Työterveyslaitos

# Development of initial REACH exposure scenarios for methanol

## Final report

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This project has received financing from The Finnish Work Environment Fund

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# DEVELOPMENT OF INITIAL REACH EXPOSURE SCENARIOS FOR METHANOL

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FOREWORD FOR THE TRANSLATION

The aim of this study was to develop REACH (Registration, Evaluation, Authorization, and Restriction of Chemicals) Exposure Scenarios (ESs) for methanol, and to test the ES development process in co-operation with companies, experts and authorities. We followed draft REACH technical guidance documents available during the years 2006-2007 for ES development. The development of ESs included mapping uses and categorizing them, according to operational conditions, into broader scenarios when needed. The exposure data and conditions of use required in the scenarios were gathered from existing measurement reports, new measurements, and through modelling. Preliminary human health and environmental hazard assessment was based on published data or modelling.

This project was successful in determining the main Finnish uses of methanol. The mapping of methanol uses in Finland revealed 62 uses, 35 of which were included in the ten exposure scenarios in this project. Five of these ESs were exposure categories comprising several applications while the remainder were detailed ESs for a single application. The identification of uses also unveiled previously unknown exposure situations to the researches. As the mapping of uses revealed new sites of exposure for which risk management measures were developed in the scenarios, the goal of REACH, i.e. the safer use of chemicals, was met. Worker exposure in industry was managed efficiently by traditional workplace measures. The measures recommended to consumers were product integrated, as was the decrease of the percentage of methanol in the preparation.

Our work was mainly to test the Exposure Scenario development process, and because of that the scenarios and categories presented here could be seen as initial. The category grouping chosen was useful in this project, but according to REACH regulation the uses could also be grouped in different ways.

This report will be also available in the internet pages of Finnish Institute of Occupational Health http://www.ttl.fi/internet/english

ECHA (European Chemicals Agency) guidances, RMM (Risk Management Measures) library and new models (like ECETOC TRA) have released after our project and can be found in the links below.

The ECHA quidances on exposure estimation (is under revision at present, December 2009) http://guidance.echa.europa.eu/docs/guidance_document/information_requirements_en.htm?time=12530981

The latest draft of the Exposure Scenario format by ECHA (2009) http://guidance.echa.europa.eu/docs/guidance_document/inforeq_csr_d_version_2_en_esformat_draft_peg_clean.pdf.

The RMM library is helpful for example in presenting the efficacy of RMM. http://cefic.org/Templates/shwStory.asp?NID=719&HID=718.

New version of ECETOC TRA has been released http://www.ecetoc.org/tra.

# INTRODUCTION

Planning of the project for developing REACH exposure scenarios began in 2005, two years before final approval of the REACH regulation. The planning group met three times and, in addition to the Finnish Institute of Occupational Health's research group, included active representation from five companies importing and/or using methanol, various authorities (Ministry of Social Affairs and Health, National Product Control Agency for Welfare and Health, Finnish Environmental Institute), labour market organizations (Chemical Industry Federation of Finland, Chemical Workers' Union, Transport Workers' Union AKT r.a.) and other expert institutes (VTT). The project received financing from the Finnish Institute of Occupational Health, Finnish Work Environment Fund and Ministry of Social Affairs and Health, and it was launched at the beginning of 2006. Along with the bodies listed above, the project management group included Ilkka Tahvanainen, representing the Finnish Work Environment Fund, and an expert group from the Finnish Institute of Occupational Health (Sanni Uuksulainen, Riitta Riala, Tiina Santonen, Pirjo Heikkilä, Beatrice Bäck and Tapani Tuomi). The management group met nine times during the project and was chaired by the Chemical Industry Federation of Finland representative, Seppo Loikkanen until spring 2007 and Juha Pyötsiä after that. Riitta Riala, who was the responsible person for the project, left the Finnish Institute of Occupational Health to take up a position with the European Chemicals Agency (ECHA). Other members of the management group were Jouni Räisänen from the National Product Control Agency for Welfare and Health, Pertti Sulasalmi from the Transport Workers' Union AKT r.a., Kari Mäkelä from the Chemical Workers' Union, Antero Laitinen from VTT and Arto Kultamaa from the Finnish Environmental Institute.

Since the REACH regulation was approved at the midpoint of the project and the final operational guidelines are still incomplete in the final stages, the project is a procedural exercise by nature and based on the application of incomplete guidelines. The project was not aimed at compiling a complete Chemical Safety Report but focused on teaching and developing the procedures and methods needed for creating exposure scenarios that comply with REACH. Fortunately, the management group was very knowledgeable and the management group work active and guidance-oriented, which benefited all parties involved.

In addition to the actual meetings, the management group has one open work meeting focusing on environmental exposure, during which Arto Kultamaa from the Finnish Environmental Institute utilised modelling to explain how to assess environmental exposure. Arto Kultamaa was also involved in writing the section of the report dealing with assessment of environmental hazard and exposure.

The Finnish Institute of Occupational Health's expert group was responsible for project implementation and the written work. The group co-operated to develop initial exposure scenarios. New exposure measurements were made by Occupational Hygienists Sanni Uuksulainen, Beatrice Bäck, Tuula Liukkonen, Jari Rajala and Ari Johansson. They were assisted in this work by Occupational Hygiene Technicians Raimo Eronen, Reijo Liukkonen and Ossi Virtanen. The earlier register data on methanol was collected by Specialised Research Scientist Pirjo Heikkilä, and Sanni Uuksulainen converted the data into a useful format. Beatrice Bäck and Chemist Urve Jakobson performed the analyses, while the exposure models were applied by Sanni Uuksulainen and Pirjo Heikkilä. Tiina Santonen, Team Leader of the Risk Assessment team, wrote the health hazard assessment. Assistant Chief Medical Officer Ari Kaukiainen and Team Leader Markku Sainio brought their medical expertise to the project. Specialised Research Scientist Juha Laitinen was responsible for the biomonitoring section. Occupational Hygienist Sanni Uuksulainen served as head researcher for the project. Tapani Tuomi, Team Leader of the Chemical Agents team, has been the responsible person for the project since autumn 2006.

## SUMMARY IN FINNISH

Työterveyslaitos ja 5 metanolia maahantuovaa tai käyttävää yritystä tekivät kaksivuotisen yhteistyöhankkeen, jossa laadittiin REACH (Registration, Evaluation and Authorization of Chemicals) -asetuksen mukaiset altistumisskenaariot eli turvallisen käytön kuvaukset usealle metanolin käyttökohteelle Suomessa. Metanoli on yksi eniten Suomessa käytetyistä kemikaaleista ja sitä tuodaan Suomeen n. 150 000 tonnia vuodessa.

Hanke toteutettiin vuosina 2006-2007, jolloin REACH -asetuksen lopulliset kemikaaliturvallisuusraporttia koskevat toimintaohjeet eivät olleet vielä valmiita, minkä vuoksi altistumisskenaarioiden kehittämisessä sovellettiin ohjeluonnoksia. Viimeisimmät hankkeessa käytetyt luonnokset olivat lokakuulta 2007. Hankkeessa ei laadittu koko kemikaaliturvallisuusraporttia, vaan sovellettiin REACH -asetuksen mukaisten altistumisskenaarioiden luomiseen tarvittavia menetelmiä ja toimintatapoja. Hankkeen altistumisskenaariot ovat luonteeltaan alustavia. Lopulliset altistumisskenaariot tekee metanolia rekisteröivien yritysten konsortio, joten raportissa esitettävät riskinhallintakeinot voivat poiketa lopullisista rekisteröijän aikanaan tekemistä altistumisskenaarioista.

Metanolin käyttökohteet selvitettiin hankkeessa olevien yritysten antamien tietojen, TTL:n mittausrekisterin, kirjallisuustietojen, internet-tietokantojen, haastattelujen sekä uusista mittauskohteista lomakkeella kerättyjen tietojen avulla. Käyttömäärätietoja saatiin KETU-rekisteristä (kemikaalirekisterin tuoterekisteri). Suomeen tuodusta metanolista suurin osa, noin 130 000 tonnia käytetään kemiallisten tuotteiden valmistukseen. Käyttökohteet jaoteltiin viiteen alustavaan altistumiskategoriaan ja viiteen alustavaan altistumisskenaarioon. Altistumiskategorioissa on mukana useampia käyttökohteita. Hankkeessa kehitettiin seuraavat kategoriat: metanolin lastaus- ja purkutyöt, metanoli lähtöaineena kemiallisten tuotteiden valmistuksessa, metanolin käyttö teollisena liuottimena uuttoprosesseissa, metanolin käyttö liuottimena teollisuudessa eri toimialoilla ja metanolin laboratoriokäyttö. Alustavia altistumisskenaarioita kehitettiin kolmelle työperäiselle käytölle: metanolin käyttö jätevedenpuhdistuksessa, metanolipitoisten lasinpesunesteiden valmistus ja metanolipitoisten lasinpesunesteiden käyttö ammattiliikenteessä. Lisäksi tehtiin altistumisskenaarioita kahdelle metanolin kuluttajakäyttökohteelle: metanolipitoisten lasinpesunesteiden käyttö ja metanolin käyttö erikoispolttonesteenä. Altistumisskenaarioille ja kategorioille määritettiin todennäköiset altistumisreitit, joiden yhteenlaskettu altistuminen otettiin huomioon riskinluonnehdinnassa.

Osana alustavien altistumisskenaarioiden laadintaa arvioitiin metanolin alustavat DNEL- ja PNEC -arvot (Derived No Effect Level eli johdettu vaikutukseton altistumistaso ja Predicted No Effect Consentration eli arvioitu vaikutukseton pitoisuus). Metanolin terveysvaaran arviointi tehtiin saatavilla olevan toksikologisen tiedon pohjalta ja tämänhetkisten vaaranarviointia koskevien REACH-asetuksen toimintaohjeluonnosten mukaisesti. Hankkeessa tehtiin suppea ympäristövaaran arviointi, jossa metanolille määritettiin alustavat haitattomat pitoisuudet vedelle, sedimentille ja maaperäeliöstölle. Hankkeessa kehitettiin alustavat DNEL-arvot työntekijöiden akuutille ja pitkäaikaiselle iho- ja hengitystiealtistumiselle sekä kuluttajien akuutille ja pitkäaikaiselle iho- ja hengitystiealtistumiselle. Työntekijöille laskettiin näiden perusteella kokonaisaltistumisen DNEL-arvot. Arvioituja altistumistasoja verrattiin skenaarioittain näihin alustaviin DNEL-arvoihin. Raportissa esitetään myös alustava metanolille ehdotettu GHS (Globally Harmonised System of classification and labelling) -luokitus ja merkintä. Varsinaisessa rekisteröinnissä REACH -asetus edellyttää kaiken olemassa olevan tutkimustiedon kokoamista ja avaintutkimusten yksityiskohtaista arviointia, jonka lisäksi metanolia rekisteröivällä konsortiolla saattaa olla vaaraominaisuustietoja, mitä ei ole julkisesti saatavilla. Rekisteröijien laatimat DNEL- ja PNEC-arvot saattavat mm. tästä syystä poiketa tässä esitetystä.

Altistumista arvioitiin mittaamalla ja mallintamalla. Mittaaminen on RIP (REACH Implementation Project) -toiminto-ohjeluonnoksissa esitetty altistumisen arvioinnin ensisijaiseksi menetelmäksi.
Altistumisen arviointi hengitystiealtistumisen osalta perustui mittaustuloksiin kaikissa altistumis- ja käyttöskenaarioissa. Olemassa olevia mittaustuloksia oli 31 käyttökohteesta (475 näytettä). Tutkimuksen aikana mitattiin ilman metanolipitoisuuksia 184 näytteestä 14 eri pääkäyttökohteessa, mukaan lukien kaksi kuluttajakäyttökohdetta. Ihoaltistumista arvioitiin mallintamalla. Mallintamisessa kokeiltiin kolmen kemikaalialtistumismallin soveltuvuutta altistumisen arvioinnissa. Käytetyt mallit olivat EUSES (eli European Union System for the Evaluation of Substances) 2.0.3, kuluttajan altistumista kuvaava ConsExpo 4.1-malli ja EcetocTra (European Centre for Ecotoxicology and Toxicology of Chemicals, Targeted Risk Assessment). Monia toiminto-ohjeluonnoksissa suositeltavia malleja (mm. Riskofderm ja EcetocTra -mallit) kehitetään parhaillaan. Ympäristön altistumista arvioitiin kahdessa altistumisskenaariossa ensin mallintamalla (EUSES 2.0.3) ja mallin antamaa tulosta varmennettiin tutkimalla vesinäytteitä.

Lisäksi hankkeessa selvitettiin biomonitoroinnin soveltuvuutta altistumisen kuvaamiseen muutamalla toimialalla. Näytteitä otettiin 28 henkilöltä. Tämän suppean aineiston perusteella biomonitoroinnista saatiin lisähyötyä metanolialtistumisen arvioinnissa lähinnä ihoaltistumisen arvioinnissa ja suojaustason varmistamisessa tilanteissa, joissa käytettiin hengityksensuojaimia. Biomonitorointia tehtiin kahdella menetelmällä (virtsan muurahaishappo ja virtsan metanoli).

Monissa käyttökohteissa työntekijöiden altistuminen ylitti jopa nykyisin käytössä olevat HTP-arvot (haitalliseksi tunnetut pitoisuudet), joten varsinkin työntekijöille ehdotetut riskinhallintatoimet ovat perusteltuja. Käyttökohteita, joissa HTP -arvot ylitettiin olivat lasinpesunesteiden valmistus, jätevesilaitosten kunnossapitotyöt ja lyhytaikaiset metanolin lastaus- ja purkutyöt. Myös muutamissa teollisissa käyttökohteissa (reaktorien lyhytaikaiset huoltotoimenpiteet, uuttoliuoskäyttö tai telojen pesuliuoskäyttö) altistuminen oli merkittävää ja ylitti osassa nykyiset HTP -arvot.

Altistumisskenaarioissa esitimme riskinhallintatoimia, joiden avulla altistuminen on mahdollista saada sen verran matalalle, että se ei todennäköisesti enää aiheuta terveysvaaraa. Riskinhallintatoimina suosittelimme henkilökohtaisten suojaimien käyttöä metanolin lastaus- ja purkutöissä. Työjärjestelyin sekä henkilökohtaisten suojaimien avulla voidaan vähentää metanolin jätevesilaitoskäytön kunnossapitotyön altistumista. Lasinpesunesteiden valmistuksessa tulisi työ tehdä tehokkaalla kohdepoistolla varustetussa hyvin ilmastoidussa tilassa ja työntekijän tulee lisäksi käyttää henkilökohtaisia suojaimia. Työjärjestelyjä, tehokasta kohdepoistoa sekä henkilökohtaisia suojaimia tarvittaisiin metanolin teollisissa uutto- ja liuotinkäytöissä sekä kemiallisten tuotteiden valmistuksen kunnossapitotöissä ja tynnyritäytöissä. Metanolin käsittely laboratorioissa tulisi arviomme mukaan tehdä aina vetokaapissa.

