individual measurements (all data included) for naphtha (0-1% benzene concentration)

Exposure scenario description	s	n	AM T (mg/m3)	PCT (95% CI) measurements (mg/m3)		T>75% PCT	T>90% PCT
				75th %ile	90th %ile		
Equipment cleaning and maintenance (CS39)	1	11	0.80	0.30 (0.10-0.60)	0.30 (0.30-0.60)	Yes	Yes
Equipment maintenance (CS5)	1	87	2.72	0.39 (0.30-0.45)	0.67 (0.45-0.92)	Yes	Yes
Laboratory activities (CS36)	1	26	0.16	0.73 (0.20-7.70)	4.80 (0.73-9.20)	No	No
Bulk closed loading (CS500)	1	30	0.48	0.50 (0.30-0.70)	0.70 (0.60-1.60)	No	No
Bulk closed unloading (CS502)	1	7	0.80	1.60*	4.60*	No	No
Bulk closed loading and unloading CS501)	1	4	0.48	0.06*	0.10*	Yes	Yes
Refuelling (CS507)	1	54	0.80	0.40 (0.30-0.40)	0.40 (0.40-0.60)	Yes	Yes
Overall	*7*	*219*	*1.44*	*0.40 (0.30-0.45)*	*0.70 (0.60-1.12)*	*Yes*	*Yes*

s= number of exposure scenarios for which data were available; n=number of measurements; AM T= arithmetic mean of the exposure estimates weighted across the number of measurements included; PCT=percentile of the measurement results; T>75th PCT=exposure estimate exceeds 75th percentile of the measurement results; T>90th PCT=exposure estimate exceeds 90th percentile of the measurement results; *= Confidence intervals not estimated due to small number of observations.

Similar results to the comparison of the 75th and 90th percentiles of the restricted dataset with the relevant exposure estimates were again found. The exposure estimate was higher than the selected percentiles for four of the eight scenario descriptions, suggesting a degree of conservatism in the estimate value. For the remaining three scenarios (again as for the restricted dataset), the estimate was lower than the 75th percentile of the measurement data, suggesting a degree of underestimation in some workplace situations. These were the exposure scenarios for Laboratory activities (CS36); Bulk closed loading (CS500) and Bulk closed unloading (CS502).

Naphtha (0-1% benzene concentration): aggregated data (all data included)

Following initial analysis a group of aggregated estimates (n=11) on CS501 (Bulk closed loading and unloading) originating from Table 5, Concawe report 4/87 appeared to have an unreasonably high estimated AM value (207.17 mg/m^3). This was a direct consequence of an unrealistically high GSD value (54.4) provided in the report, most likely as a result of a typographical error. This estimate was excluded from the analysis. Sensitivity analysis examining the influence of this extreme outlier on the results of the comparison did not reveal systematic differences in the estimated proportion of aggregated measurements exceeding the exposure estimate neither in overall terms (19.9% vs 19.9% for the analysis with and without the outlier respectively) nor for the specific scenario involved (49.2% vs 49.3% for the analysis with and without the outlier, respectively). However, this was not the case for the estimated values of central tendencies which appeared to increase by almost an order of a magnitude in size.

The full set of aggregated data for Naphtha (0-1% benzene concentration), i.e. with all data included, after exclusion of the extreme outlier is summarised in Table A3.16, with the corresponding exposure estimates also given. It is evident from the table that the inclusion of older, concentration-modified aggregated data greatly increased the number and type of comparisons possible (n= 5947 compared with n=47 for the restricted dataset. The additional data included for the following analyses (i.e. those from before 2000) are summarised in the Supplementary material, Table S1.23.

Table A3.16 Overview of aggregated measurement data (all data included) and corresponding exposure estimates from the CSA available for comparison for naphtha (0-1% benzene concentration) by exposure scenario description

Exposure scenario description	**s**	**g**	**n**	**Measurements**			**Exposure estimates**		
				Mean AM (mg/m3)	**Min AM (mg/m3)**	**Max AM (mg/m3)**	**AM T (mg/m3)**	**Min T (mg/m3)**	**Max T (mg/m3)**
Equipment cleaning and maintenance (CS39)									
Overall	2	6	221	0.60	0.09	1.25	0.80	0.80	0.80
Manufacture of substance	1	4	157	0.82	0.40	1.25	0.80	0.80	0.80
Distribution of substance	1	2	64	0.18	0.09	0.26	0.80	0.80	0.80
Equipment maintenance (CS5)	1	1	2	0.28	0.28	0.28	2.72	2.72	2.72
Laboratory activities (CS36)	1	1	628	0.15	0.15	0.15	0.16	0.16	0.16
Bulk closed unloading (CS502)	1	18	1392	0.64	0.14	2.55	0.80	0.80	0.80
Bulk closed loading and unloading (CS501)	1	24	1255	1.03	0.08	3.15	0.48	0.48	0.48
Refuelling (CS507)	1	9	668	0.27	0.12	0.50	0.80	0.80	0.80
General exposures with sample collection (CS15 + CS56).	1	12	1665	0.66	0.09	2.60	1.60	1.60	1.60
Storage (CS67)	1	1	27	0.50	0.50	0.50	1.12	1.12	1.12
Process sampling (CS2)	1	2	89	0.25	0.2	0.31	0.16	0.16	0.16
Overall	*10*	*74*	*5947*	*0.69*	*0.08*	*3.15*	*0.83*	*0.16*	*2.72*

s= number of exposure scenarios for which data were available; g=number of aggregates (arithmetic mean estimates); n=number of measurements; Mean AM=mean of the arithmetic means of the measurement results; Min AM=lowest arithmetic mean value of the aggregated measurement results; Max AM= highest arithmetic mean value of the aggregated measurement results; AM T=arithmetic mean of the exposure estimates weighted across the number of aggregates included; Min T=lowest exposure estimate; Max T=highest exposure estimate.

The arithmetic means of the aggregated data were again calculated by exposure scenario description and compared with the estimates. The ratios of the measured data to the estimates are shown in Table A3.17, and illustrated in Figure A3.4.

Table A3.17 Summary of the ratios of the arithmetic mean of the aggregated measurement results (all data included) over the exposure estimate and predicted percentage of measurements exceeding the exposure estimate (%M>T) for naphtha (0-1% benzene concentration)

Exposure scenario description	s	n	AM	GM	GSD	Min	Max	%M>T
Equipment cleaning and maintenance (CS39)								
Overall	2	221	0.75	0.55	2.64	0.11	1.56	22
Manufacture of substance	1	157	1.02	0.92	1.70	0.50	1.56	28
Distribution of substance	1	64	0.22	0.19	2.12	0.11	0.33	6
Bulk closed loading and unloading (CS501)	1	1255	2.08	1.36	2.70	0.17	6.56	49
Equipment maintenance (CS5)	1	2	0.10	0.10	-	0.10	0.10	0
Laboratory activities (CS36)	1	628	0.94	0.94	-	0.94	0.94	35
Bulk closed unloading (CS502)	1	1392	0.79	0.60	2.08	0.17	3.19	15
Refuelling (CS507)	1	668	0.33	0.30	1.59	0.15	0.63	1
General exposures with sample collection (CS15 + CS56)	1	1665	0.41	0.29	2.40	0.05	1.63	4
Storage (CS67)	1	27	0.45	0.45		0.45	0.45	6
Process sampling (CS2)	1	89	1.59	1.56	1.36	1.25	1.94	17
Overall	*10*	*5947*	*1.10*	*0.64*	*2.81*	*0.05*	*6.56*	*20*

s= number of exposure scenarios for which data were available, n=number of measurements; AM=arithmetic mean of the ratio of the measurement result over the exposure estimates; GM=geometric mean of the ratio of the measurement result over the exposure estimates; GSD=geometric standard deviation of the ratios; min=lowest measurement/ exposure estimate ratio; max=highest measurement/ exposure estimate ratio; %M>T=percentage of the measurements that exceed the relevant exposure estimate.

The results from these comparisons are to an extent similar to those for the individual measurements for the restricted dataset, in the type of activity where exceedance of the exposure estimate occurs: bulk loading and unloading tasks and laboratory work. However, comparison with the results in Table A3.24 below (relating to exposure to naphtha concentration 1-5%) also show a high degree of similarity. As the aggregated dataset (all data included) for the naphtha 0-1% benzene concentration and the restricted aggregated dataset for naphtha (1-5% benzene concentration) are very similar, this is in principle expected. It does, however, suggest that the data may be more representative of older work practices rather than more modern approaches to risk control. Only limited conclusions can therefore be drawn in relation to the degree of conservatism or representativeness of the exposure estimates.