Työntekijäaltistumisen ja kuluttajan altistumisen käyttökohteet menivät päällekkäin metanolin lasinpesunestekäytössä taksiliikenteessä. Tällöin taksiliikenteen ja muun ammattiliikenteen käyttöön sovellettiin kuluttajakäytön raja-arvoja ja riskinhallintakeinoja. Kuluttajien altistuminen lasinpesunesteiden metanolille arvioitiin liialliseksi. Altistumista voidaan vähentää alentamalla kuluttajille myytävien lasinpesunesteiden metanolipitoisuutta, koska kuluttajille suositetaan ensi sijassa tuotteeseen sidottuja riskinhallintatoimenpiteitä. Hankkeessa tehtiin myös vertailtavien etanoli- ja isopropanolipohjaisten lasinpesunesteiden altistumismittauksia, joiden mukaan kokonaisaltistuminen liuotinaineille vertailutuotteita käytettäessä oli useita kertaluokkia pienempää.
Kuluttajien erikoispolttoainekäytön katsottiin olevan erityisempi kuluttajakäyttökohde, ammattikäytön ja kuluttajakäytön rajatapaus, jolloin altistumisskenaariossa ehdotimme suojakäsineitä turvallisen käytön turvaamiseksi.
Metanolista ei aiheudu nykyisen kaltaisissa käyttöolosuhteissa liiallisia ympäristöpäästöjä lasinpesunestekäytössä tai jätevedenpuhdistamokäytössä.

## SUMMARY

### Developing REACH Exposure Scenarios for Methanol

The Finnish Institute of Occupational Health (FIOH) and five companies importing or using methanol carried out a two-year collaboration project in which exposure scenarios or instructions for safe use for several applications of methanol in Finland were prepared. The exposure scenarios were prepared based on the REACH (Registration, Evaluation and Authorization of Chemicals) legislation. Methanol is one of the most widely used chemicals in Finland, with a volume of import of about 150 000 tons per year.

The project was conducted in 2006–2007, when the final guidance documents of the REACH regulation concerning the chemicals safety report were not yet completed, and drafts of guidance documents were therefore used in the development of exposure scenarios. The latest drafts used in the project were from October 2007. A complete chemical safety report was not prepared in the project, but the methods suggested for creating exposure scenarios that comply with the REACH legislation were applied. The exposure scenarios created in the project are initial in nature. Because the final exposure scenarios are prepared by the consortium of companies to register methanol, the risk management measures presented in the report may differ from the final exposure scenarios to be prepared by the registering body.

The different uses of methanol were mapped based on information given by companies involved in the project, FIOH's measurement register, literature, search engines, interviews, and information on new measurement targets collected by a questionnaire. Information on the amounts of use was sought from the Product Register of Chemicals (KETU). The majority of the methanol imported into Finland, about 130 000 tons, is used in the manufacturing of chemical products. The applications were divided into five initial exposure categories and five initial exposure scenarios. The exposure categories include several applications. The following categories were created: loading and unloading of methanol, methanol as the original substance in the manufacturing of chemical products, use of methanol as an industrial solvent in extraction processes, use of methanol as solvent in different fields of industry, and laboratory use of methanol. Initial exposure scenarios were developed for three work-related uses: use of methanol in wastewater treatment, manufacturing of windshield washer fluids containing methanol, and use of windshield washer fluids containing methanol in professional traffic. In addition, exposure scenarios were prepared for two consumer applications of methanol: use of windshield washer fluids containing methanol and use of methanol as fuel. Probable exposure routes were defined for the exposure scenarios and categories, and the combined exposures of these routes were accounted for in risk characterization.

As part of the preparation of initial exposure scenarios, preliminary DNEL and PNEC (Derived No Effect Level and Predicted No Effect Concentration) values were prepared for methanol. Assessment of the health hazards of methanol was carried out based on the available toxicological information and according to current REACH draft guidance documents on hazard assessment. The project also carried out a limited assessment of environmental hazards and defined preliminary harmless concentrations of methanol for water, sediment, and organisms in the soil. Preliminary DNEL values were determined for acute and long-term dermal and inhalation exposure of workers and acute and long-term dermal and inhalation exposure of consumers. Based on these, DNEL values for overall exposure were calculated for workers. The estimated exposure levels in each scenario were compared to these preliminary DNEL values. In the study report, a preliminary proposal for a GHS (Globally Harmonised System of classification and labelling) classification and labelling of methanol is also presented. In the case of actual registration, the REACH legislation requires the compilation of all existing research information and a detailed analysis of key studies. In addition, the consortium registering methanol may possess information that is not publicly

available. The DNEL and PNEC values determined by the registering bodies may for this reason differ from those used here.

Exposure was assessed through measuring and modelling. In the RIP (REACH Implementation Project) guidance document drafts, measuring is presented as the primary method for exposure assessment.

Exposure assessment for inhalation exposure was based on measurement results in all exposure and use scenarios. Measurement results existed for 31 applications (475 samples). Concentrations of methanol in air were measured in 184 samples in 14 different main applications, including two consumer applications. Dermal exposure was assessed through modelling. In the modelling, we tested the usefulness of three chemicals exposure models in the assessment of exposure. The models used were EUSES (the European Union System for the Evaluation of Substances) 2.0.3, ConsExpo 4.1 model describing consumer exposure, and EcetocTra (European Centre for Ecotoxicology and Toxicology of Chemicals, Targeted Risk Assessment). Many of the models recommended in the draft for guidance document (e.g. Riskofderm and EcetocTra models) are currently under development.

Environmental exposure was assessed in two exposure scenarios by modelling (EUSES 2.0.3), and the result gained from the model was verified by studying water samples.

In addition, the project evaluated the usability of biomonitoring for exposure assessment in different fields. Samples were taken from 28 persons. Based on this limited data, biomonitoring of methanol produced additional value mainly for the assessment of dermal exposure and for the ensurance of the level of protection in situations where respiratory protection was used. Two different methods were used for biomonitoring: measurements of formic acid in urine and of methanol in urine.

In many applications, workers' exposure exceeded even the current Finnish occupational exposure levels (OELs), meaning that risk management measures for workers are justified. Applications where the current OELs were exceeded included the manufacturing of windshield washer fluids, maintenance work in wastewater treatment plants, and the short-duration tasks of loading and unloading of methanol. In some industrial applications (short-duration maintenance procedures on reactors, use in extraction fluids, or washing of rollers), the exposure was significant and exceeded current OELs.

In the exposure scenarios, we proposed risk management measures that can reduce exposure to a level where it would not be likely to pose a health hazard. As risk management measures, we recommended the use of personal protective equipment when loading and unloading methanol. New work arrangements and use of personal protective equipment can reduce exposure to methanol in maintenance work in wastewater processing plants. In the manufacturing of windshield washer fluids, the work should be carried out in a well-ventilated space fitted with an efficient local exhaust ventilation system, and the worker must also use personal protective equipment. Working arrangements, efficient local exhaust ventilation system, and personal protective equipment would be necessary in industrial extraction and solvent use of methanol and in maintenance work and barrel fillings in chemical products manufacturing. According to our estimate, the processing of methanol in laboratories should always be carried out inside a fume cupboard.

The applications of worker and consumer exposure overlapped in the use of methanol in windshield washer fluids in taxis. In this case, consumer limit values and consumer risk management measures were applied in taxis and other professional traffic. Consumer exposure to methanol in windshield washer fluids was assessed as excessive. Exposure can be reduced by lowering the methanol content of windshield washer fluids sold to consumers, because the risk management measures recommended to consumers are mainly product-specific. The project also carried out comparative measurements of ethanol and isopropanol-based windshield washer fluids. Based on the measurements, the overall exposure to solvents when using the products assessed was several times smaller compared to occasions where products with methanol were used. Consumers' use of methanol-based fuels was considered to be a more specific consumer application, a borderline case between professional and consumer use, in which case we proposed the use of protective gloves to ensure safe use.

In the current circumstances of use, no excessive environmental emissions result from the use of methanol in windshield washer fluids or wastewater processing plants.

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## ABBREVIATIONS

| | |
|---|---|
| ACGIH | American Conference of Governmental Industrial Hygienist |
| BAT | Biologische Arbeitsstoff Toleranz |
| BEI | Biological Exposure Indice |
| CalEPA | California Environmental Protection Agency |
| CERHR-NTP | Center for the Evaluation of Risks to Human Reproduction- National Toxicity Program |
| COSHH | Control of Substances Hazardous to Health |
| DECOS | Dutch Expert Committee on Occupational Standards |
| DNEL | Derived No Effect Level |
| EcetocTra | European Centre for Ecotoxicology and Tocxicology of Chemicals - Targeted Risk Assessment |
| $EC_{50}$ | Median effectice consentration (required to induce a 50 % effect) |
| ECHA | European Chemical Agency (Helsinki) |
| ES | Exposure scenario |
| EUSES | European Union System for the Evaluation of Substances |
| GHS | Globally Harminised System og Classification and Labelling of Chemicals |
| HPLC | High Pressure Liquid Chromatography |
| HTP | Haitalliseksi tunnettu pitoisuus (Finnsh occupational exposure level) |
| IDHL | Immediately dangerous to life and health |
| IPCS | International Programme on Chemical Safety |
| KETU | Kemikaalirekisterin tuoterekisteri, STTV ṡ Product Register of Chemicals |
| KETSU | Kemian työsuojeluneuvottelukunta (labour protection advisory board for chemicals) |
| $LD_{50}$ | Lethal consentration (kills 50 % of test animals) |
| LOAEL | Lowest-observed Adverse Effect Level |
| MTBE | methyl tertiary butyl ether |
| NIOSH | National Institution of Occupational Safety and Health |
| NOAEL | No-observed Adverse effect Level |
| OECD | Organisation for Economic Co-operation and Development |
| OEHHA | California Office of Environmental Health Hazard Assessment |
| OSHA | Occupational Safety and Health Administration |
| PBT | Persistent, Bioaccumulative and Toxic |
| PEC | Predicted Environmental Concentration |
| PNEC | Predicted No Effect Consentration |
| REACH | Registration, Evaluation and authorisation of Chemicals |
| RIP | REACH Implementation Project |
| RMM | Risk Managament Measures |
| SEG | Stakeholder Expert Group |
| SIEF | Substance Information Exchange Forum |
| SIDS | Screening Information Data Set |
| STEL | Short-term exposure limit |
| STTV | Sosiaali- ja terveydenhuollon tuotevalvontakeskus, The National Product Control Agency for Welfare and Health (STTV), which is now known as Valvira (National Supervisory Authority for Welfare and Health) |
| TAME | tertiary amyl methyl ether |
| TGD | Tecnical Quidance Document |
| TOL | Toimialaluokka, Finland's national Standard Industrial Classification |
| TLV | Treshold Limit Value |
| TWA | Time-weighted average |
| VOC | Volatile organic compounds |
| VTT | Valtion tekninen tutkimuskeskus, Technical Research Centre of Finland |

# 1 BACKGROUND

The EU's new Chemicals Decree REACH (Registration, Evaluation, Authorisation of Chemicals) 1907/2006 entered into force on 1 June 2007. The decree had an extensive effect on monitoring and assessment procedures for chemical agents. Substances imported to the EU area and manufactured inside the EU must be registered by the manufacturer or importer. In conjunction with registration, the essential information about the substance and its safe use are provided in the so-called Chemical Safety Report. This report assesses the risk posed by the substance to workers, consumers and the environment during production, downstream use and the entire life-cycle of the chemical. Possible exposure must be assessed in all exposure and use situations, and the user provided with safe risk management measures that either prevent exposure or reduce it to a safe level. Exposure assessments in different use situations are called exposure scenarios, and these are required in the safety report for dangerous substances imported or manufactured in quantities starting at 10 tonnes per year. The exposure assessment, which includes the compiling of exposure scenarios and an estimate of exposure, is part of the Chemical Safety Report. The Chemical Safety Report is submitted to the European Chemicals Agency in conjunction with registration of the substance. According to the REACH legislation, the Chemical Safety Report can be compiled by the manufacturer or importer of the substance, a Substance Information Exchange Forum (SIEF) or a consortium of these parties. External experts can be used when compiling the report. All substances manufactured or imported into the EU area in amounts starting at one ton must be registered. In order to take advantage of the so-called phase-in registration, a substance had to be pre-registered between 1 June 2008 and 1 December 2008. Phase-in registration must be registered within 11 years of the entry into force of REACH. The substances present in the largest amounts are registered first.

Implementation of REACH will require that the manufacturers and importers of substances provide extensive reports and assessments concerning the properties of the substances, their health and environmental impacts, exposure of workers and consumers, dispersion of the substances into the environments and the possibilities of human exposure via the environment as well as estimates of the risks that exposure situations can cause. The regulation also includes new obligations for downstream users.

Methanol was selected as the model substance for the development of exposure scenarios in this project. In the EU, methanol is classified as a toxic and flammable chemical. Methanol is extensively used in Finland, and the majority of the substance is imported from Russia. Because Russia is not a member of the EU, the importer is responsible for compiling the safety report. Methanol is not manufactured in Finland at this time. The companies, experts from FIOH and other organizations, and the authorities participated in compiling the exposure scenarios for methanol, which was the model substance in the project.

Although the chemical industry is important in Finland, it is a small player on a global and EU scale. This project was inspired by the idea that it would be beneficial for companies in the chemical industry to co-operate when developing and applying the measures required by REACH. Failure to prepare for the requirements of the new chemical legislation could make it difficult to maintain domestic chemical manufacturing and for small companies to continue their operations.

# 2 OBJECTIVES

The objective of the project was for Finnish chemical companies, experts and authorities to co-operate to develop exposure scenarios for different uses of methanol in Finland as required by the European Union's new REACH legislation, and thus practice using the methods needed to develop exposure scenarios so that they could be applied to other substances. The development of exposure scenarios requires diverse expertise and experience in the fields of chemistry, toxicology, eco-toxicology and environmental science and often the acquisition of new information (for example, exposure data). As the work progressed, it became apparent that the project would develop initial rather than final exposure scenarios. A consortium of companies that is registering methanol will eventually develop the final exposure scenarios for methanol. The project was intended to develop exposure scenarios, not to compile the Chemical Safety Report required to register methanol. Exposure scenarios are one part of the chemical safety report. An assessment of the health and environmental hazards of methanol was also performed while compiling the initial exposure scenarios. This provided preliminary DNEL and PNEC values for methanol.

The model substance used in the development process for initial exposure scenarios was methanol, which is a toxic solvent extensively used as a raw material and solvent in the chemical industry. Another aim of the project was to gather more exposure data about methanol. In addition to the working population, consumers are exposed to methanol. Exposure and the necessary risk management were assessed in the Finnish distribution chain and use situations. Initial exposure scenarios were drawn up for workers 'exposure when handling methanol and methanol products at the workplace and for consumer exposure when using windshield washer fluids containing methanol and methanol-based fuels. The environmental exposure of methanol was also examined by means of two initial exposure scenarios.

This project was also intended to address the process of compiling the exposure scenarios required by REACH and, because the instructions for this are still incomplete, to also develop methods for compiling exposure scenarios. The final report for this project has been written on basis of draft guidelines because the final guidelines were not complete when the report was being written. Exposure, risk assessment and management were described in initial exposure scenarios that complied with the October 2007 REACH draft guidance (RIP 3.2-2 SEG 5 06 cTGD-Part D Oct 2007).

Measurement was the primary means of assessing exposure, but the applicability of various chemical exposure models to describing initial exposure scenarios for methanol was also tested. Furthermore, the suitability of biomonitoring for describing exposure was examined in a few sectors, and new methanol air concentration measurements were also taken in these areas. Contrary to the project plan, biomonitoring was performed using two methods, but the analysis costs for the newer (U-methanol) method were not charged to the project.

The project also tested the functionality of the consortium idea and how it worked between several Finnish importers and users. In conjunction with this, all members of the management group signed confidentiality agreements.

The comparative exposure studies for ethanol- and isopropanol-based windshield washing fluids described in the project plan were also carried out, and this provided a comprehensive picture of the hazards associated with the use of such windshield washing fluids. This section was not specifically related to compiling the REACH exposure scenarios, and a more detailed report of the methanol–based and other comparative studies on windshield washing fluids is available in the interim project report published in December 2006.

The project plan included a symptom questionnaire for workers exposed to methanol, and some of these people also underwent methanol biomonitoring. Both the questionnaire and the biomonitoring section for the interviewees had to be left out because it was impossible to find a suitable target group. The target group would have been suitable for methanol, but not for a group of workers exposed to other chemicals.

# 3 SAFETY ASSESSMENT AND GENERATION OF EXPOSURE SCENARIOS ACCORDING TO THE REACH REGULATION

A chemical safety assessment is performed if more than 10 tons of a substance is manufactured or imported each year. A chemical safety assessment performed by a manufacturer or an importer for a substance must contain the parts specified in Appendix 1 of the Reach regulation:

1. Human health hazard assessment.
2. Human health hazard assessment of physicochemical properties.
3. Environmental hazard assessment.
4. PBT and vPvB assessment.

If as a result of steps 1-4 a manufacturer or an importer concludes that the substance or preparation meets the criteria for classification as dangerous or is assessed to be a PBT or vPvB, the chemical safety assessment shall also consider the following steps:

5. Exposure assessment
   - 5.1 The generation of exposure scenarios or the generation of relevant use or exposure categories if appropriate.
   - 5.2 Exposure estimation.
6. Risk characterisation

According to Annex 1 of the Reach regulation, an exposure scenario is the set of conditions that describe how the substance is manufactured or used during its life-cycle. It describes how the manufacturer or importer controls, or recommends downstream users to control, exposures of humans and the environment. These sets of conditions contain a description of both the risk management measures and operational conditions which the manufacturer or importer has implemented or recommends to be implemented by downstream users. If the substance is placed on the market, the relevant exposure scenarios, including the risk management measures and operational conditions, shall be included in an annex to the safety data sheet.

Annex 1 of the Reach regulation provides some freedom regarding the level of detail in the exposure scenarios. The content can vary from case to case depending on the use of the substance, its hazardous properties and the amount of information available to the manufacturer or importer. A single exposure scenario can also cover a large range of processes or uses, in which case it can be referred to as an exposure category.

The development of an exposure scenario is described in the June 2007 REACH draft guidance (RIP 3.2-2 A4. ES-TOOL VERSION 12 JUNE 2007) IT Tools for exposure scenarios. The instructions for developing an exposure scenario have five steps:

1. Identify, study and group the uses of the substance.

- in-house use at the corporate level

- own markets and customer's markets
- downstream uses in the supply chain (uses after the primary customer)
- assign an appropriate short title for the uses (according to the RIP guidance: sector of use, application, use and intended use of the object if appropriate)
-identify the most important routes of exposure and effects (endpoints)
-identify the current risk management measures

2. Develop one or several initial exposure scenarios for substance use in the most typical actual operational conditions. Collect information from inside the company, by asking customers or other sources, and from the information submitted by downstream users.
- do a brief process description and select an appropriate name for the use or process
- list the most important operational conditions and determine typical values for the variables for the modelling programs used to assess tier 1 exposure
- list the risk management measures used and their presumed efficiency
- justify the grouping of identified uses into categories
- justify the exclusion of certain routes of exposure or effects (endpoints)
- select a suitable exposure modelling tool for the most significant routes of exposure in tier 1 assessment

3. Determine exposure and risk, select an iteration strategy
-determine the exposure estimation and compare it to the PNEC and DNEL values
-decide how to proceed in order to reduce the risk to below the PNEC or DNEL values:
  - collect more information about use or exposure, or
  - modify the risk management measures or operational conditions, or
  - refine the hazard assessment, do more testing, or
  - do not support use of the application

4. Repeat the procedure in section 3 until the final scenario is ready

5. Report the exposure scenario in the chemical safety report and transfer the information to the safety data sheet.

The template presented in the RIP 3.2.2 October 2007 version of the guidance was used as the template for the exposure scenario in this report (RIP 3.2-2 SEG 5 06 cTGD-Part D Oct 2007).

According to REACH, exposure is first divided into work-related exposure, consumer exposure and environmental exposure. In addition, indirect human exposure via the environment should also be examined, which in this case has been done by collecting the existing information. If necessary, REACH also calls for the examination of secondary exposure through the food chain and exposure to substances released from articles.

### *3.1 ASSESSMENT OF WORK-RELATED EXPOSURE AND METHODS*

The October 2007 draft guidance (RIP 3.2-2 SEG 5 09a rTGD-Part D-Occupational Oct 2007) describes the background and methods for assessing exposure. The draft guidance specifies the assessment of exposure based on measurements as the primary method of evaluation. In this case, the personal exposure data or biomonitoring data must be of high quality, in other words, it should describe personal exposure, be properly collected and analysed using approved methods, and the variables with an essential impact on exposure must be appended to the data.

If measurement information is not available, deductions made using similar substances are proposed as a secondary method, but in this case it may be difficult to draw conclusions and additional information is required to ensure safe use, especially if the assessed concentration levels are close to the DNEL levels. Use of measurement information that is average in terms of quality is also proposed as a secondary method (for example, use of static sampling when assessing the exposure of a person).

An exposure assessment performed using suitable models is a third possible method. In this case, the source data must correspond to the uses presented in the scenario. Methods of this level also describe the use of data collected using measurements of poorer quality (such as that collected from static sampling and insufficient description of the conditions) or by drawing conclusions based on the use of data of average quality.

When the measurement information is not representative, an exposure assessment suitable for the purpose can be obtained by combining measurement data and modelling. Exposure data based on biological monitoring can be used to assess exposure just as well as other kinds of information, for example, exposure data based on air concentration measurements.

### 3.1.1 ROUTES OF EXPOSURE

Work-related exposure to a substance can occur through inhalation, skin or oral exposure. Exposure is often measured in terms of the external dose. The actual dose that is effective in the system is the absorbed dose. Exposure can occur as single, repetitive or continuous exposure. Assessment of exposure levels must also take into consideration the duration and repetitiveness of exposure as well as the number of people exposed. Substances that cause local effects must also be taken into account.

Inhalation exposure is reported as the concentration of the substance in the breathing zone atmosphere. All-day exposure is reported as the average concentration for eight hours. Exposure resulting from different phases of work during this time also has to be taken into consideration. Acute exposure also has to be assessed if the substance has acute effects or if the exposure time is short. Inhalation exposure can occur with gases, vapours and aerosols (liquid and solid).

Dermal exposure is described as potential or actual dermal exposure. Potential dermal exposure is an overall assessment of the amount of a substance that has fallen on the work clothing and various parts of the skin. Actual dermal exposure assesses the amount of contamination that has fallen on the skin. Dermal exposure is generally described as potential, or external, dermal exposure. Absorption through the skin can result from local contamination or dirty clothing or via the air if the substance has a high vapour concentration. Factors affecting dermal exposure are the concentration of the substance, surface area of the exposed skin, and the duration and frequency of exposure. There are three routes of dermal exposure: deposit, direct contact and contact with a contaminated surface.

There are no approved methods for describing exposure that occurs only by the oral route. Oral exposure can occur whenever there is exposure to aerosols. Contaminated protective clothing can also lead to oral exposure. Oral exposure is not taken into account at workplaces because eating is generally forbidden in work spaces and there are guidelines concerning washing of hands before eating. ConsExpo modelling can be used to assess oral exposure if necessary. Biological monitoring can also be helpful, because in theory it describes the total dose for all exposure routes.

### 3.1.2 REQUIRED EXPOSURE DATA

Work-related exposure depends on the properties of the substance or product, the process, work method, conditions and risk management measures used. In order to conduct a proper exposure assessment, the following basic information is always needed in tier 1 assessment:

- where the product is used (a description of the work, process and product)
- composition of the compounds, preparations and products (% amounts)
- how the substance or product is used (phases of exposure and amounts used)
- amount of the substance in the process components and the end product
- state of the substance when used (powder, pellet, solvent, etc.)
- number of workers exposed
- operating conditions (work description, frequency of use, duration of use, duration and frequency of exposure
- the technical or personal risk management measures that are used and what should be used during the exposing phases of work
- information about the suitability of personal protective equipment and proof that personal protective measures are only used as the last possible risk management measure as well as recommendations for the correct use of personal protective equipment

The sources of this information must also be reported. Risk management measures aimed at downstream users must be practical and properly dimensioned in relation to the risk.

### 3.1.3 EXPOSURE ASSESSMENT BASED ON MEASUREMENTS

Assessment of human exposure must be based on scientific assessment in accordance with the October 2007 draft guidance (RIP 3.2-2 SEG 5 09a rTGD-Part D-Occupational Oct 2007). The worst possible situation and a typical exposure situation must be examined by scenario. Accident situations are not taken into account. Exposure is understood to be external and is reported in units of external exposure. Suitable measurement information includes data collected from databases, occupational hygiene measurements or material about the substance collected by the manufacturer, importer, distributor or an organization. Measurement information from specific uses included in the scenario is often needed when developing the final exposure scenario. The Guidance Document also contains more detailed background information and instructions concerning measurement and reporting. A recommendation concerning the minimum number of samples has been made: 12 samples per company for air concentration samples and 12-20 samples for biological samples.

#### 3.1.3.1 Air concentration measurements made in the project

In this project, exposure assessment for inhalation exposure was based on existing and new measurement data in all exposure and use scenarios. The existing measurement data consisted of 475 measurements from 31 applications (from 21 sectors of use and from 56 companies). A total of 184 new air methanol measurements were taken in 14 different main applications (including two consumer applications).

A pump (Model SKC 222-3) was used to collect the air samples for methanol determination from the worker's breathing zone atmosphere into silica gel sorbent tubes (SKC ST 226-10-03) at a rate of 50 ml/min. When studying substitutes for windshield washing fluids containing methanol, the other solvents were collected from the air into Anasorb carbon sorbent tubes (SKC 226-83). The methanol was extracted from the adsorbent with dimethyl formamide and the other solvents with a mixture of dimethyl formamide and carbon bisulphide (60/40). The samples were analysed using a gas chromatograph equipped with a flame ionisation detector. The compounds were separated using two different columns. The concentrations of the compounds were specified from the samples using clean reference substances (the analysis method used was FIOH's internal UUTYO-003 method and applicable parts of OSHA Method 91).

#### 3.1.3.2 Biomonitoring performed in the project

Biomonitoring samples were taken from four applications in the project: methanol-based fuels (drag racing use and speedway drivers), production of windshield washing fluids, pharmaceutical solvent, and laboratory use (mass spectrometers, chromosome laboratory work, HPLC work). Air samples were also taken for these applications. Biomonitoring samples were taken from 28 people.

In this study, worker exposure to methanol was evaluated by measuring the concentration of methanol and formic acid, which is the metabolic product of methanol responsible for its adverse effects, in the workers' urine. The methanol samples from urine (U-MeOH) were taken before exposure and immediately after exposure because methanol is rapidly eliminated from the system. The concentration of formic acid (U-Form) in the urine was measured before exposure and the morning following exposure because formic acid is eliminated from the system slowly and maximum excretion occurs at that time. The methanol samples from urine were gas chromatographically analysed from a head-space specimen using a mass selective detector (Accorsi, Barbieri et al. 2001). The formic acid samples were gas chromatographically analysed with an electron capture detector (Liesivuori 1986).

### 3.1.4 EXPOSURE ASSESSMENT BY MODELLING

Models for evaluating chemical exposure, which are often presented as computer applications, were in a phase of strong development as the REACH registration times drew nearer. Many model developers had announced that revised versions would be available by the end of 2008.

The REACH draft implementation guidance from October 2007 (RIP 3.2-2 SEG 5 09a rTGD-Part D-Occupational Oct 2007) recommends that work-related exposure be assessed using the ECETOC TRA model and the British COSSH method or the German Easy-to-use workplace control scheme for hazardous substances program, which is based on the British COSHH Essentials program. The programs are available online at:
https://www.ecetoc-tra.org/public/login/index.asp
http://www.coshh-essentials.org.uk/
http://www.baua.de/nn_37642/sid_EEFC07D867E24D8EFD899D42BE191020/nsc_true/en/Topics-from-A-to-Z/Hazardous-Substances/workplace-control-scheme.pdf.
The tier 1 source data required in the models is also listed on page 11 in section D of the cTGD from October 2007 (RIP 3.2-2 SEG 5 06 cTGD-Part D Oct 2007).

The ECETOC TRA (Targeted Risk Assessment) program is particularly recommended for describing inhalation exposure. This program also assesses dermal exposure, but the model is not as well suited for this kind of modelling, particularly if local exhaust ventilation is used. The program takes a tiered approach to exposure assessment, using the default values for use scenarios entered into the program to provide values for both work-related and consumer exposure. The program calculations are based on the EASE model. At this time, use of the paper version of the program is recommended because the current online version does not fully correspond to the actual program.

The online version of the ECETOC TRA program is presently under revision. The model was tested for several scenarios in the project, and the modelling results are presented in the report under each initial scenario.