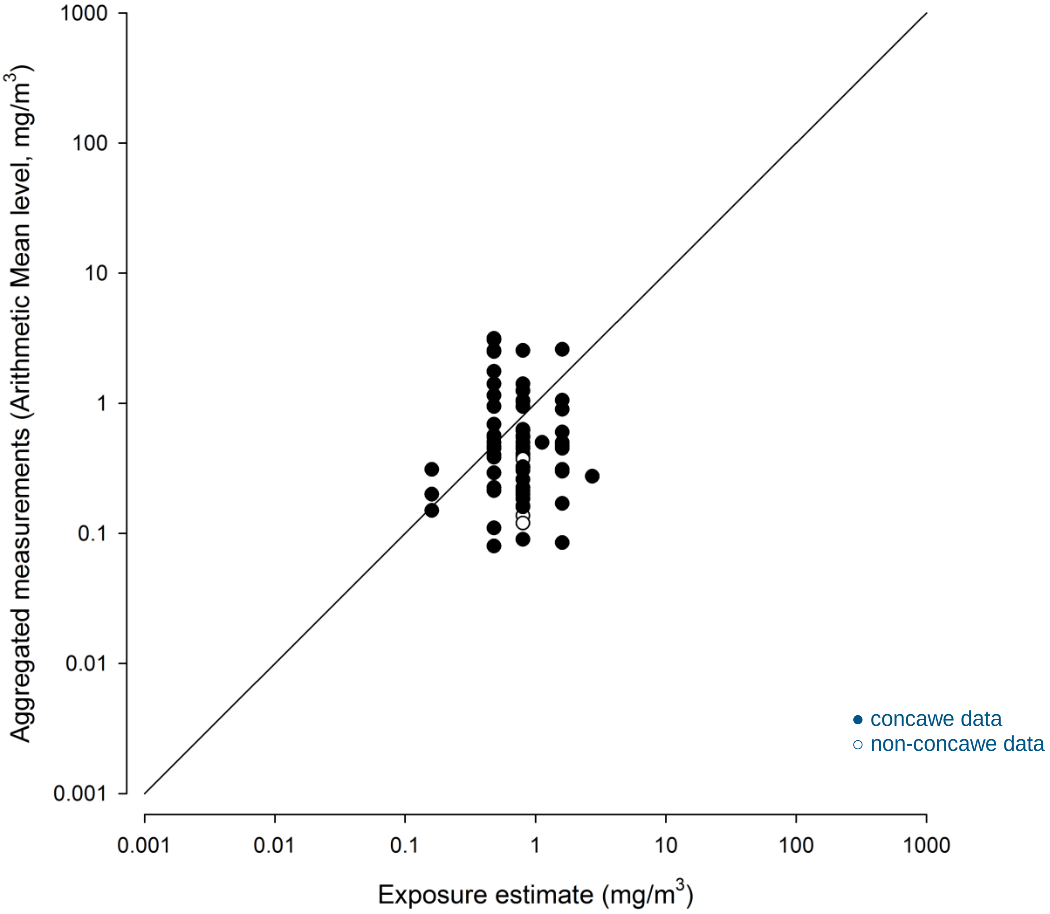

Figure A3.4 Comparison of the arithmetic means of the aggregated data (all data included) with the exposure estimates for exposure to naphtha (0-1% benzene concentration) (mg/m3)

Similarly, comparison of the 75th and 90th percentiles of the distribution of the aggregated measurements (all data included) with the corresponding exposure estimates generated results which resembled those for the restricted aggregated dataset for naphtha (1-5% benzene concentration). Discussions with Concawe suggest that the level of uncertainty associated with this older dataset is high, thus hindering definitive interpretation of the results in the context of more modern work practices.

Table A3.18 Comparison by exposure scenario description of the exposure estimates with the 75th and 90th percentile values of the distribution of the available aggregated measurement data (all data included) for naphtha (0-1% benzene concentration)

Exposure scenario description	s	g	AM T (mg/m3)	PCT (95% CI) measurements (mg/m3)		T>75th PCT	T>90th PCT
				75th %ile	90th %ile		
Equipment cleaning and maintenance (CS39)							
Overall	2	6	0.80	1.05*	1.25*	No	No
Manufacture of substance	1	4	0.80	1.15*	1.25*	No	No
Distribution of substance	1	2	0.80	0.18*	0.26*	Yes	Yes
Equipment maintenance (CS5)	1	1	2.72	0.28*	0.28*	Yes	Yes
Laboratory activities (CS36)	1	1	0.16	0.15*	0.15*	Yes	Yes
Bulk closed unloading (CS502)	1	18	0.80	0.63 (0.47-2.55)	1.41 (0.63-2.55)	Yes	No
Bulk closed loading and unloading (CS501)	1	24	0.48	1.28 (0.69-3.08)	2.55 (1.80-3.15)	No	No
Refuelling (CS507)	1	9	0.80	0.33*	0.50*	Yes	Yes
General exposures with sample collection (CS15 + CS56).	1	12	1.60	0.75 (0.46-2.60)	*1.06 (0.90-2.60)*	Yes	Yes
Storage (CS67)	1	1	1.12	0.50*	0.50*	Yes	Yes
Process sampling (CS2)	1	2	0.16	0.31*	0.31*	No	No
Overall	*10*	*74*	*0.83*	*0.90 (0.55-1.15)*	*1.41 (1.06-2.60)*	*No*	*No*

s= number of exposure scenarios for which data were available; g=number of aggregates; AM T= arithmetic mean of the exposure estimates weighted across the number of measurements included; PCT=percentile of the arithmetic means of the measurement results; T>75th PCT=exposure estimate exceeds 75th percentile of the arithmetic means of the measurement results; T>90th PCT=exposure estimate exceeds 90th percentile of the arithmetic means of the measurement results; *= Confidence intervals not estimated due to small number of observations.

Naphtha (0-1% benzene concentration): individual and aggregated data combined (all data included)

The revised (all data included) individual and aggregated datasets were combined prior to further comparison with the relevant estimates, with the results shown in Table A3.19.

Table A3.19 Overall percentage of measurements of naphtha (0-1% benzene concentration) exceeding the exposure estimates by exposure scenario (individual and aggregated data combined, all data included)

Exposure scenario description	s	n	nM>T	%M>T
Equipment cleaning and maintenance (CS39)				
Overall	2	232	48	21
Manufacture of substance	1	168	44	26
Distribution of substance	1	64	4	6
Bulk closed loading and unloading (CS501)	1	1259	619	49
Equipment maintenance (CS5)	1	89	1	1
Laboratory activities (CS36)	1	654	232	35
Bulk closed unloading (CS502)	1	1399	208	15
Refuelling (CS507)	1	722	7	1
General exposures with sample collection (CS15 + CS56).	1	1665	64	4
Storage (CS67)	1	27	2	6
Process sampling (CS2)	1	89	15	17
Bulk closed loading (CS500)	1	30	9	30
Overall	*11*	*6166*	*1205*	*20*

s= number of exposure scenarios for which data were available; n=number of measurements; nM>T=number of measurements that exceed the relevant exposure estimate; %M>T=percentage of the measurements that exceed the relevant exposure estimate.

Table A3.19 indicates that, overall, similar patterns emerge for the combined data set as for the aggregated data when considered separately, with the numbers of aggregated data dominating the combined results. As noted above, the degree to which these older data match modern practices is difficult to determine, therefore the overall comparison results for the combined dataset (all data included) should be treated with caution.

Naphtha (1-5% benzene concentration)

Fewer data were available for comparison with the CSA exposure estimates for naphtha (1-5% benzene concentration) than for the lower benzene content naphtha (0-1% benzene). To increase the numbers of comparator data available, a data gathering and analytical approach comparable to the one for the 0-1% benzene content was applied. The datasets, estimates and comparisons are described below.

As noted previously, benzene concentrations in naphtha (as gasoline) were generally higher prior to the year 2000, with concentrations of a maximum of 5% commonplace. The data from this period were therefore considered suitable for direct comparison with the exposure estimates for naphtha (1-5% benzene concentration). Consequently, at a first step, a dataset comprising of measurement data strictly collected before the year 2000 (hereafter called the “restricted dataset”) was established and used.

At a second step the use of additional data dating from after 2000, when benzene concentrations are assumed to have decreased, was allowed to increase power in the analysis. All relevant pre- and post-2000 measurements were included in a combined dataset (hereafter called the full dataset) and the analysis was repeated in full. Prior to the comparisons, measurements collected after 2000 were increased by 100% (correction factor of 2) to be comparable to a higher benzene concentration of 1-5%. Similar to the analysis for naphtha with 0-1% benzene content, the inclusion of measurements with a date-related concentration modifier applied may have greatly increased the uncertainty in the comparison exercise. Therefore, the analysis using all measurements available (i.e. full dataset) should be considered as less reliable compared to the one using only the pre-2000 available measurements. Interpretations of its results should be made with caution.

The outcomes of all comparisons performed are presented below, starting from those of the more reliable restricted dataset.

Naphtha (1-5% benzene concentration): individual measurement data (restricted dataset)

The following individual data were collected (Table A3.20) and compared with the given exposure estimates.

Table A3.20 Overview of individual measurements (restricted dataset) and corresponding exposure estimates from the CSA available for comparison for naphtha (1-5% benzene concentration) (by exposure scenario description)

Exposure scenario description	s	n	Measurements					Exposure estimates (T)				
			AM (mg/m3)	GM (mg/m3)	GSD	Min (mg/m3)	Max (mg/m3)	AM* (mg/m3)	GM* (mg/m3)	GSD	Min (mg/m3)	Max (mg/m3)
Bulk closed loading and unloading (CS501)	1	39	0.88	0.59	2.31	0.20	5.40	0.96	-	-	0.96	0.96

s= number of exposure scenarios for which data were available; n=number of measurements; AM=arithmetic mean; GM=geometric mean; GSD=geometric standard deviation; min=lowest value; max=highest value; *estimate weighted across the number of measurements included.