Both COSHH and the Easy-to-use program are based on three variables (volatility or dustiness of the substance, amount of the substance or product used and the risk management measures utilised). The Easy-to-use model is only suitable for describing inhalation exposure. The online versions of the program do not provide quantitative exposure assessments yet, which means that they cannot be used as such in REACH-compliant exposure assessments.

In this project, dermal exposure is also described using a program developed in the Riskofderm project: Toolkit for Assessment and Management of Risks from Occupational Dermal Exposure to Hazardous Substances (http://www.eurofins.com/research-development/occupational_hygiene/riskofderm.asp). This program was used to model exposure during the mixing stage of windshield washing fluids containing methanol. The selected risk management measures (including reducing the concentration of the substance or reducing the exposure time but not the use of personal protective equipment) helped to lower the exposure level. The program recommended the replacement of methanol whenever possible. Rather than providing concentration levels, the Riskofderm program version currently available online provides an evaluation of the health hazard caused by use of the substance, which means that it is not yet suitable for use in developing exposure scenarios. A program version that provides concentration levels is currently being tested.

The SK2 program developed by FIOH and based on safety data sheet information was tested in the assessment of windshield washing fluids, where the risk of exposure could not be reduced to a tolerable level without replacing methanol with some other substance. The program does not take the amount of the substance used or the exposure time into consideration. This program does not provide concentration levels either; instead it only evaluates the health hazard level caused by use.

The other models mentioned in the October 2007 draft guidance (RIP 3.2-2 SEG 5 09a rTGD-Part D-Occupational Oct 2007) that are currently under development are the Stoffenmanager exposure model, which can be used to describe the initial phase of inhalation exposure assessment, the new version of the EASE model, and the Riskofderm version that describes dermal exposure, which can provide concentration levels.

In the long term, the EU is aiming to develop the modelling methods into a single tool that is generally suitable making initial exposure assessments. The short-term plan is to improve ECETOC TRA, which is recommended for assessing worker and consumer exposure.

### *3.2 METHODS FOR ASSESSING CONSUMER EXPOSURE*

Consumer exposure occurs via inhalation, the skin and/or orally. Volatile compounds mainly cause inhalation exposure while non-volatile substances are more likely to enter the system through the mouth or skin. Consumers are simultaneously exposed through several sources and it is common for exposure commonly to also occur after using the actual product. Consumer exposure can consist of a single or many different exposure situations and the frequency of exposure may vary a lot. Exposure that lasts less than one day is considered to be acute consumer exposure. Acceptable risk management measures in a consumer product are primarily measures taken by the manufacturer concerning the composition of the product (such as the percentage of the substance in the product, package size).

The October 2007 draft guidance (RIP 3.2-2 SEG 5 06 cTGD-Part D Oct 2007) recommends that modelling be done using the EUSES program or ConsExpo 4.1. The instructions also list the tier 1 source data required in the models. When using ConsExpo for inhalation exposure, direct evaporation should be selected and the ventilation rate must be zero. The document states that for dermal exposure instant application, in which case the product is applied to the skin all at one time, or migration, in which the substance migrates from material in contact with the skin should be selected. In this project, air measurements were used to assess consumer exposure in two applications. The dilution phase of consumer windshield washing fluids was modelled with ConsExpo and the EUSES program in section 8.1.

### *3.3 METHODS FOR ASSESSING ENVIRONMENTAL EXPOSURE*

Environmental exposure is based on an emissions assessment and an assessment of partitioning. According to RIP 3.2-2, the assessment should be performed using the EUSES and TDG Exel programs. In contrast to EUSES, which utilises default values, the TDG Exel program requires emissions data. The EUSES program is very extensive in nature and its use requires a good knowledge of the program. The tier 1 source data required in the EUSES model is also listed on page 12 in section D of the cTGD (RIP 3.2-2 SEG 5 06 cTGD-Part D Oct 2007).

Based on the input data provided, the EUSES model calculates the predicted environmental concentration (PEC) for the chemical emission in different environments, which are soil, fresh water, salt water, ground water, sediment and air. These PEC values can further lead to the exposure amounts for organisms in different parts of the environment. Based on the results of toxicity tests and assessment factors, the model also assesses the harmless concentrations of the chemical in different parts of the environment (PNEC, Predicted No-Effect Concentration), in which case no adverse effects are expected to occur. The input data required by the model includes information about the chemical being assessed, its use and the model environment. The program includes a lot of default values concerning environmental conditions, waste water treatment plants, number of inhabitants in an area, etc. (Koskela, Seppälä et al. 2006).

In the project, environmental exposure assessment was performed with the EUSES program in two scenarios, which were methanol use as an auxiliary substance in waste water treatment and use in windshield washing fluids.

### *3.4 INDIRECT HUMAN EXPOSURE VIA THE ENVIRONMENT*

This project uses data from the WHO summary report (WHO 1997) as the values for indirect human exposure. According to these values, background methanol concentrations in the air range between 3-60 µg/m$^3$ in towns and outside them. Methanol also comes from foodstuffs. Methanol values ranging between 1-140 mg/l have been measured in both fresh and canned fruit juices. Methanol levels in beer have been measured at 6-27 mg/l, in wines at 96-321 mg/l and in distilled alcohol at 10-220 mg/l. The methanol in distilled alcohol comes from pectin in the raw material, which is broken down by the pectin methylase enzyme during the process. The highest permitted concentration of methanol in grape wines (brand) in the USA, Canada and Italy is 6-7 g/ethanol litre. Methanol in dried legumes was analyzed at 1.5-7.9 mg/kg. Methanol was also found in the steam from several cooked foods. Aspartame is hydrolysed into methanol in the digestive tract. Soft drinks containing aspartame have approximately 555 mg of aspartame per litre, which corresponds to about 56 mg of methanol per litre, which means that about 10% of the aspartame is converted into methanol in the digestive tract. Methanol, acetone and formaldehyde metabolise into formic acid in the system. According to WHO, the normal background concentration of formic acid in the blood is 0.07-0.4 mM. Tobacco smoke studies show that methanol content in tobacco is 180 µg per cigarette.

# 4 METHANOL APPLICATIONS

## *4.1 USE OF METHANOL IN FINLAND*

Any registrant of a dangerous substance must submit a REACH-compliant description for every application being registered. A Chemical Safety Report and exposure scenarios are made for the identified uses of a dangerous substance if the amount of the substance being manufactured or imported exceeds 10 tons per year. The registrants generally know the applications and amounts at the beginning of the use chain and the necessary risk management measures. Such information can be considered to be within the scope of a trade secret. The form presented in Appendix 2 was used to collect information from the project's target companies, where we took exposure measurements and made assessments. The level of the information obtained varied. For the most part, the information was sufficient to develop a initial exposure scenario for occupational exposure in a single use. Less information was received about environmental emissions or environmental exposure.

General sources of information were also used to find applications and assess the quantity of the substances used. These included the Tullihallituksen tilastopalvelu (Finnish Customs' Statistics Service) and information and statistics from STTV's Product Register of Chemicals (STTV is now known as Valvira). In this project, the indicative data concerning the amounts used in different applications is mainly based on information from the Product Register of Chemicals. The list of applications and the exposure information for the applications measured are based on the Finnish Database of Occupational Exposure Measurements (FDEOM) and measurement reports carried out by FIOH at the request of companies.. The applications are also outlined on the basis of a book published by the Chemical Industry Federation of Finland (Riistama, Laitinen et al. 2005).

It is possible that registrants may not have possession of all the information about downstream or end user applications for their substance. The REACH legislation states that downstream users are obliged to pass on information about their use to the registrant at least 12 months before the registration of the substance concerned ends in order that it can be taken into consideration during registration (REACH Regulation, Article 37). According to the REACH principles, information should be passed down the supply chain from the registrant to the downstream and end user and back up the chain from the end user to the registrant. If the downstream user's use is not included in the exposure scenario or the conditions of use for the substance differ from those proposed, the downstream user can prepare a chemical safety report for that use if he wants to continue using the substance in the same manner. Users at the lower end of the supply chain should also check with the manufacturer, importer or distributor to ensure that the information about use has been identified.

Tullihallituksen tilastopalvelu(Finnish Customs' Statistics Service) provided information about the amounts of methanol imported in 1990, 1995 and 2001 - 2006 (Tullihallituksen tilastopalvelu 2006; Tullihallituksen tilastopalvelu 2007). The importing of methanol was mainly divided into two groups: 2905110, also known as methyl alcohol, and 38070090, also known as brewer's pitch, and similar preparations based on rosin, resin acids or vegetable pitch (wood tar oils, wood creosote, wood naptha, but excluding wood tar). Furthermore, methanol in group 38159010 (catalysts comprising a methanol solvent of ethyl phosphonium acetate) is imported in certain years. Table 1 presents the import statistics according to the two main groups. The share of the main import country Russia is presented separately.

Table 1. Amounts of methanol imported in 1990, 1995 and 2001-2006 for the two main groups (Tullihallituksen tilastopalvelu 2006; Tullihallituksen tilastopalvelu 2007).

| Year | Methanol 29051100 all countries, 1,000 kg | Methanol 29051100 Russia 1,000 kg | CN 38070090 all countries 1,000 kg | Total imported methanol 1,000 kg |
|---|---|---|---|---|
| 1990 | 83648 | 45545 | 28 | 83676 |
| 1995 | 97269 | 95113 | 133 | 97402 |
| 2000 | 127492 | 108916 | 40 | 127532 |
| 2001 | 126447 | 126343 | 108 | 126555 |
| 2002 | 204313 | 204282 | 1468 | 205781 |
| 2003 | 148027 | 147981 | 6501 | 154528 |
| 2004 | 142244 | 142196 | 6238 | 148482 |
| 2005 | 153306 | 153224 | 4137 | 157443 |
| 2006 | 478090 | 477961 | 10330 | 488420 |

There has been a clear increase in the amounts of methanol imported since 2000. The amounts imported in 2004-2005 averaged 150,000 tons per year. In 2006, methanol imports from Russia increased, and export statistics show that some of this increase may be due to the fact that methanol imported into Finland would probably have continued on to other EU countries (Tullihallituksen tilastopalvelu 2007).

The National Product Control Agency for Welfare and Health (STTV), which is now known as Valvira (National Supervisory Authority for Welfare and Health) maintains the Product Register of Chemicals (KETU), which includes information about chemicals available on the Finnish market. The information is based on the chemicals data submitted by manufacturers and importers. The Product Register contains information about more than 100,000 chemical products. Nearly 30,000 of these are currently on the market. The KETU register is used by authorities and research institutes, and FIOH uses the database via TietoEnator's ePortti. Although the amount of a single preparation that is produced or imported annually is not public information, the aggregate amounts of substances contained in the preparations are available to the public. However, if a substance is only contained in three or less preparations, the amount of the substance is not public information (STTV 2004).

According to the Product Register, methanol is one of the 20 most used substances in Finland (Top 20 substances) as measured by tonnage. For the most part, the most common substances with a concentration of 90% or more in a preparation by tonnage are the same as the Top 20 substances (STTV 2004).

The manufacturer or importer reports the amounts of the preparation used annually to the KETU register. The concentration of the substance can be reported as a concentration range and the classification provided can also be used in this case. Approximately half of the companies provide exact amounts. Thus, the figures in the KETU register are not precise but provide a general picture of quantity. Methanol amounts classified according to use (table 3) or standard industrial classification (TOL) (table 4) are available as a statistics service. If several TOL categories or uses are reported for a product, a total is recorded for all of these, which can skew the information about amounts. However, the register also provides more accurate information about amounts for all products containing methanol, and this is presented in table 2.

Table 2. Information on amounts as reported to the KETU register for all products containing methanol in 2001-2006. Product refers to a manufactured or imported product (STTV 2007).

| Year | Number of products | Product t | Methanol in the products t |
|---|---|---|---|
| 2001 | 362 | 4765898 | 539873 |
| 2002 | 371 | 417759 | 153370 |
| 2003 | 382 | 569313 | 145629 |
| 2004 | 402 | 575139 | 125148 |
| 2005 | 399 | 561647 | 116441 |
| 2006 | 468 | 614698 | 125819 |

Table 3. Information on amounts as reported to the KETU register for products containing methanol and the amounts of methanol in products classified according to application in 2006. Product refers to a manufactured or imported product (STTV 2007).

| Intended use | 2006 Number of products | 2006 Product t | 2006 Methanol in the products t | Average methanol concentration in the products % |
|---|---|---|---|---|
| KETU register information 2006 | 468 | 614698 | 125819 | |
| totals for information below | 445+(at least 17) | 754124 | 206933 | |
| 48 Solvents | 28 | 82098 | 81669 | 100 |
| 55 Other chemicals | 71 | 69279 | 58239 | 84 |
| 5 Antifreeze substances | 4 | 50011 | 50010 | 100 |
| 2 Adhesives and binding agents | 136 | 252180 | 5802 | 2 |
| 27 Fuels | 7 | 5096 | 4230 | 83 |
| 9 Cleaning and washing agents | 56 | 3780 | 1761 | 47 |
| 28 Fuel additives | 7 | 167010 | 1680 | 1 |
| 39.1 Disinfectants and general biocide preparations | 10 | 62600 | 1424 | 2 |
| 39 Biocide preparations | 10 | 60121 | 1201 | 2 |
| 43 Process regulators | 5 | 1005 | 698 | 69 |
| 10 Dyes | 8 | 401 | 153 | 38 |
| 34 Laboratory chemicals | 37 | 234 | 57 | 24 |
| 17 Electric galvanisation substances | 5 | 10 | 5 | 50 |
| 39.4 Other biocide preparations | 4 | 187 | 2 | 1 |
| 59 Paints, coatings and varnishes | 16 | 30 | 1 | 3 |
| 14 Corrosion inhibitors | 14 | 62 | 1 | 2 |
| 61 Surface treatment agents | 13 | 8 | 0 | 0 |
| 35 Lubricants and additives | 7 | 12 | 0 | 0 |
| 39.2 Preservatives | 7 | 0 | 0 | 0 |
| 17 other applications with <4 products | | | | |
| 36 applications in total | | | | |

Table 4. Information on amounts as reported to the KETU register for products containing methanol and the amounts of methanol in products classified according to industry category in 2006. Product refers to a manufactured or imported product (STTV 2007).

| TOL | Industry<br>- and the applications for the products used | Number of products | Products t | Methanol t |
|---|---|---|---|---|
| | KETU register information 2006 | 468 | 614698 | 125819 |
| | Total for items below | | | 173211 |
| D | Manufacturing<br>- Nearly half of methanol from solvent use | 10 | 25 | 1 |
| 17 | Manufacture of textiles<br>- incl. fuel additives, binding agents, impregnating agents | 10 | 22 | 10 |
| 202 | Manufacture of plywood and other wood panels<br>- glue and binding agents | 51 | 177820 | 3963 |
| 203 | Manufacture of builders 'carpentry and joinery<br>- glue and binding agents | 9 | 2410 | 17 |
| 21 | Manufacture of pulp, paper and paper products<br>- 4 other chemicals, remainder are biocide preparations, preservatives and glue and binding agents | 10 | 759 | 8 |
| 211 | Manufacture of pulp, paper and paperboard<br>- incl. biocides, disinfectants and preservatives, glue and binding agents, reducing agents | 23 | 9300 | 26 |
| 212 | Manufacture of articles of paper and paperboard, other chemicals<br>- glue and binding agents | 34 | 27260 | 1542 |
| 232 | Manufacture of refined petroleum products (information from 2004)<br>- fuels, fuel additives and other chemicals | 4 | 166000 | 30370 |
| 24 | Manufacture of chemicals, chemical products and man-made fibres<br>- nearly all methanol used as solvents | 14 | 93815 | 32205 |
| 244 | Manufacture of medicinal chemicals and pharmaceutical products<br>- disinfectants and biocide preparations, pharmaceuticals and their raw materials, reducing agents and other chemicals | 6 | 1606 | 86 |
| 245 | Manufacture of washing agents, cosmetic and toilet products<br>- perfumes, cleaning and washing agents and other chemicals | 6 | 663 | 375 |
| 243 | Manufacture of paints and printing ink | 5 | 121 | 75 |
| 246 | Manufacture of other chemical products, group 1<br>- glue and binding agents, fluidiser agents in casting and soldering, laboratory chemicals, solvents, surface-active agents and other chemicals | 19 | 60730 | 51740 |
| 246 | Manufacture of other chemical products, group 2<br>- Dyes, fuel additives, laboratory chemicals, disinfectants and biocide preparations, photographic chemicals, stabilisers, antifreeze agents, cleaning and washing agents, glues and binding agents, fuels, reprographic agents, solvents | 34 | 112675 | 51768 |
| 268 | Manufacture of other non-metallic mineral products | 5 | 29157 | 146 |
| 275 | Casting of metals<br>- methanol mainly from glues and binding agents | 7 | 2210 | 15 |
| 28 | Manufacture of fabricated metal products | 7 | 314 | 9 |
| 285 | Treatment and coating of metals<br>- electric galvanisation agents, glues and binding agents, paints, coatings and varnishes, surface treatment agents and other chemicals | 11 | 20 | 6 |
| 321 | Manufacture of electronic valves and tubes and other electronic components<br>- dyes, corrosion inhibitors, electric galvanisation agents, surface treatment agents and other chemicals | 8 | 100 | 15 |
| 341 | Manufacture of motor vehicles<br>- incl. corrosion inhibitors, solvents | 5 | 30 | 1 |
| 50 | Sales, maintenance and repair of motor vehicles<br>- the majority of methanol comes from cleaning and washing agents | 12 | 232 | 128 |
| 502 | Maintenance and repair of motor vehicles<br>- the majority of methanol comes from cleaning and washing agents | 36 | 760 | 375 |
| 503 | Sale of motor vehicle parts and accessories<br>- cleaning and washing agents | 5 | 322 | 114 |
| 516 | Wholesale of machinery, equipment and supplies<br>- methanol from solvents, some from dyes and cleaning and washing agents | 8 | 13 | 6 |
| 73 | Research and development<br>- laboratory chemicals | 17 | 47 | 41 |
| 851 | Human health activities where methanol comes from laboratory chemicals, some from cleaning and washing agents or other chemicals | 13 | 114 | 14 |
| 99 | Industry unknown | 23 | 568 | 155 |
| | 27 industries are listed above, and approximately 40 other industries exist | | | |

Table 4 above shows the industries using the largest amounts of methanol in Finland. Methanol can be in the statistics several times, first as a raw material used industrially and then in the finished product. On the other hand, in comparison to the Finnish Customs 'statistics, the reporting limits for the KETU register cause some deviation with regard to the information on amounts. Classification according to TOL can also be somewhat misleading, because many companies report the company's industry as the TOL rather than reporting where the product is used. However, the table does provide the order of magnitudes, and these numbers can be used to compare different applications. The following information on amounts was selected from the table:

- Manufacturing of chemical products (TOL 246 1 and 2) and oil products (TOL 232) approximately 130,000 tons
- Solvent use approximately 30,000 tons (TOL 24)
- Pharmaceutical industry use approximately 90 tons (TOL 244)
- Laboratory use approximately 50 tons (TOL 73 and 851)

A search of the updated KETU register using ePortti (April 2007) found 522 preparations in use that contained methanol. One hundred of these products were glues or binding agents, 40 were biocide preparations, 9 were inkjet toners and 28 preparations were paints or paint removal products.

Safety data sheets for windshield washing fluids on the market were collected in the project. A total of 48 different windshield washing fluid products containing methanol were on the market in spring 2006. The amounts used of the windshield washing fluids on the market that were reported to the KETU register were obtained as a separate service. The register contained information about 36 products in September 2006. A total of 3,534 tons of these windshield washing fluids containing methanol were used, for a total of 1,620 tons of methanol. In table 4 above, windshield washing fluids are probably placed in different industry categories (for example, 50, 502), and this classification makes it impossible to get an accurate picture of the total amount in use. According to table 3, 56 washing and cleaning agents were reported to the register in 2006 and the total amount of use for the products was 3,780 tons, which in turn contained 1,761 tons of methanol. In April 2007, the DETU register most likely contained all (48) of the windshield washing fluids containing methanol that were on the market.

### 4.1.1 METHANOL AS A RESIDUE OF FORMALDEHYDE

Table 3 shows that although adhesives and binding agents are the most used (136 products) and the annual amount of use is nearly 250,000 tons, the amount of methanol contained in the products is only about 6,000 tons per year. The methanol in glues and binding agents (resins) comes from formaldehyde, which is used in the production of resins. These adhesives and binding agents are used in many different industries. Such industries in the KETU register include:

- manufacturing of plywood and wood panels and manufacturing of builders 'carpentry and joinery
- manufacture of wood and wood products and manufacture of furniture
- construction finishing work
- manufacture of pulp, paper and paperboard
- casting of metal and treatment and coating of metals
- manufacture of chemical products
- maintenance and repair of motor vehicles and sales of motor vehicles
- manufacture of motor vehicles and trailers and service centre activities
- manufacture of other non-metallic mineral products (for example, mineral and glass fibre)
- manufacture of textile products
- manufacture of rubber and plastic products

Furthermore, formaldehyde is used in the manufacturing of other products. This methanol should be taken into consideration in methanol registration if the methanol contained in the product exceeds the 1% preparation limit. Possible applications for formaldehyde are outlined in tree diagram 2a (section 4.1.2).

### 4.1.2 FINNISH DATABASE OF OCCUPATIONAL EXPOSURE MEASUREMENTS (FDOEM), APPLICATIONS AND OCCURRENCES OF METHANOL AND TREE DIAGRAM

The Finnish Database of Occupational Exposure Measurements (FDIEM) contains air impurity results from the past 50 years. The measurement register information from 1994-2003 (Heikkilä and Saalo 2005) and more recent information from measurement reports carried out by FIOH’s at the request of companies were used to assist in mapping the applications and occurrences of methanol and in assessing exposure levels. On the basis of this information, data collected during the project and literature (Riistama, Laitinen et al. 2005), tables for applications and occurrences of methanol were compiled (Appendices 1a-1d). The exposure levels were separately assessed in each category (section 8).

A total of 55 work-related methanol exposure applications and occurrences were found. Earlier measurement information from FIOH or the companies showed 31 applications or occurrences. A total of 12 new investigations concerning work-related use and 2 concerning consumer use were conducted during the project. Seven consumer applications were found. Additional investigations were performed in four old work-related applications in which there was little FIOH measurement data. Furthermore, 17 methanol applications and occurrences for which there was no exposure measurement data were added to tables 1a-1d. Only those uses for which methanol is actually sold, including the loading and unloading of methanol, were included in the methanol exposure scenarios. This comprised a total of 33 applications. Exposure scenarios were not created for the use of products containing methanol, because there was little information about these applications. According to FIOH’s old measurement results, methanol occurs in conjunction with the use of resin, for example, in the production of plywood, chipboard, fibreboard and wood panels as well as in the coating industry and in foundries. Concentrations of methanol in the air during glue spreading work have been as high as 80 $mg/m^3$. Significant methanol levels also occurred at coating plants and foundries. Use of methanol as a solvent can also be included in methanol measurements in glue spreading work and at coating plants and foundries.

The tree diagrams presented below (images 1-9) illustrate the utilisation chain and registration obligations for methanol. The tree diagrams present all the utilisation chains for methanol on the basis of the information collected. According to REACH, the registering body must describe the utilisation chain for its product, not the whole market situation (unless the case involves a consortium of all manufacturers or importers). The diagrams also include several other substances that must be registered, such as chlorine dioxide, potassium methylate and sodium methylate, trimethyl borate and MTBE. Biodiesel may be exempted from registration, because the valid list of substances exempted from registration (Appendix IV of the REACH regulation) currently includes coconut, tallow and unsaturated fatty acid (C16-18 and C18) methyl esters (Luhtanen 2007). Even if methanol does occur in the utilisation chain of other substances requiring registration, according to the REACH regulation, exposure to methanol should be described throughout the utilisation chain in methanol exposure scenarios, although this has not been done in this project.

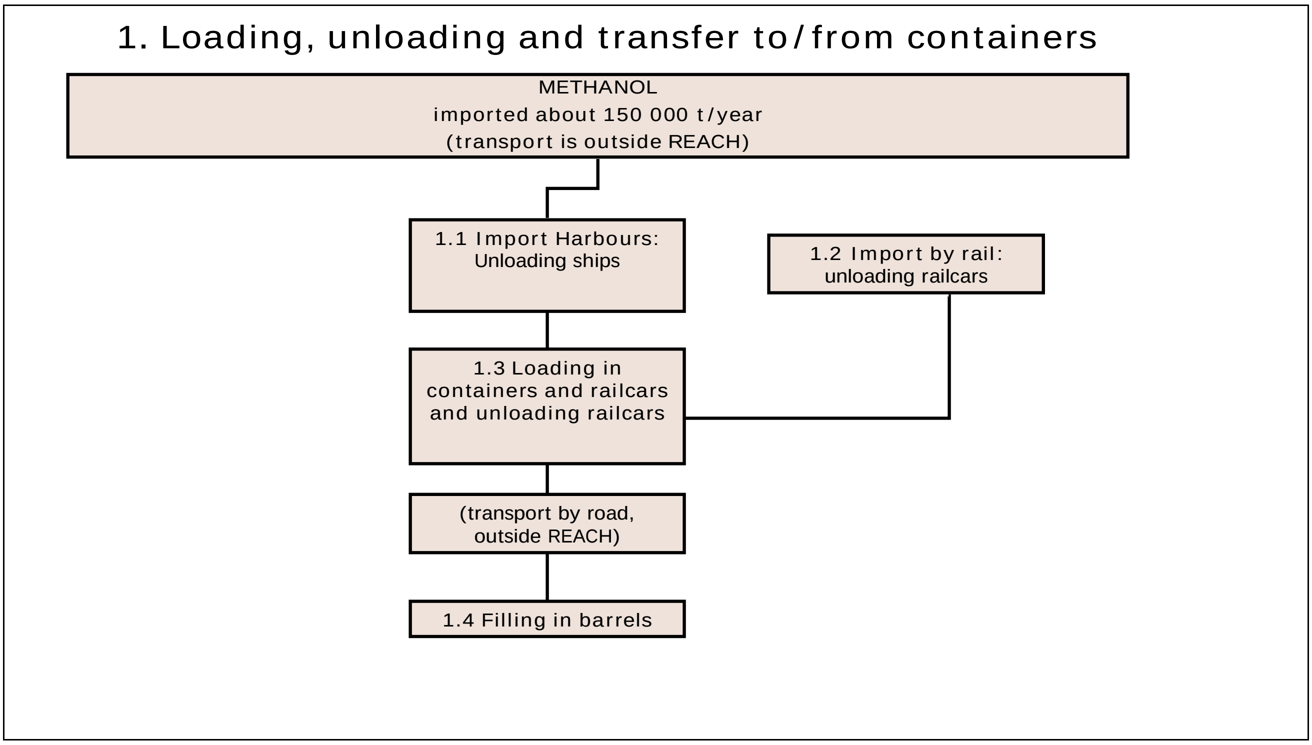


Figure 1. Tree diagram of hierarchy of uses: loading, unloading and transfer to/from containers.

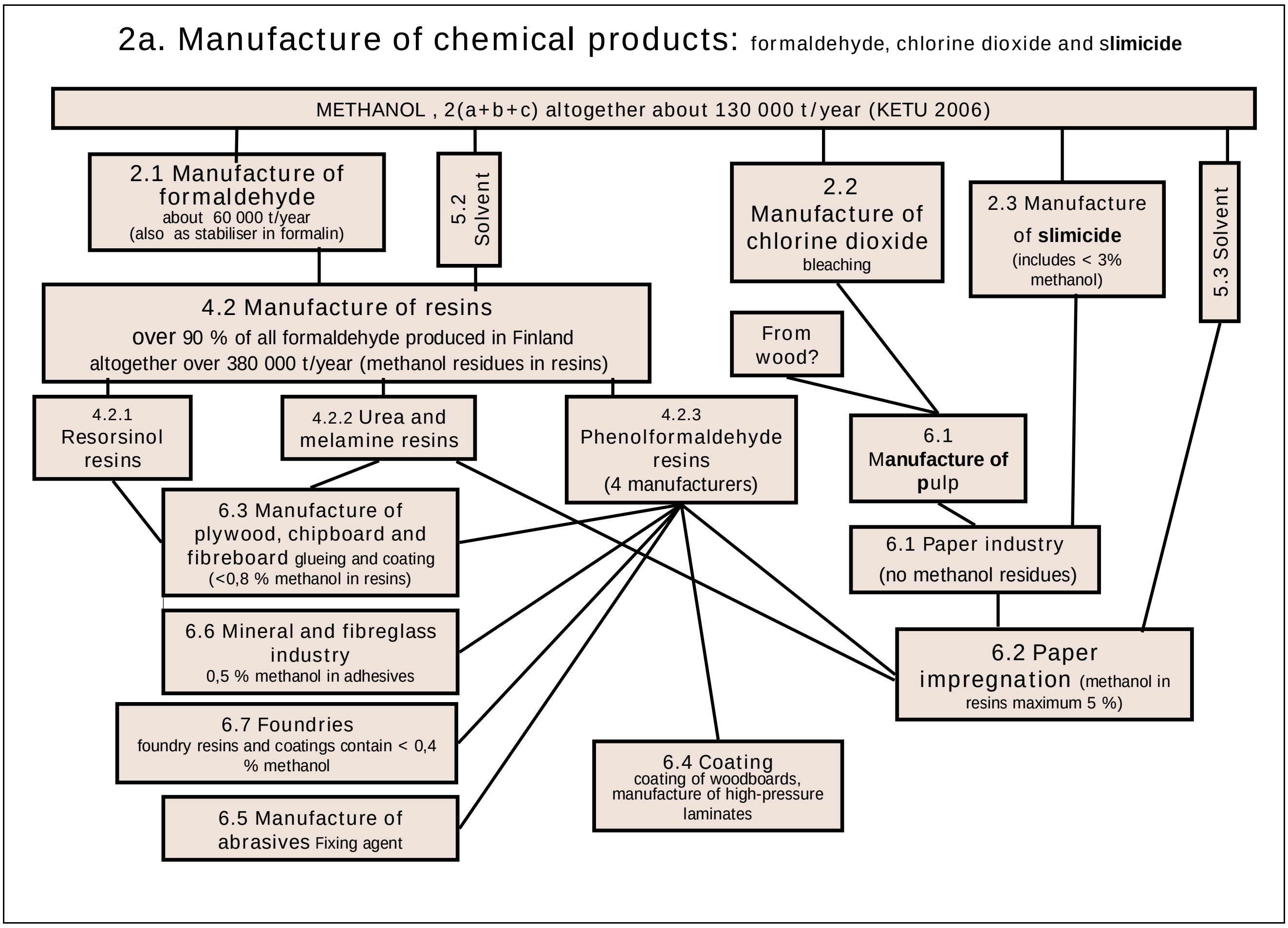


Figure 2a. Tree diagram of hierarchy of uses: manufacture of chemical products (formaldehyde, chlorine dioxide and slimicide) and use of methanol as a solvent.