The ratios of the measurement data over the exposure estimates were calculated, with the results tabulated in Table A3.21 and shown on the scatterplot in Figure A3.5.

Table A3.21 Summary of the ratios of the individual measurement results (restricted dataset) over the exposure estimates and percentage of measurements exceeding the exposure estimate (%M>T) for naphtha (1-5% benzene concentration)

Exposure scenario description	s	n	AM	GM	GSD	Min	Max	%M>T
Bulk closed loading and unloading (CS501)	1	39	0.92	0.61	2.31	0.21	5.63	23

n=number of measurements, AM=arithmetic mean of the ratio of the measurement result over the exposure estimate; GM=geometric mean of the ratio of the measurement result over the exposure estimates; GSD=geometric standard deviation of the ratios; min=lowest measurement/ exposure estimate ratio; max=highest measurement/ exposure estimate ratio; %M>T=percentage of the measurements that exceed the relevant exposure estimate.

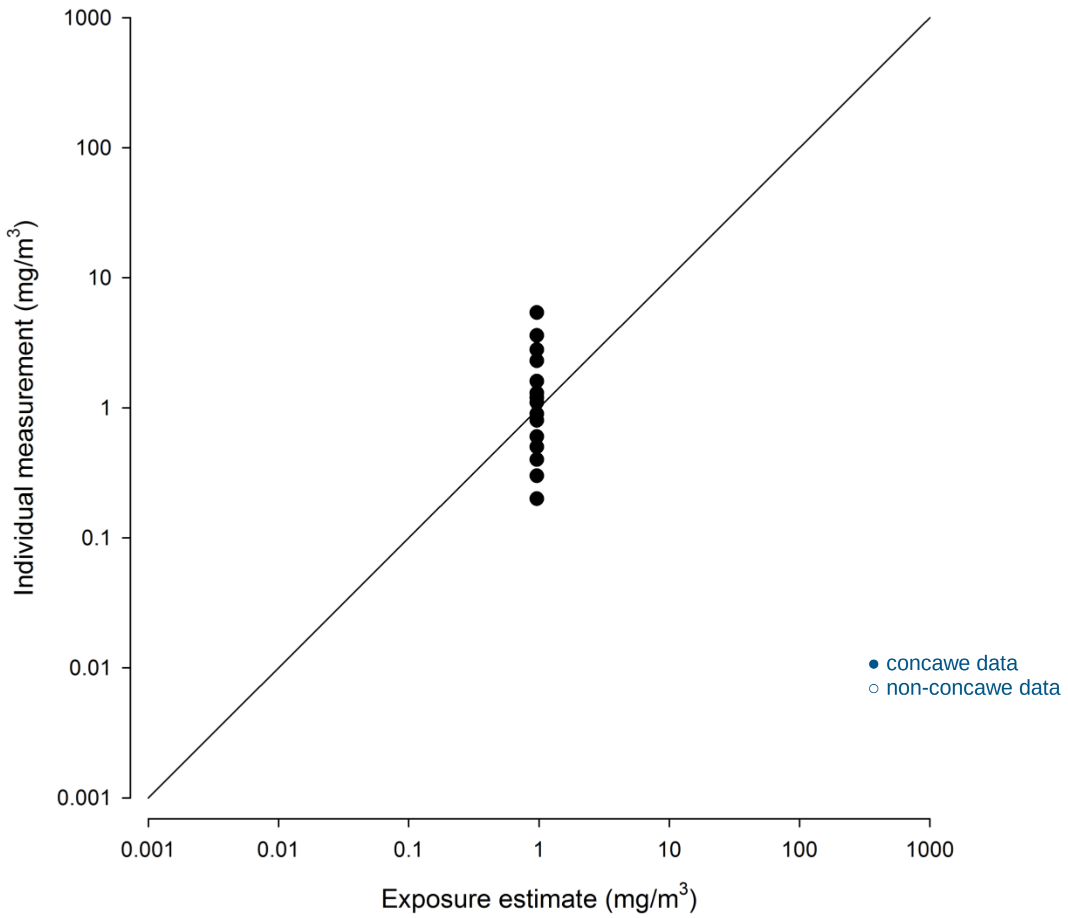

Figure A3.5 Measured data (restricted dataset|) vs. exposure estimate for naphtha (1-5% benzene concentration)

Around 23% of the data points for the exposure scenario “Bulk closed loading and unloading (CS501)” lay above the 1:1 line, indicating that although the AM of the ratios was close to 1, and the GM was also <1, a sizeable proportion of measurements were in excess of the exposure estimates.

The 75th and 90th percentiles of the distribution of the individual measurement restricted dataset were calculated, and again compared with the exposure estimate (Table A3.22). The exposure estimate lay between the 75th and 90th percentile of the measurement set, which is in accordance with expectations for estimates generated using the ECETOC TRA tools.

Table A3.22 Comparison by exposure scenario description of the exposure estimates with the 75th and 90th percentile values of the distribution of the available individual measurements (restricted dataset) for naphtha (1-5% benzene concentration)

Exposure scenario description	s	n	AM T (mg/m3)	PCT (95% CI) measurements (mg/m3)		T>75th PCT	T>90th PCT
				75th %ile	90th %ile		
Bulk closed loading and unloading (CS501)	1	39	0.96	0.90 (0.80-1.60)	2.30 (1.10-5.40)	Yes	No

s= number of exposure scenarios for which data were available; n=number of measurements; AM T= arithmetic mean of the exposure estimates weighted across the number of measurements included; PCT=percentile of the measurement results; T>75th PCT=exposure estimate exceeds 75th percentile of the measurement results; T>90th PCT=exposure estimate exceeds 90th percentile of the measurement results.

Naphtha (1-5% benzene concentration): aggregated data (restricted dataset)

Similar comparisons of the exposure estimates were carried out with the restricted aggregate dataset, with a summary of the measurements and estimates given in Table A3.23. During the analysis of these aggregated data, the same summary estimate identified as an extreme outlier for naphtha 0-1% benzene concentration was identified on ES_ID: N_1-5p_14 (from Table 5 of Concawe Report 4-87). This value was subsequently excluded from the analyses. Sensitivity analyses showed that the exclusion of this value did not affect the overall (56.6% vs 56.6% for the analysis with and without the outlier, respectively) and scenario specific (38.7% vs 38.7% for the analysis with and without the outlier, respectively) proportions of aggregated measurements exceeding the exposure estimate.

Table A3.23 Overview of aggregated measurement data (restricted dataset) and corresponding exposure estimates from the CSA available for comparison for naphtha (1-5% benzene concentration) (by exposure scenario description)

Exposure scenario description	**s**	**g**	**n**	**Measurements**			**Exposure estimates (T)**		
				Mean AM (mg/m3)	**Min AM (mg/m3)**	**Max AM (mg/m3)**	**AM T (mg/m3)**	**Min T (mg/m3)**	**Max T (mg/m3)**
General exposures with sample collection (CS15 + CS56).	1	12	1665	1.32	0.17	5.20	0.16	0.16	0.16
Equipment cleaning and maintenance (CS39)									
Overall	*3*	*7*	*223*	*1.11*	*0.18*	*2.50*	*1.60*	*1.60*	*1.60*
Formulation of substance	1	1	2	0.55	0.55	0.55	1.60	1.60	1.60
Manufacture of substance	1	4	157	1.63	0.80	2.50	1.60	1.60	1.60
Distribution of substance	1	2	64	0.35	0.18	0.52	1.60	1.60	1.60
Bulk closed loading and unloading (CS501)	1	37	2223	1.64	0.22	6.30	0.96	0.96	0.96
Laboratory activities (CS36)	1	1	628	0.30	0.30	0.30	0.32	0.32	0.32
Storage (CS67)	1	1	27	1.00	1.00	1.00	0.16	0.16	0.16
Overall	*7*	*58*	*4766*	*1.48*	*0.17*	*6.30*	*0.85*	*0.16*	*1.60*

s= number of exposure scenarios for which data were available; g=number of aggregates (arithmetic mean estimates); n=number of measurements; Mean AM=mean of the arithmetic means of the measurement results; Min AM=lowest arithmetic mean value of the aggregated measurement results; Max AM= highest arithmetic mean value of the aggregated measurement results; AM T=arithmetic mean of the exposure estimates weighted across the number of aggregates included; Min T=lowest exposure estimate; Max T=highest exposure estimate.

The ratios of the AMs of the aggregated data to the exposure estimates were calculated and given in Table A3.24. The results of the comparison are also illustrated in Figure A3.6, where it can be seen that a substantial number of data points were above the 1:1 line.

Table A3.24 Summary of the ratios of the arithmetic mean of the aggregated measurement results (restricted dataset) over the exposure estimates and predicted percentage of measurements exceeding the exposure estimates (%M>T) for naphtha (1-5% benzene concentration)

Exposure scenario description	s	n	AM	GM	GSD	Min	Max	%M>T
General exposures with sample collection (CS15 + CS56). Equipment cleaning and maintenance (CS39)	1	1665	8.23	5.79	2.40	1.06	32.50	93
Overall	3	223	0.69	0.51	2.47	0.11	1.56	22
Formulation of substance	1	2	0.34	-	-	0.34	0.34	0
Manufacture of substance	1	157	1.02	0.92	1.70	0.50	1.56	28
Distribution of substance	1	64	0.22	0.19	2.12	0.11	0.33	6
Bulk closed loading and unloading (CS501)	1	2223	1.71	1.19	2.32	0.23	6.56	39
Laboratory activities (CS36)	1	628	0.94	-	-	0.94	0.94	35
Storage (CS67)	1	27	6.25	-	-	6.25	6.25	50
Overall	*7*	*4766*	*3.00*	*1.53*	*3.10*	*0.11*	*32.50*	*57*

s= number of exposure scenarios for which data were available; n=number of measurements; AM=arithmetic mean of the ratio of the measurement result over the exposure estimate; GM=geometric mean of the ratio of the measurement result over the exposure estimate; GSD=geometric standard deviation of the ratios; min=lowest measurement/ exposure estimate ratio; max=highest measurement/ exposure estimate ratio; %M>T=percentage of the measurements that exceed the relevant exposure estimate.

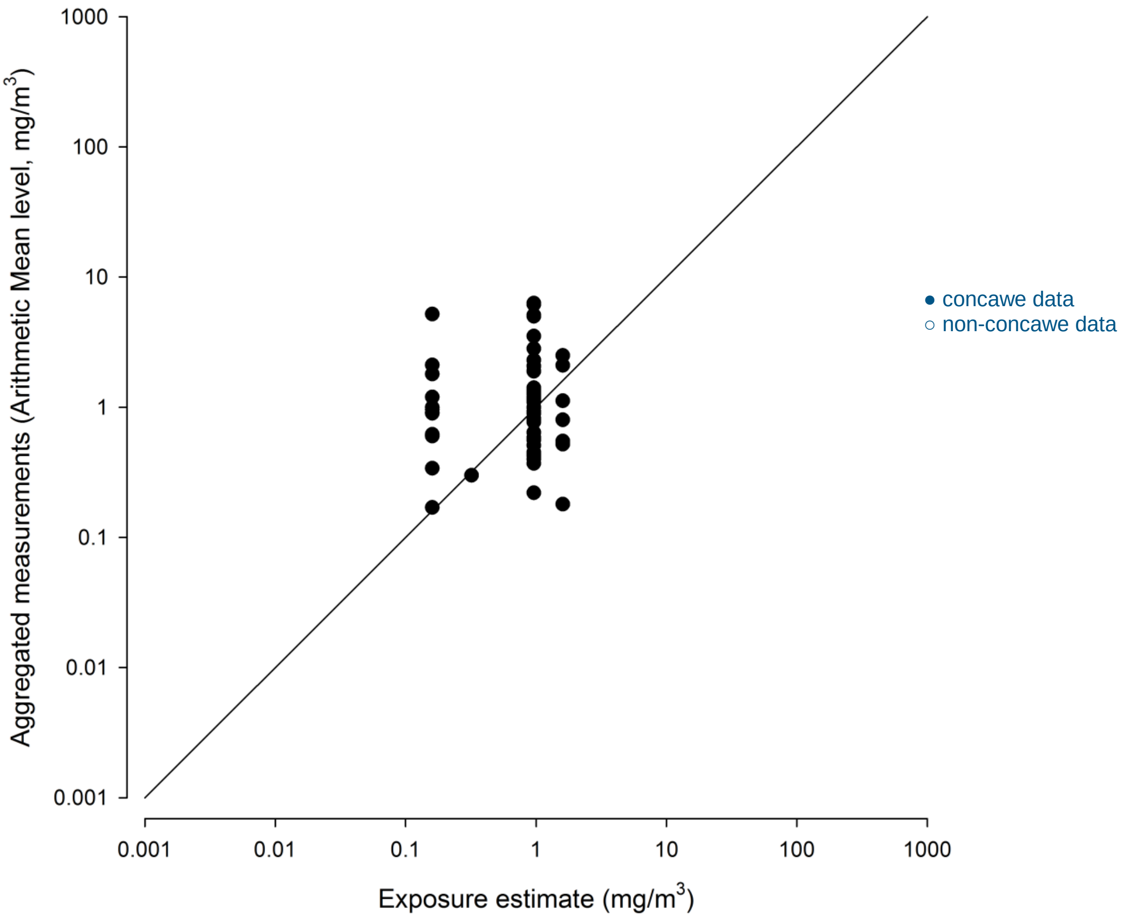

Figure A3.6 Comparison of the arithmetic means of the aggregated data (restricted dataset) with the exposure estimates for naphtha (1-5% benzene concentration)

In general, the data points which exceed the exposure estimates relate to industrial sites and activities during manufacture and distribution of the substance, in particular during general exposure sampling and bulk loading activities, where the AMs of the ratios of the measurements over the estimate greatly exceed 1 and equipment cleaning and maintenance work and materials storage, where again the AMs of the ratios are >1. More detail on the specific aggregated data situations where exceedances occur can be found in the Supplementary material, Table S1.20. It should be noted that many of the data originate from pre-2000, therefore whilst the concentration of benzene in the substance may be similar to current levels, the activities and level of risk control may not be fully representative of more modern work practices.

Further comparisons of the estimates with the 75th and 90th percentiles of the measured data were carried out. From the results in Table A3.25, it can be seen that the exposure estimates for “General exposures with sample collection”; “Equipment cleaning and maintenance (manufacture of substance)”; “Bulk closed loading and unloading” and “Storage” are lower than the 75th percentile of the distribution of the measured data allocated to these scenarios for the comparison. A review of the options used in the exposure estimation process for these scenarios may therefore be required.

Table A3.25 Comparison by exposure scenario description of the exposure estimates with the 75th and 90th percentile values of the distribution of the available aggregated measurement data for naphtha (1-5% benzene concentration)

Exposure scenario description	**s**	**g**	**AM T (mg/m3)**	**PCT (95% CI) measurements (mg/m3)**		**T>75th PCT**	**T>90th PCT**
				75th %ile	**90th %ile**		
General exposures with sample collection (CS15 + CS56). Equipment cleaning and maintenance (CS39)	1	12	0.16	1.50 (0.91-5.20)	2.11 (1.80-5.20)	No	No
Overall	3	7	1.60	2.10*	2.50*	No	No
Formulation of substance	1	1	1.60	0.55*	0.55*	Yes	Yes
Manufacture of substance	1	4	1.60	2.30*	2.50*	No	No
Distribution of substance	1	2	1.60	0.52*	0.52*	Yes	Yes
Bulk closed loading and unloading (CS501)	1	37	0.96	1.90 (1.29-5.00)	5.00 (2.30-6.30)	No	No
Laboratory activities (CS36)	1	1	0.32	0.30*	0.30*	Yes	Yes
Storage (CS67)	1	1	0.16	1.00*	1.00*	No	No
Overall	*7*	*58*	*0.85*	*1.89 (1.20-2.30)*	*3.52 (2.11-6.16)*	*No*	*No*

s= number of exposure scenarios for which data were available; g=number of aggregates; AM T= arithmetic mean of the exposure estimates weighted across the number of measurements included; PCT=percentile of the arithmetic means of the measurement results; T>75th PCT=exposure estimate exceeds 75th percentile of the arithmetic means of the measurement results; T>90th PCT=exposure estimate exceeds 90th percentile of the arithmetic means of the measurement results; *= Confidence intervals not estimated due to small number of observations.

Naphtha (1-5% benzene concentration): individual and aggregated data combined (restricted dataset)

All of the measurements in the individual and aggregated restricted datasets were combined and used for a further comparison (Table A3.26). Overall, the results are similar to the datasets when considered in isolation in terms of the patterns and percentages of exceedance of the estimates.

Table A3.26 Overall percentage of measurements of naphtha (1-5% benzene concentration) exceeding the exposure estimate by exposure scenario (individual and aggregated data combined-restricted dataset)

Exposure scenario description	**s**	**n**	**nM>T**	**%M>T**
General exposures with sample collection (CS15 + CS56).	1	1665	1553	93
Equipment cleaning and maintenance (CS39)				
Overall	3	223	48	22
Formulation of substance	1	2	0	0
Manufacture of substance	1	157	44	28
Distribution of substance	1	64	4	6
Bulk closed loading and unloading (CS501)	1	2262	870	39
Laboratory activities (CS36)	1	628	220	35
Storage (CS67)	1	27	14	50
Overall	*7*	*4805*	*2705*	*56*

s= number of exposure scenarios for which data were available; n=number of measurements; nM>T=number of measurements that exceed the relevant exposure estimate; %M>T=percentage of the measurements that exceed the relevant exposure estimate.

Additional comparisons between the exposure estimates for naphtha (1-5% benzene concentration) were carried out with data collected after the year 2000, to which a concentration adjustment modifying factor of 2 had been applied. The use of this data changed only the individual measurement dataset, as no relevant aggregated post-2000 data were identified for use in the comparison.