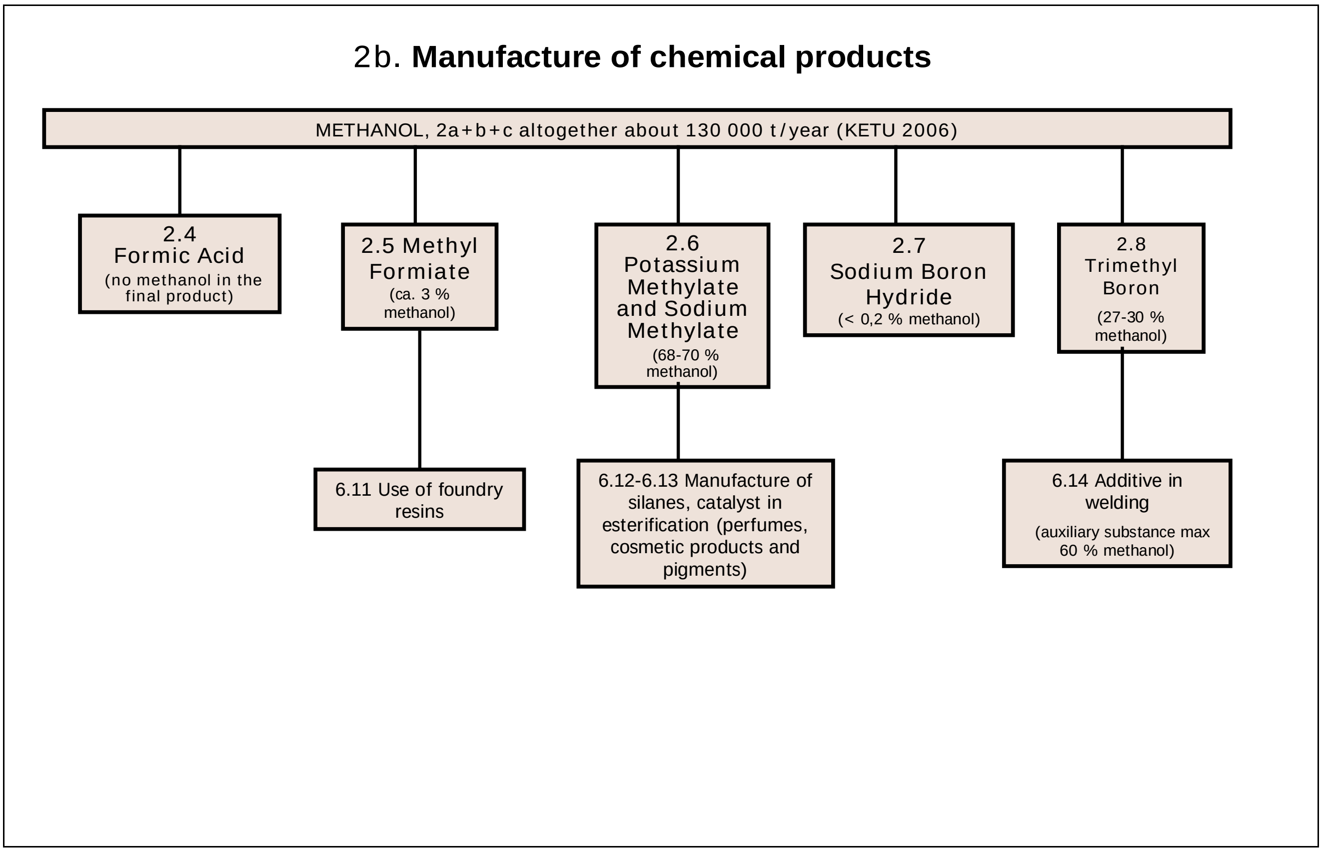


Figure 2b. Tree diagram of hierarchy of uses: manufacture of chemical products (formic acid, methyl formiate, potassium methylate and sodium methylate, sodium boron hydride, trimethyl boron).

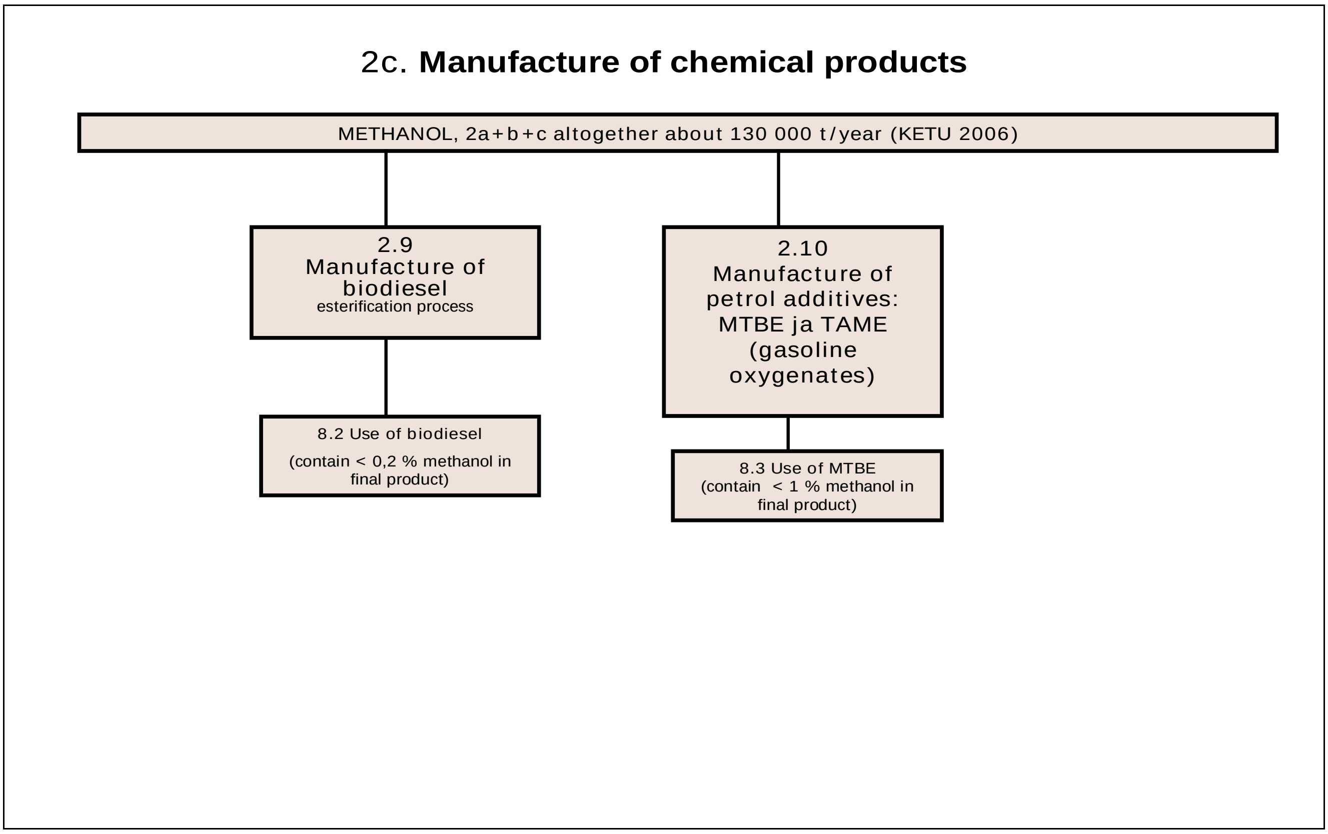


Figure 2c. Tree diagram of hierarchy of uses: manufacture of chemical products (biodiesel and petrol additives MTBE and TAME).

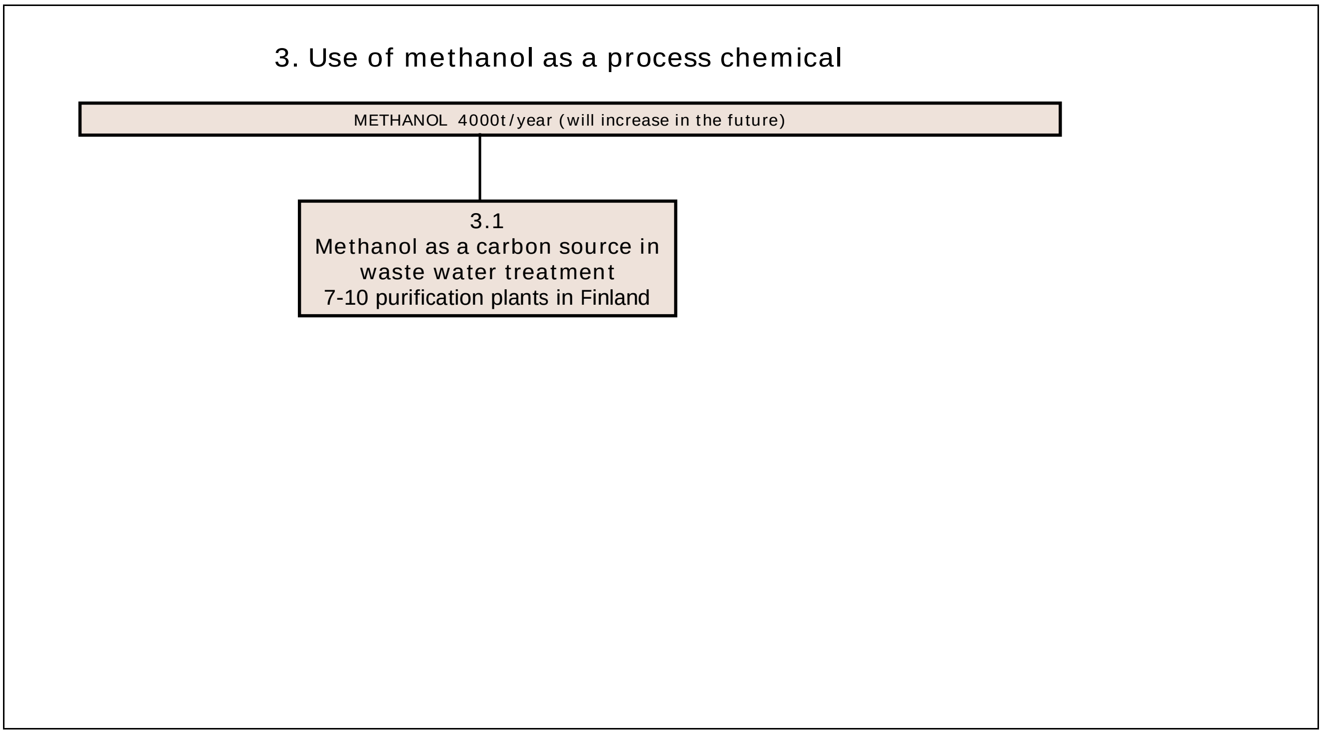


Figure 3. Tree diagram of hierarchy of uses: use of methanol as a process chemical

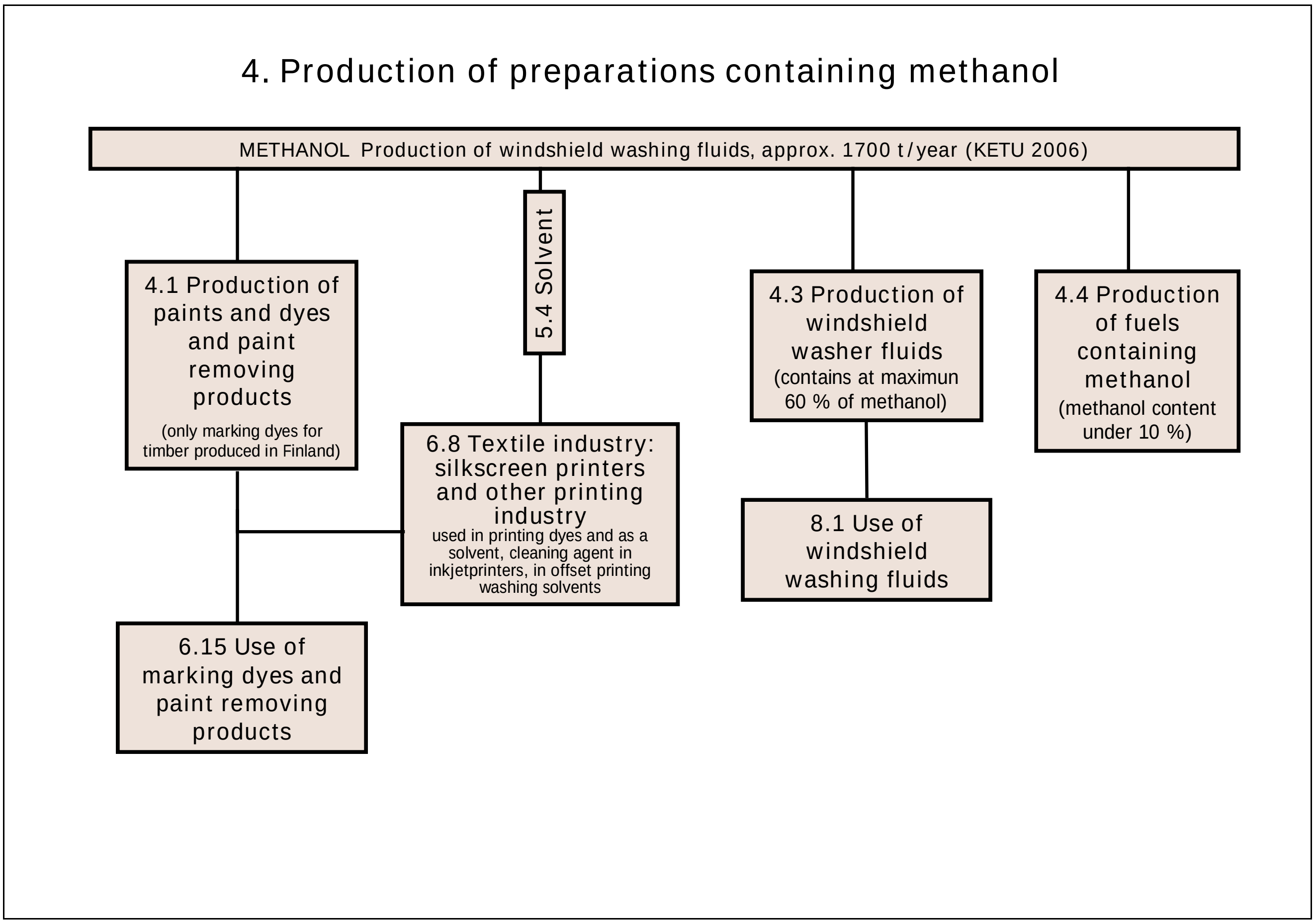


Figure 4. Tree diagram of hierarchy of uses: production of preparations containing methanol (paints, dyes, paint removing products, windshield washer fluids, fuels) and use of methanol as a solvent.

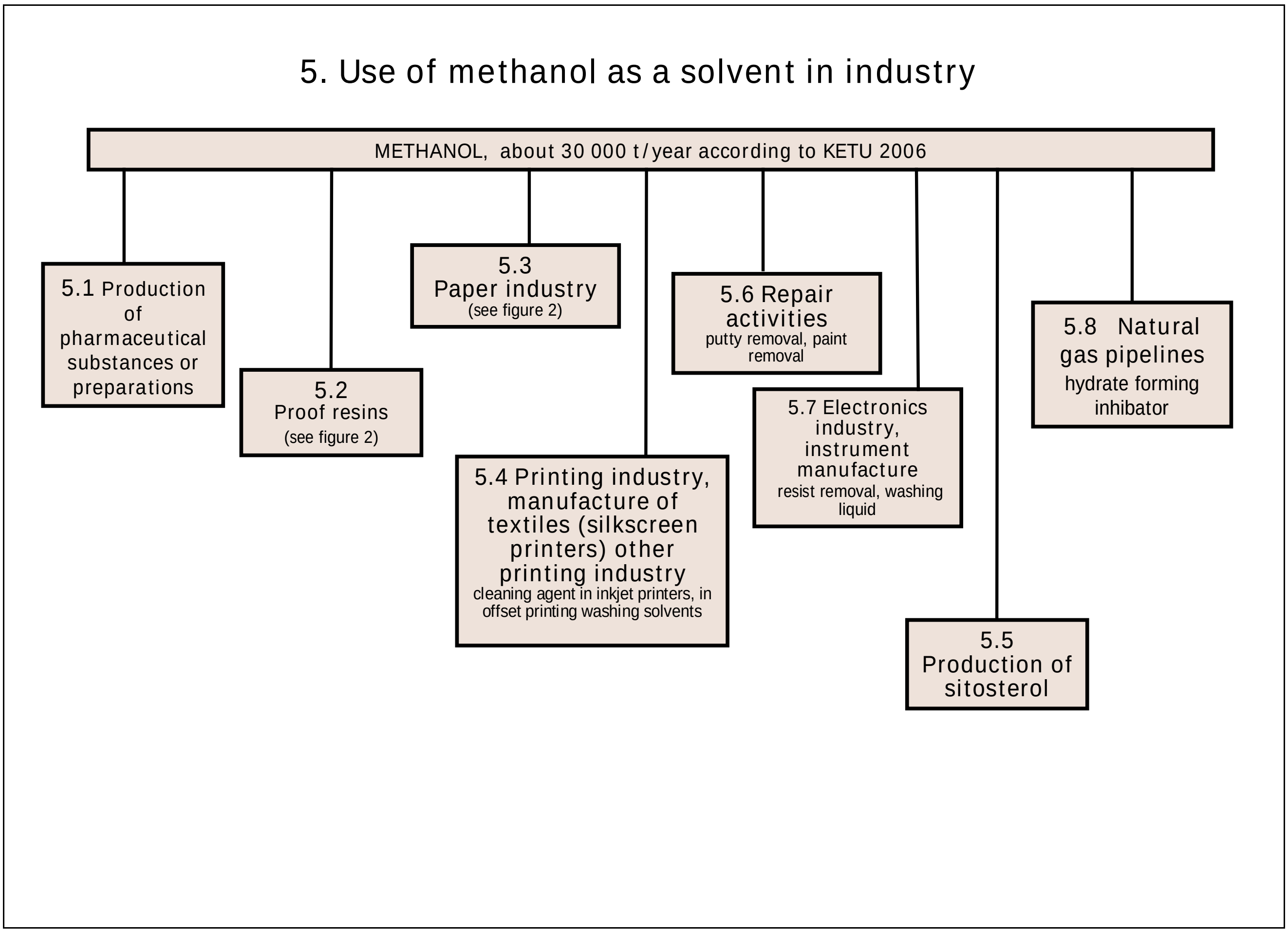


Figure 5. Use of methanol as a solvent.

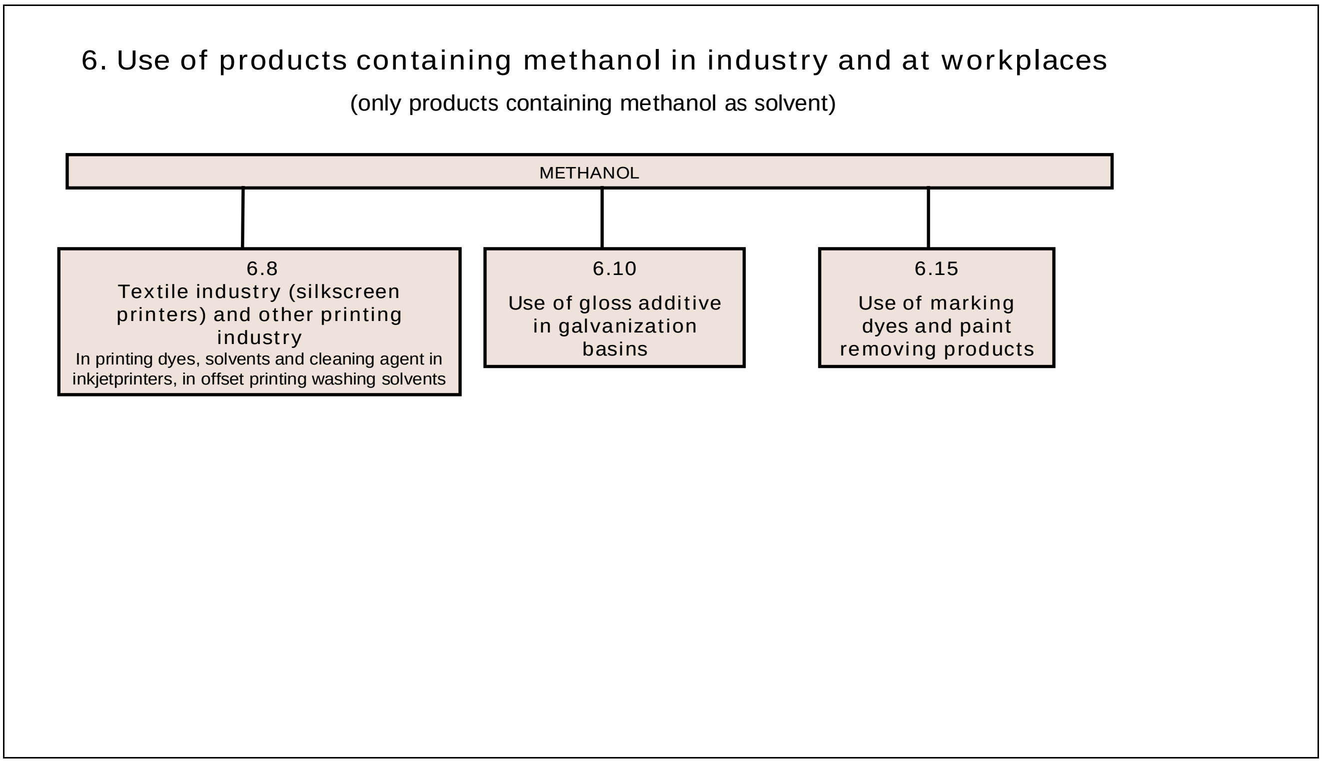


Figure 6. Tree diagram of hierarchy of uses: use of products containing methanol in industry and at workplaces.

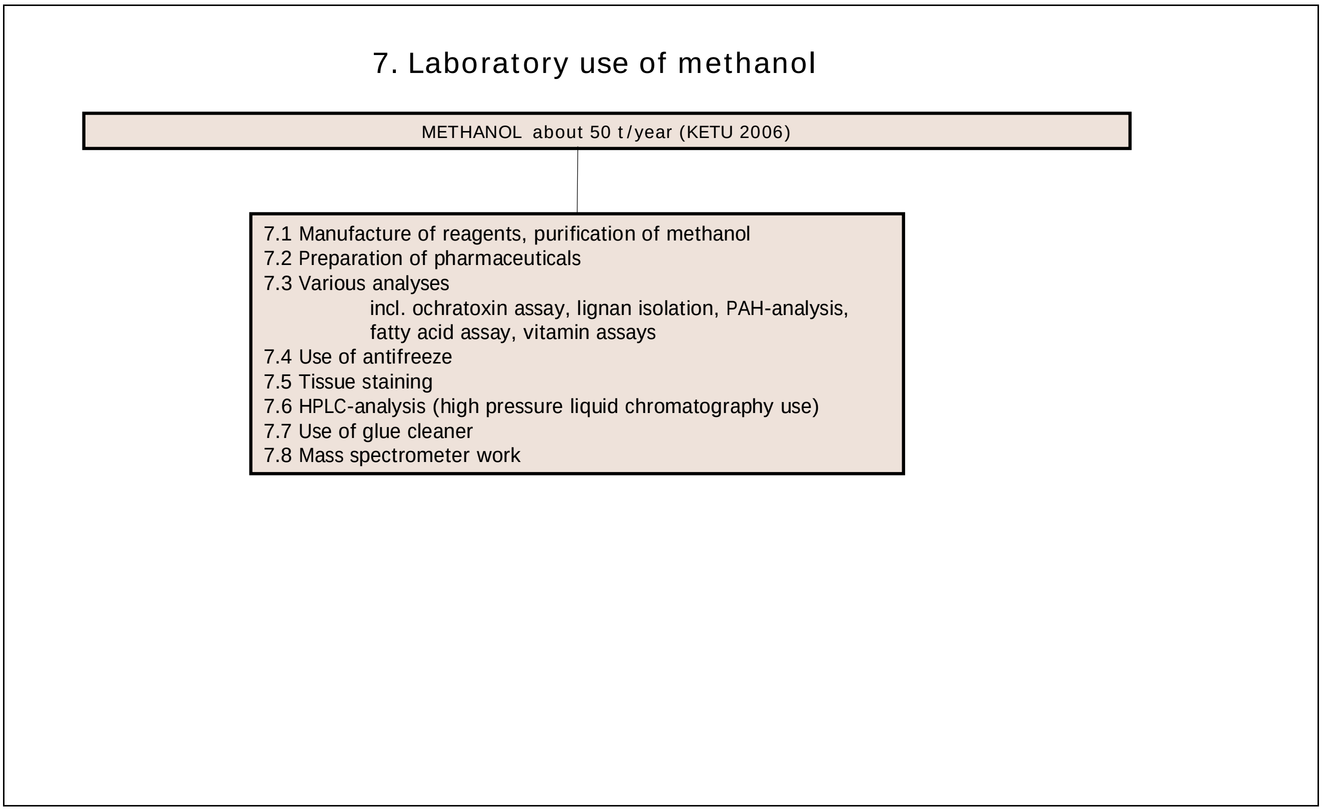


Figure 7. Tree diagram of hierarchy of uses: laboratory use of methanol.

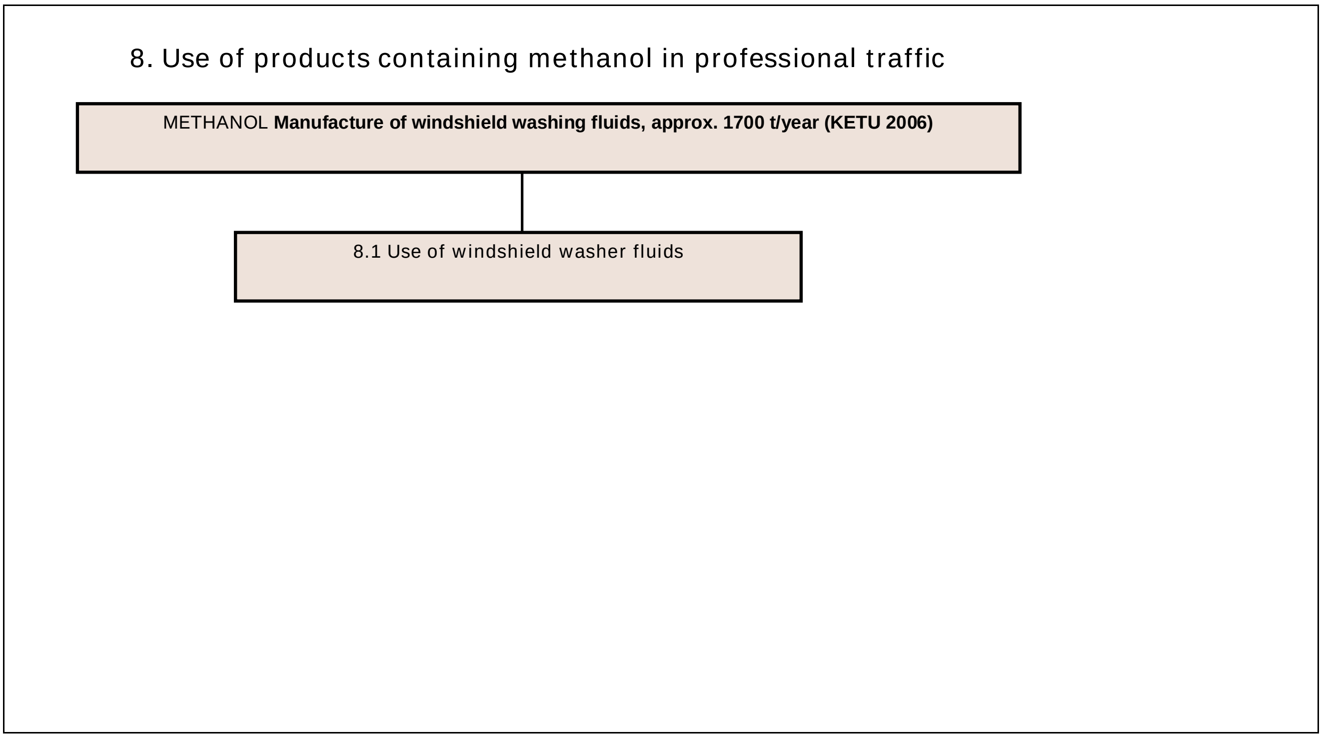


Figure 8. Tree diagram of hierarchy of uses: use of products containing methanol in professional traffic.