Naphtha (1-5% benzene concentration): individual measurement data (all data included)

An overview of the exposure scenarios and exposure estimates for additional data were available is shown in Table A3.27.

Table A3.27 Overview of individual measurements (all data included) and corresponding exposure estimates from the CSA available for comparison for naphtha (1-5% benzene concentration) (by exposure scenario description)

Exposure scenario description	s	n	Measurements					Exposure estimates (T)				
			AM (mg/m3)	GM (mg/m3)	GSD	Min (mg/m3)	Max (mg/m3)	AM* (mg/m3)	GM* (mg/m3)	GSD*	Min (mg/m3)	Max (mg/m3)
Bulk closed loading and unloading (CS501)	1	39	0.88	0.59	2.31	0.20	5.40	0.96	-	-	0.96	0.96
Laboratory activities (CS36)	1	26	2.36	0.42	6.89	0.01	18.40	0.32	-	-	0.32	0.32
Equipment cleaning and maintenance (CS39)	1	11	0.30	0.14	4.56	0.01	1.20	1.60	-	-	1.60	1.60
Overall	*3*	*76*	*1.30*	*0.42*	*4.33*	*0.01*	*18.40*	*0.83*	*0.71*	*1.83*	*0.32*	*1.60*

s= number of exposure scenarios for which data were available; n=number of measurements; AM=arithmetic mean; GM=geometric mean; GSD=geometric standard deviation; min=lowest value; max=highest value; *estimate weighted across the number of measurements included.

Comparisons of the ratio of the measured data to the corresponding exposure estimate are given in Table A3.28 and shown in Figure A3.7. When the results in Table A3.27 are compared to those in Table A3.13, it can be seen that the results from the naphtha (0-1% benzene concentration) are very similar. Discussions with Concawe during the project have suggested more confidence in the later data (post-2000). Assuming that the date-related concentration modifying factor (x2) is appropriate, results in Table A3.28 are considered a valid comparison between the exposure estimate and measured data. The assumptions made in the exposure estimates for "Laboratory activities" should therefore be reviewed.

Table A3.28 Summary of the ratios of the individual measurement results (all data included) over the exposure estimates and percentage of measurements exceeding the exposure estimate (%M>T) for naphtha (1-5% benzene concentration)

Exposure scenario description	**s**	**n**	**AM**	**GM**	**GSD**	**Min**	**Max**	**%M>T**
Bulk closed loading and unloading (CS501)	1	39	0.92	0.61	2.31	0.21	5.63	23
Laboratory activities (CS36)	1	26	7.37	1.31	6.89	0.04	57.50	46
Equipment cleaning and maintenance (CS39)	1	11	0.19	0.09	4.56	0.01	0.75	0
Overall	*3*	*76*	*3.02*	*0.60*	*5.12*	*0.01*	*57.50*	*28*

n=number of measurements, AM=arithmetic mean of the ratio of the measurement result over the exposure estimate; GM=geometric mean of the ratio of the measurement result over the exposure estimates; GSD=geometric standard deviation of the ratios; min=lowest measurement/ exposure estimate ratio; max=highest measurement/ exposure estimate ratio; %M>T=percentage of the measurements that exceed the relevant exposure estimate.

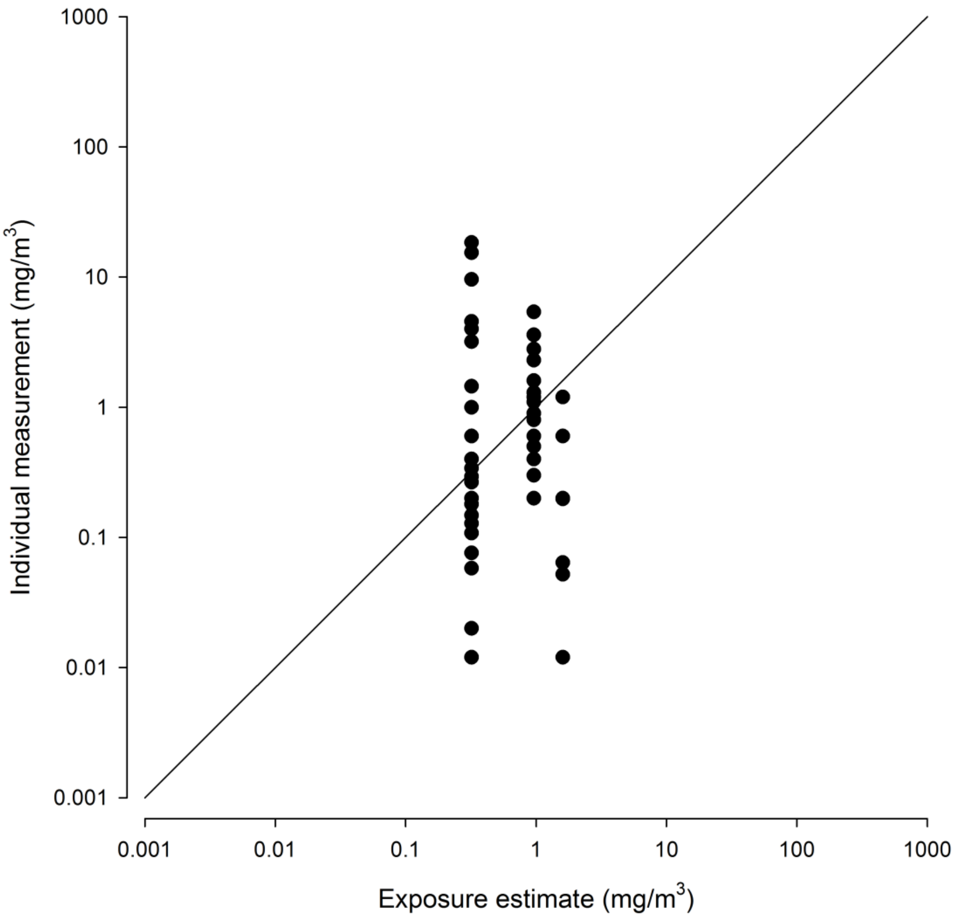

Figure A3.7 Measured data (all data included) vs. exposure estimate for naphtha (1-5% benzene concentration)

A comparison of the 75th and 90th percentiles of the exposure distribution of the individual data set (with all data included) is reported in Table A3.29. It can be seen that the exposure estimate for "Laboratory activities" is again lower than the 75th percentile of the distribution of the measured data, suggesting that a review of the exposure assessment may be beneficial.

Table A3.29 Comparison by exposure scenario description of the exposure estimates with the 75th and 90th percentile values of the distribution of the available individual measurements (all data included) for naphtha (1-5% benzene concentration)

Exposure scenario description	s	n	AM T (mg/m3)	PCT (95% CI) measurements (mg/m3) 75th %ile	90th %ile	T>75th PCT	T>90th PCT
Bulk closed loading and unloading (CS501)	1	39	0.96	0.90 (0.80-1.60)	2.30 (1.10-5.40)	Yes	No
Laboratory activities (CS36)	1	26	0.32	1.45 (0.40-15.40)	9.60 (1.45-18.40)	No	No
Equipment cleaning and maintenance (CS39)	1	11	1.60	0.60 (0.20-1.20)	0.60 (0.60-1.20)	Yes	Yes
Overall	*3*	*76*	*0.83*	0.85 (0.60-1.45)	3.20 (1.20-9.60)	No	No

s= number of exposure scenarios for which data were available; n=number of measurements; AM T= arithmetic mean of the exposure estimates weighted across the number of measurements included; PCT=percentile of the measurement results; T>75th PCT=exposure estimate exceeds 75th percentile of the measurement results; T>90th PCT=exposure estimate exceeds 90th percentile of the measurement results.

Other lubricant base oils

The data collected for OLBOs related solely to the use of metal working fluids in metal machining processes. Both aerosol and vapour data were collected, and were compared separately with the relevant exposure estimate for their physical form. Discussions with Concawe indicated that a duration modifier (x0.6) had been applied during generation of the exposure estimate to specify allowed task times. This modifier was removed prior to comparison with the measured data. The data collected for OLBOs are shown in more detail in the Supplementary material 1A and 1B and Table S1.21. To transform the estimates from ppm to mg/m^3, the molecular weight of n-tetradecane (198.40 g/mol) was used. This compound is suggested as a major component in the vapour phase of metal working fluids (Simpson, 2000) [3].

Other lubricant base oils: individual measurement data

A very small number of individual measurement data were collected for exposure to OLBOs in the form of aerosols from metal working fluids. These are described in Table A3.30, along with the corresponding exposure estimate.

Table A3.30 Overview of individual measurements and corresponding exposure estimates from the CSA available for comparison for other lubricant base oils (as metal working fluids)

Exposure scenario description	s	n	Measurements					Exposure estimates (T)				
			AM (mg/m3)	GM (mg/m3)	GSD	Min (mg/m3)	Max (mg/m3)	AM* (mg/m3)	GM* (mg/m3)	GSD*	Min (mg/m3)	Max (mg/m3)
Metal machining operations (CS79)-aerosol	1	4	1.15	0.91	2.31	0.30	2.30	7.50	-	-	7.50	7.50

s= number of exposure scenarios for which data were available; n=number of measurements; AM=arithmetic mean; GM=geometric mean; GSD=geometric standard deviation; min=lowest value; max=highest value; *estimate weighted across the number of measurements included.

The ratios of the individual measurement data to the exposure estimate are shown in Table 4.10 (main report), where the low AM and GM of the ratios suggest that the estimate was conservative in comparison to the workplace data. This can also be seen on the graphical representation of the comparisons (Figure 4.4).

The exposure estimate was also higher than the 75th and 90th percentiles of the measurement data distribution, again suggesting appropriate conservatism (Table 4.11).

Other lubricant base oils: aggregated data

A higher amount of aggregated data were collected for OLBOs, again relating to exposure to aerosol and vapours for metal working fluids. These are shown in Table A3.31 below, with the relevant exposure estimates also given.

Table A3.31 Overview of aggregated measurement data and corresponding exposure estimates from the CSA available for comparison for other lubricant base oils as metal working fluids

Exposure scenario description	s	g	n	Measurements			Exposure estimates (T)		
				Mean AM (mg/m3)	Min AM (mg/m3)	Max AM (mg/m3)	AM T (mg/m3)	Min T (mg/m3)	Max T (mg/m3)
Metal machining operations (CS79) - vapour	1	15	6601	7.79	2.79	20.83	60.00	60.00	60.00
Metal machining operations (CS79) - aerosol	1	9	856	0.54	0.23	1.61	7.50	7.50	7.50

s= number of exposure scenarios for which data were available; g=number of aggregates (arithmetic mean estimates); n=number of measurements; Mean AM=mean of the arithmetic means of the measurement results; Min AM=lowest arithmetic mean value of the aggregated measurement results; Max AM= highest arithmetic mean value of the aggregated measurement results; AM T=arithmetic mean of the exposure estimates weighted across the number of aggregates included; Min T=lowest exposure estimate; Max T=highest exposure estimate.

The ratios of the arithmetic means of the aggregated data over the exposure estimates (for vapours and aerosols) are shown in Table A3.32, with the comparison also illustrated visually in Figures A3.8 and A3.9.

From the Table and plots, it is evident that the estimates are higher than the measured data in the vast majority of cases, and can therefore be considered appropriately conservative.

Table A3.32 Summary of the ratios of the AM of the aggregated measurement results over the exposure estimates and predicted percentage of measurements exceeding the exposure estimates (%M>T) for other lubricant base oils (as metal working fluids)

Exposure scenario description	s	n	AM	GM	GSD	Min	Max	%M>T
Metal machining operations (CS79) - vapour	1	6601	0.13	0.12	1.54	0.05	0.35	1
Metal machining operations (CS79) - aerosol	1	856	0.07	0.06	1.87	0.03	0.21	0

s= number of exposure scenarios for which data were available; n=number of measurements; AM=arithmetic mean of the ratio of the measurement result over the exposure estimate; GM=geometric mean of the ratio of the measurement result over the exposure estimate; GSD=geometric standard deviation of the ratios; min=lowest measurement/ exposure estimate ratio; max=highest measurement/ exposure estimate ratio; %M>T=percentage of the measurements that exceed the relevant exposure estimate.

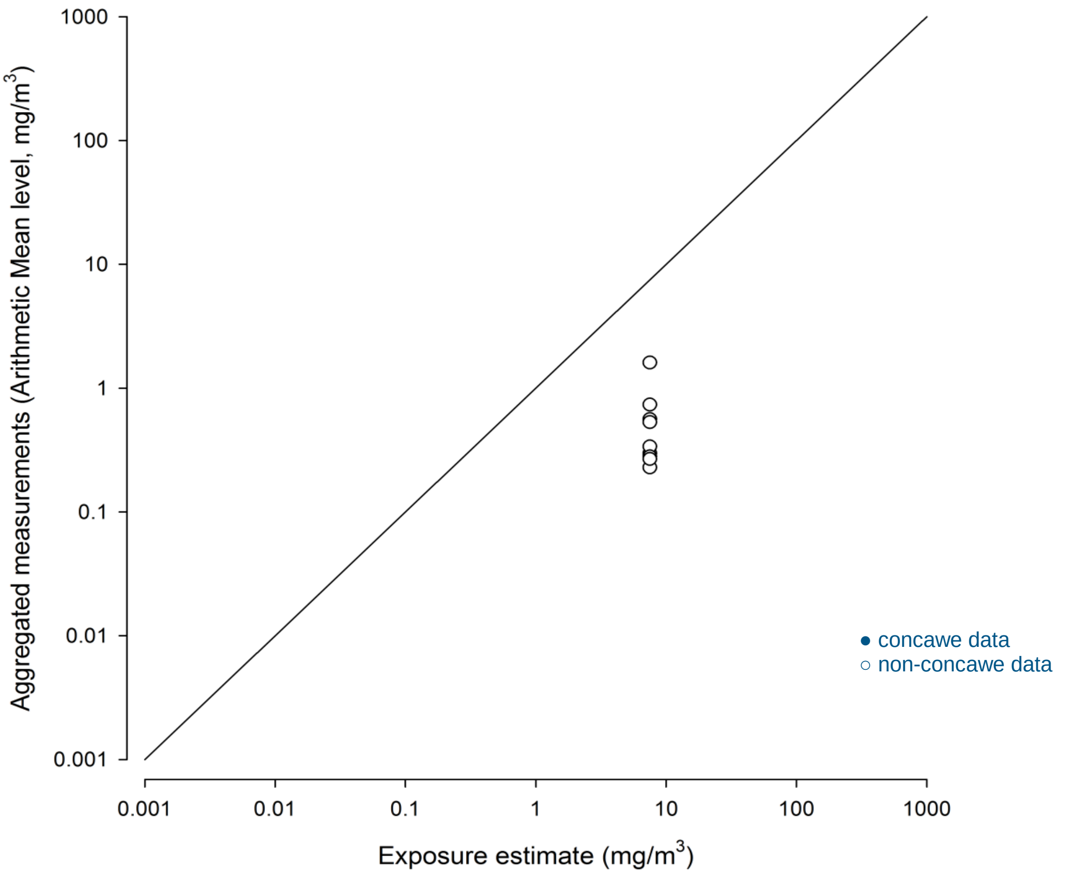

Figure A3.8 Comparison of the arithmetic means of the aggregated data with the exposure estimates for other lubricant base oils (as metal working fluids) - aerosol

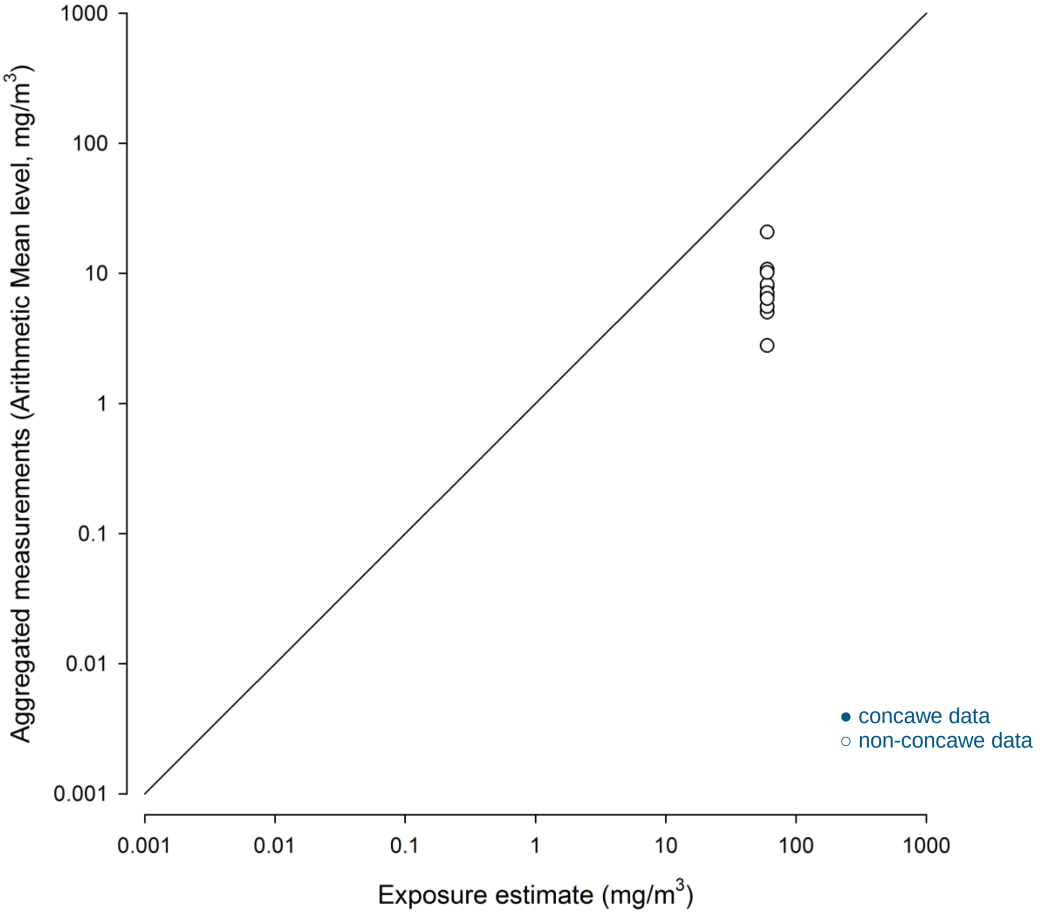

Figure A3.9 Comparison of the arithmetic means of the aggregated data with the exposure estimates for other lubricant base oils (as metal working fluids) - vapour

A further comparison of the exposure estimates with the 75th and 90th percentiles of the distribution of the measurement data was undertaken, with the results given in Table A3.33.

Table A3.33 Comparison by exposure scenario description of the exposure estimates with the 75th and 90th percentile values of the distribution of the available aggregated measurement data for other lubricant base oils (as metal working fluids)

Exposure scenario description	s	g	AM T (mg/m3)	PCT (95% CI) measurements (mg/m3)		T>75th PCT	T>90th PCT
				75th %ile	90th %ile		
Metal machining operations (CS79) - vapour	1	15	60.00	8.22 (6.73-20.83)	10.78 (10.17-20.83)	Yes	Yes
Metal machining operations (CS79) - aerosol	1	9	7.50	0.56*	1.61*	Yes	Yes

s= number of exposure scenarios for which data were available; g=number of aggregates; AM T= arithmetic mean of the exposure estimates weighted across the number of measurements included; PCT=percentile of the arithmetic means of the measurement results; T>75th PCT=exposure estimate exceeds 75th percentile of the arithmetic means of the measurement results; T>90th PCT=exposure estimate exceeds 90th percentile of the arithmetic means of the measurement results; *= Confidence intervals not estimated due to small number of observations.

Other lubricant base oils: individual and aggregated data combined

Following combination of the individual and aggregated measurement data for OLBOs, and comparison of the resulting combined data set, the overall level of conservatism of the exposure estimate is high in the context of the validation dataset, as shown in Table A3.34.

Table A3.34 Overall percentage of measurements of other lubricant base oils (as metal working fluids) exceeding the exposure estimate (individual and aggregated data combined)

Exposure scenario description	s	n	nM>T	%M>T
Metal machining operations (CS79) - vapour	1	6601	44	1
Metal machining operations (CS79) - aerosol	1	860	2	0

s= number of exposure scenarios for which data were available; n=number of measurements; nM>T=number of measurements that exceed the relevant exposure estimate; %M>T=percentage of the measurements that exceed the relevant exposure estimate.

OVERALL SUMMARY OF COMBINED INDIVIDUAL AND AGGREGATED DATA COMPARISONS

Table A3.35 Overall proportion of measurements exceeding the exposure estimates across all substances (individual and aggregated data combined)

Substance	s	n	nM>T	%M>T
Kerosine	4	226	3	1
Heavy oil fuel	1	5	3	60
Naphtha (0-1% benzene)	7	236	28	12
Naphtha (1-5% benzene)	7	4805	2705	56
Other lubricant base oils-vapour	1	6601	44	1
Other lubricant base oils-aerosol	1	860	2	0

s= number of exposure scenarios; n=number of measurements; nM>T=number of measurements that exceed the relevant exposure estimate; %M>T=percentage of the measurements that exceed the relevant exposure estimate.

As can be seen from Table A3.35 above, there is some variation in the percentage of measurements exceeding the exposure estimates for the different petroleum substances, with relatively higher percentages of underestimation for naphtha (1-5% benzene concentration) and heavy fuel oil. More detailed consideration should be given to these substances and the possibility of collecting additional comparator data to facilitate a further, more comprehensive validation should be examined.

APPENDIX 3B: RESULTS OF COMPARISON EXERCISE – OVERALL SUMMARY PER SCENARIO

All exposure estimates are recalculations in order to check CSA estimates and analyse which RMMs and operational conditions have been used. Small deviations between the values displayed here and the values from the CSAs which have been used for comparison are usually rounding errors.

For scenarios where duration modifier has been used two results are given (with and without duration modifier).

RESTRICTED DATASET

Table A3.36 Scenarios for validation: basic results of comparison (restricted dataset)

Substance	ES_ID	PROC	Situation	General description of situation	Typical exposure conditions	n	N M>T	% M>T	estimate	initial estimate (mg/m³)	modifiers	Conditions used for exposure assessment	RMM use for exposure assessment	estimate (mg/m3)
Kerosine	ES_K_1	PROC 8a Transfer of substance or preparation (charging/discharging) from/to vessels/large containers at non-dedicated facilities.	CS39 Equipment cleaning and maintenance	Manufacture of substance	Daily; 15 min -1 hour; product temp; Indoor/Outdoor. Enclosed lines; collection of line waste in container; retain wash down in sealed storage pending disposal or use as recycled material for subsequent formulation. PPE.	11	1	9	vapour	261.75	0.2	>4 hours, ambient temp.	Drain down system prior to equipment break-in or maintenance. E65. (80%)	52.35
Kerosine	ES_K_27	PROC 8b Transfer of a substance or preparation (charging /discharging) from/to vessels/large containers at	CS14 Bulk transfers	use as fuel / professional	Outdoor; Daily; 1 - 4 hours; product temp (ambient). Enclosed transfers, clear lines prior to decoupling	175	0	0	vapour	261.75	0.595	>4 hours, ambient temp. outdoors (30%)	Ensure operatives are trained to minimise exposures. EI19. (15%).	155.74125

Substance	ES_ID	PROC	Situation	General description of situation	Typical exposure conditions	n	N M>T	% M>T	estimate	initial estimate (mg/m³)	modifiers	Conditions used for exposure assessment	RMM use for exposure assessment	estimate (mg/m3)
		dedicated facilities												
Kerosine	ES_K_28	PROC 8a Transfer of substance or preparation (charging/discharging) from/to vessels/large containers at non-dedicated facilities.	CS39 Equipment cleaning and maintenance. Equipment maintenance e.g. Vehicle, boiler, pump maintenance, pump calibration.	use as fuel / professional	Indoor/Outdoor; Daily; >4 hours, to 100%. operator training, PPE	32	1	3	vapour	523.5	0.2	>4 hours, ambient temp.	Drain down system prior to equipment break-in or maintenance. E65. (80%)	104.7
Kerosine	ES_K_38	PROC 13 Treatment of articles by dipping and pouring	CS4 Dipping, immersion and pouring	use in road and construction applications/ professional	Daily; >4 hours, product temp (ambient) Outdoor	8	1	13	vapour	523.5	0.357	1-4 hours (*0.6), ambient temp. outdoors (30%)	Ensure operatives are trained to minimise exposures. EI19. (15%)	186.9 (311.5)

Substance	ES_ID	PROC	Situation	General description of situation	Typical exposure conditions	n	N M>T	% M>T	estimate	initial estimate (mg/m³)	modifiers	Conditions used for exposure assessment	RMM use for exposure assessment	estimate (mg/m3)
Heavy fuel oil	ES_HFO_1	PROC8b Transfer of substance or preparation (charging /discharging) from/to vessels/large containers at dedicated facilities.	CS_new Marine vessel/barge (un)loading	ES2 - Distribution of substance - industrial	Daily; 1 - 4 hours; Outdoor OT 55-90dC (low volatile); outdoors (-30%)	5	3	60	aerosol	0.064	0.6	<4 hours (*0.6), moderately elevated temp.		0.0384 (0.064)
Naphtha 0-1% benzene	N_0-1p_1	PROC 8a Transfer of substance or preparation (charging/discharging) from/to vessels/large containers at non-dedicated facilities.	CS39 Equipment cleaning and maintenance	Manufacture of substance - Industrial	Daily; 8 hours; product temp; collection of line waste in container; Outdoor. Enclosed lines; retain wash down in sealed storage pending disposal or use as recycled material for subsequent formulation. PPE.	11	0	0	vapour	797.5	0.001	>4 hours; ambient temp. , concentration modifier 0.01.	Drain down and flush system prior to equipment break-in or maintenance. E55. (90%)	0.7975
Naphtha 0-1% benzene	N_0-1p_10	PROC 8b Transfer of a substance or preparation (charging /discharging) from/to vessels/large containers at dedicated facilities	CS500 Bulk closed loading. Bulk closed loading and unloading (e.g. road/rail car bottom loading/ unloading; marine vessel/barge	Distribution of substance - Industrial	Daily; 15 min -1 hour; product temp.; exposure potential during breaking of hose connection; Outdoor. Enclosed transfers, clear lines prior to decoupling	30	9	30	vapour	478.5	0.001	>4 hours, ambient temp. concentration modifier 0.01.	LEV or containment E66 (90%)	0.4785

Substance	ES_ID	PROC	Situation	General description of situation	Typical exposure conditions	n	N M>T	% M>T	estimate	initial estimate (mg/m³)	modifiers	Conditions used for exposure assessment	RMM use for exposure assessment	estimate (mg/m3)
			loading/unloading)											
Naphtha 0-1% benzene	N_0-1p_11	PROC 8b Transfer of a substance or preparation (charging /discharging) from/to vessels/large containers at dedicated facilities	CS501 Bulk closed loading and unloading. Bulk closed loading (e.g. road/rail car bottom loading; marine vessel/barge loading)	Distribution of substance - Industrial	Daily; 15 min -1 hour; product temp.; exposure potential during breaking of hose connection; Outdoor. Enclosed transfers, clear lines prior to decoupling	4	0	0	vapour	478.5	0.001	>4 hours, ambient temp. concentration modifier 0.01.	LEV or containment E66 (90%)	0.4785

Substance	ES_ID	PROC	Situation	General description of situation	Typical exposure conditions	n	N M>T	% M>T	estimate	initial estimate (mg/m³)	modifiers	Conditions used for exposure assessment	RMM use for exposure assessment	estimate (mg/m3)
Naphtha 0-1% benzene	N_0-1p_13	PROC 8a Transfer of substance or preparation (charging/discharging) from/to vessels/large containers at non-dedicated facilities.	CS5 Equipment maintenance. Equipment maintenance e.g. Vehicle, boiler, pump maintenance, pump calibration	Use as a fuel - Professional	Daily; >4 hours, to 100%; Outdoor. PPE. Operator training.	58	1	2	vapour	1595	0.0017	> 4 hours daily; ambient temp. concentration modifier 0.01. Intended to cover usual incidental exposures plus injector strip down and work on fuel tank.	Drain down system prior to equipment break-in or maintenance. E65. (80%) Ensure operatives are trained to minimise exposures. EI19. (15%).	2.7115
Naphtha 0-1% benzene	N_0-1p_15	PROC 15 Use as laboratory reagent	CS36 Laboratory activities	manufacture of substance - industrial	Daily; 1-4 hours; product temp.; Indoor. Fume cupboard. PPE.	26	12	46	vapour	159.5	0.001	>4 hours, ambient temp. concentration modifier 0.01.	With LEV (90%),	0.1595

Substance	ES_ID	PROC	Situation	General description of situation	Typical exposure conditions	n	N M>T	% M>T	estimate	initial estimate (mg/m³)	modifiers	Conditions used for exposure assessment	RMM use for exposure assessment	estimate (mg/m3)
Naphtha 0-1% benzene	N_0-1p_16	PROC 8b Transfer of a substance or preparation (charging /discharging) from/to vessels/large containers at dedicated facilities	CS502 Bulk closed unloading. Bulk delivery (closed) (e.g. heating oil, diesel, bunker fuel deliveries)	Use as a fuel - Professional	Outdoor; Daily; 1 - 4 hours; product temp (ambient) . Enclosed transfers, clear lines prior to decoupling	35	6	18	vapour	797.5	0.001	>4 hours, ambient temp. concentration modifier 0.01.	No lev but Extract Ventilation (90%),	0.7975
Naphtha 0-1% benzene	N_0-1p_17	PROC 8b Transfer of a substance or preparation (charging/ discharging) from/to vessels/large containers at dedicated facilities	CS507 Refuelling. Refuelling vehicles, light aircraft or marine	Use as a fuel - Professional	Outdoor; Daily; >4 hours, to 100%. Pumped transfer to vehicle; with or without vapour recovery	73	0	0	vapour	797.5	0.001	daily; ambient temp. No lev. But Extract Ventilation (90%), concentration modifier 0.01.		0.7975
Naphtha 1-5% benzene	N_1-5p_1	PROC 2 Use in closed, continuous process with occasional controlled exposure (e.g. sampling)	CS15 General exposures (closed systems). + CS56 With sample collection.	Manufacture of substance – Industrial	Continuous; daily; 15 min -1 hour; product temp. Outdoor. Enclosed process; Outdoor location; closed/semi-closed sampling point	1665	1553	93	vapour	159.5	0.001	>4 hours, ambient temp. , concentration modifier 0.02.	Sample via a closed loop system. E8. (95%)	0.1595

Substance	ES_ID	PROC	Situation	General description of situation	Typical exposure conditions	n	N M>T	% M>T	estimate	initial estimate (mg/m³)	modifiers	Conditions used for exposure assessment	RMM use for exposure assessment	estimate (mg/m3)
Naphtha 1-5% benzene	N_1-5p_2	PROC 8a Transfer of substance or preparation (charging/discharging) from/to vessels/large containers at non-dedicated facilities.	CS39 Equipment cleaning and maintenance	Manufacture of substance – Industrial	Daily; 8 hours; product temp; collection of line waste in container; Outdoor. Enclosed lines; retain wash down in sealed storage pending disposal or use as recycled material for subsequent formulation. PPE.	157	44	28	vapour	797.5	0.002	>4 hours, ambient temp. , concentration modifier 0.02.	Drain down and flush system prior to equipment break-in or maintenance. E55. (90%)	1.595
Naphtha 1-5% benzene	N_1-5p_3	PROC 2 Use in closed, continuous process with occasional controlled exposure (e.g. sampling)	CS67 Storage	Manufacture of substance - Industrial	Daily; 8 hrs; product temp; Outdoor Samples collected at dedicated sample points (incl. tank dipping)	27	14	50	vapour	159.5	0.001	>4 hours, ambient temp. , concentration modifier 0.02.	Store substance within a closed system. E84. (95%)	0.1595
Naphtha 1-5% benzene	N_1-5p_15	PROC 15 Use as laboratory reagent	CS36 Laboratory activities	Manufacture of substance - Industrial	Daily; 1-4 hours; product temp.; Indoor. Fume cupboard. PPE	628	220	35	vapour	159.5	0.002	>4 hours, ambient temp. concentration modifier 0.02.	With LEV (90%)	0.319
Naphtha 1-5% benzene	N_1-5p_9	PROC 8a Transfer of substance or preparation (charging/discharging)	CS39 Equipment cleaning and maintenance	Distribution of substance - Industrial	Daily; 15 min -1 hour; product temp; collection of line waste in container; Indoor. Enclosed lines; retain wash down in sealed storage pending disposal or use	64	4	6	vapour	797.5	0.002	daily; ambient temp. concentration	Drain down and flush system prior to equipment break-in or	1.595

Substance	ES_ID	PROC	Situation	General description of situation	Typical exposure conditions	n	N M>T	% M>T	estimate	initial estimate (mg/m³)	modifiers	Conditions used for exposure assessment	RMM use for exposure assessment	estimate (mg/m3)
		from/to vessels/large containers at non-dedicated facilities.			as recycled material for subsequent formulation. PPE.							modifier 0.02.	maintenance. E55. (90%)	
Naphtha 1-5% benzene	N_1-5p_13	PROC 8a Transfer of substance or preparation (charging/discharging) from/to vessels/large containers at non-dedicated facilities.	CS39 Equipment cleaning and maintenance	Formulation & (re)packing of substances and mixtures - Industrial	Daily; 1 - 4 hours; product temp; collection of line waste in container; Indoor. Enclosed lines; retain wash down in sealed storage pending disposal or use as recycled material for subsequent formulation. PPE.	2	0	0	vapour	797.5	0.002	daily; ambient temp. temp. concentration modifier 0.02.	Drain down and flush system prior to equipment break-in or maintenance. E55. (90%)	1.595
Naphtha 1-5% benzene	N_1-5p_14	PROC 8b Transfer of a substance or preparation (charging /discharging) from/to vessels/large containers at dedicated facilities	CS501 Bulk closed loading and unloading. Bulk closed loading (e.g. road/rail car bottom loading; marine vessel/barge loading)	Distribution of substance - Industrial	Daily; 15 min -1 hour; product temp.; exposure potential during breaking of hose connection; Outdoor. Enclosed transfers, clear lines prior to decoupling	2262	870	39	vapour	478.5	0.002	>4 hours, ambient temp. concentration modifier 0.02.	No LEV but Extract Ventilation (90%)	0.957
Other lubricant base oils - aerosol	ES_OLBO_16+17	PROC 17 Lubrication at high energy conditions	CS79 Metal machining operations	Metal working fluids / rolling oils professional	Indoor, Daily; 8 hours; ambient temp. LEV; PPE	860	2	0	aerosol	50	0.0918	1-4 hrs, ambient temp. < 4hrs	Ensure operatives trained to minimise	4.59 (7.65)

Substance	ES_ID	PROC	Situation	General description of situation	Typical exposure conditions	n	N M>T	% M>T	estimate	initial estimate (mg/m³)	modifiers	Conditions used for exposure assessment	RMM use for exposure assessment	estimate (mg/m3)
		and in partly open process										duration (0.6x);	exposures EI19 (15%) + Enhanced general ventilation (0.3x); <25% concn (0.6x); resulting in overall 91% reduction.	
Other lubricant base oils - vapour	ES_OLBO _16+17	PROC 17 Lubrication at high energy conditions and in partly open process	CS79 Metal machining operations	Metal working fluids / rolling oils professional	Indoor, Daily; 8 hours; ambient temp. LEV; PPE	6601	44	1	vapour	667	0.0918	1-4 hrs, ambient temp. < 4hrs duration (0.6x);	Ensure operatives trained to minimise exposures EI19 (15%) + Enhanced general ventilation (0.3x); <25% concn (0.6x); resulting in overall 91% reduction.	61.2 (102)

Environmental Science for European Refining

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