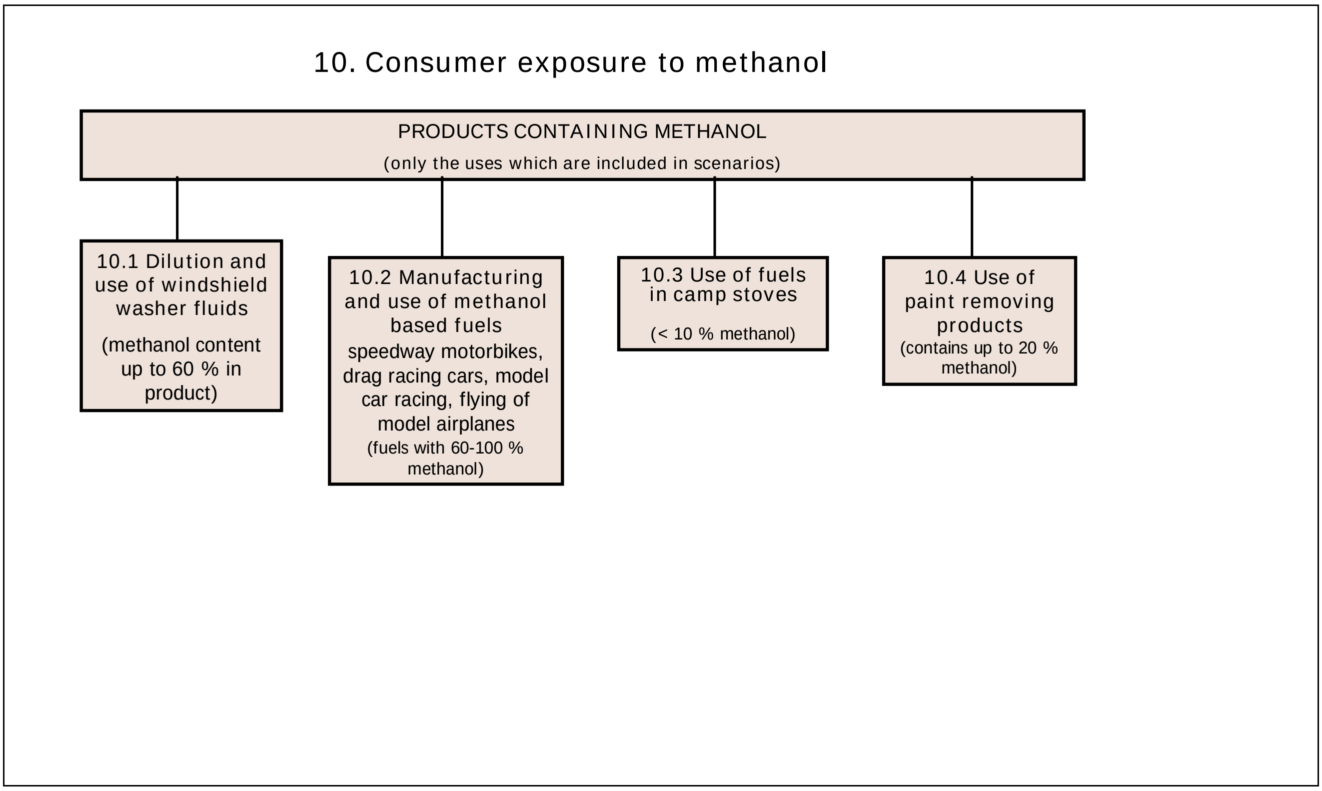


Figure 9. Tree diagram of hierarchy of uses: consumer exposure to methanol.

### *4.2 EXPOSURE SCENARIOS AND CATEGORIES*

In accordance with sections 5.1.1 and 5.2.2 of appendix 1 of the REACH regulation, the exposure scenarios must include all production in the community and all identified uses and the waste phase if necessary. The REACH regulation also provides the opportunity to group different applications into appropriate application or exposure categories. A total of 10 exposure scenarios were made in this project, 5 of which were categories comprising several applications while the remainder were more detailed exposure scenarios for a single application.

Exposure scenarios were not done for all applications, because the required information was not available. Such applications included manufacturing of products containing methanol as a solvent (excluding manufacturing of windshield washer fluids) and the use of products containing methanol in industry and at workplaces. These applications are described in more detail in section 4 of appendix 1a and section 6 of appendix 1b. It is probable that other products containing methanol will be imported into Finland. Products containing methanol often include other substances that also require registration. The manufacturer of such a product can compile its own exposure scenario for the product users that outlines the hazards of all the substances contained in the product. Preparation of an exposure scenario for the product does not exempt the registering body from creating an exposure scenario for all uses. The exposure scenario for the product includes substances with classification limits that exceed those outlined in article 14 of the REACH regulation. At this time, the lowest limit for methanol is determined according to 1% in the product. The appendices to the draft of the GHS regulation also present 1% as the concentration limit for target organ toxicity effects. Guidelines regarding the actions of downstream users and chemical safety reports have been prepared in the RIP project (RIP 3.5-2 SEG meeting 3 June 19 2007).

According to REACH, the grounds for categorisation must be briefly described. Transportation of methanol is not specifically included in REACH, but exposure occurs during the loading and unloading phases and it would be advisable to take this into consideration when creating the exposure scenarios.

Uses of methanol in the production of chemical products can be grouped into a separate application and exposure category, under which similar and repetitive exposing work phases that require more detailed risk management measures are specified.

Methanol is used as a solvent in many applications, and it is appropriate to group this use into a separate category. This project has divided the use of methanol as an industrial solvent in extraction processes into a separate category, because exposure during these processes, particularly in the pharmaceutical industry, is greater and thus requires more effective risk management measures.

Use of methanol in laboratories can be combined into a separate use category because the amounts used in individual laboratories are similar in size and the methods used to manage exposure are the same in different laboratories.

The remainder of work-related application categories are more detailed exposure scenarios for single applications: methanol as a carbon source in wastewater treatment, manufacturing of windshield washer fluids containing methanol, and use of products containing methanol in professional traffic.

Exposure scenarios for the two most important methanol sources were created for consumers: use of windshield washer fluids containing methanol in traffic and use of methanol-based fuels.

According to the implementation guidelines for exposure scenarios that are currently under preparation, (RIP 3.2-2 SEG 5 06 cTGD-Part D Oct 2007), as of October 2007 a so-called short title shall be created for the exposure scenarios. This briefly describes the use of the substance and simultaneously serves as the title for the exposure scenario. The short title comprises 1) sector of use 2) product category 3) process category and 4) article category. The table below outlines the short title for scenarios in accordance with the October 2007 draft of the implementation guideline (3-stage titles in this case because methanol is not present in articles manufactured in downstream use of methanol). Consumer use has been included in the description of process category although it was not yet included in the guideline version.

Table 5. Exposure scenarios (es) and categories (ec) created in the project and a 4-stage description, in other words, a short title in accordance with the guideline (RIP 3.2-2 SEG 5 06 cTGD-Part D Oct 2007) (use of the chemical in articles, has been excluded as unnecessary in this case).

| | Final report title (and what processes and practices this includes) | *Sector of use D-A.1<br><br>NACE 2007 | *Product category D-A.2 | *Process category D-A.3 |
|---|---|---|---|---|
| 1 ec | Loading and unloading of methanol | H Transportation and storage | PC 35 washing and cleaning products, solvent products (raw material not on the list as such) | PROC 8 Transfer of preparation or substance to/from large containers/vessels at a non-dedicated facility. Industrial or professional use. |
| 2 ec | Methanol as the original substance in the manufacturing of chemical products: the process itself, maintenance, sampling, transfer to/from small containers and waste treatment, methanol regeneration<br>- formaldehyde, chlorine dioxide<br>- formic acid, methyl formate<br>- potassium methylate, sodium methylate, - sodium boron hydride, trimethyl borate<br>- MTBE, TAME, biodiesel (RME etc) | 20.1 Basic chemical manufacturing | PC 35 washing and cleaning products, solvent products (raw material not on the list as such) | PROC 2 Closed, continuous process with occasional controlled exposure.<br><br>Industrial use. |
| 3 es | Methanol as a carbon source in waste water treatment | E Water supply and waste water treatment | PC 37 Water treatment chemical | PROC 2 Closed, continuous process with occasional controlled exposure. Industrial use. |
| 4 es | As a solvent in the manufacturing of products containing methanol:<br>- manufacturing of windshield washer fluids | 20.4 Manufacturing of cleaning and polishing products | | PROC 5 Mixing or blending in batch processes for formulation of preparations or articles. Industrial setting. |
| 5 ec | Use of methanol as an industrial solvent in extraction processes | 21 Manufacturing of pharmaceutical substances and products and other sectors | PC 2 adsorbents | PROC 4 Use in batch or other process where opportunity for exposure arises. Industrial use. |
| 6 ec | Use of methanol as a solvent in different fields of industry<br>- also includes natural gas use | 20 Manufacturing of chemical products | PC 2 adsorbents | PROC 2 Closed, continuous process with occasional controlled exposure. Industrial use. |
| 7 ec | Laboratory use of methanol<br>- includes ms analysis, HLPC, tissue staining, fatty acid analysis, glue removal, freezing point specification, chromosome laboratory work, as a stabilising fluid in film development | M Natural sciences and technology research | PC 21 Laboratory chemicals | PROC 15 Use as laboratory reagent.<br><br>Professional use. |
| 8 es | Use of windshield washer fluids containing methanol in professional traffic<br>- use of windshield washer fluids | G Vehicle sales and repair, T Private use by entrepreneurs and households | PC 35 washing and cleaning products | PROC 11 Spraying techniques. Professional use. |
| 9 es | Consumer use of products containing methanol<br>- use of windshield washer fluids | Z Consumer use | PC 35 washing and cleaning products | PROC 11 Spraying techniques. Consumer use. |
| 10 es | Consumer use of products containing methanol<br>- use of methanol-based fuels | Z Consumer use | PC 13 fuels | PROC 16 Using material as fuel sources, limited exposure to unburned product. Consumer use. |

## 5 HAZARD ASSESSMENT

### *5.1 METHANOL CLASSIFICATION AND EXISTING OCCUPATIONAL EXPOSURE LIMITS AND INDICES*

#### 5.1.1 CLASSIFICATION

At this time, methanol is classified and labelled in the EU as follows:
F-Flammable, R11 (Highly flammable)
T - Toxic, R23/24/25 (Toxic by inhalation, in contact with skin and if swallowed.) and R39/23/24/25 (Toxic: danger of very serious irreversible effect through inhalation, in contact with skin and if swallowed.)

In addition to REACH, the implementation of the Globally Harmonised Classification and Labelling System of Chemicals (GHS) has been prepared in the EU. The EC Commission made a proposal concerning the Regulation on 27 June 2007, and the aim is to begin observing the new classification and labelling regulation on 1 October 2010 for substances and 1 June 2015 for mixtures. The new regulation will change the hazard pictograms for substances and the hazard and precautionary statements and precautionary measures that describe the hazardous properties and preventive measures related to the substances. Annex VI of the GHS Regulation Proposal (European parliament and of the council 27.6.2007) suggests the following GHS-compliant classification for methanol:

Flammable Liquid, category 2, hazard statement no. H225 (Highly flammable liquid and vapour)
Acute Toxicity, category 3, hazard statements H331, H311, H301 (Toxic if swallowed, in contact with skin and if inhaled)
Single exposure target organ toxicity, category 1 hazard statement H370 (Causes damage to [specify target organs])

Based on this, the hazard pictograms, signal words and precautionary statements are as follows:

Danger, Highly flammable liquid and vapour

Danger, Toxic if swallowed, in contact with skin and if inhaled*

Danger, Causes damage to [ocular system and blood acid-base balance**]

** The GHS Regulation Proposal does not indicate what target organs would be specified for methanol, and the ocular system and blood acid-base balance have been used in a demonstrative manner to provide an example of how the statement would look for methanol.

According to the GHS criteria, there will be no environmental classification for methanol.

### 5.1.2 OCCUPATIONAL HYGIENE LIMIT VALUES FOR METHANOL CONCENTRATIONS IN THE AIR

The table below provides a summary of reference values for occupational hygiene. Each year, the American Conference of Governmental Industrial Hygienists publishes TLV values (Treshold Limit Values) for concentrations of impurities in the air and BEI values (Biological Exposure Indices) for biomonitoring. The methods presented for calculating exposure to air impurities are TWA (time-weighted average, concentration calculated for an 8-hour working day and a 40-hour working week) or STEL (short-term exposure limit) for shorter periods (15 min.).

Table 6. OEL (occupational exposure limits) and IDHL (immediately dangerous to life and health) values for methanol (ACGIH 2006). Converted values in parenthesis.

| TWA ppm | TWA $mg/m^3$ | STEL ppm | STEL $mg/m^3$ | County and year | organzations |
|---|---|---|---|---|---|
| 200 | (270 ) | 250 | (330) | Canada (Alberta) 2003, Canada British Columbia 2003, Australia 2005, Belgium 2006, Finland 2005 (same value in 2007), Hong Kong 2002, Ireland 2002, Japan 2007, Malesia 2000, Mexico 2003, New-Zealand 2002, Quebec Canada 2004, South-Africa 2006, Spain 2006, Sweden 2005, Great--Britain 2005 | ACGIH 2006 USA NIOSH REL |
| 200 | (270) | - | - | USA OSHA 2005 | |
| 200 | (270) | 800 | (1060) | Germany 2005 | |
| 200 | (270) | 400 | (530) | Holland 2006 | |
| 156 | (207) | - | - | Brazil 2006 (48 hour week) | |
| (18) | 25 | (37) | 50 | China 2002 | |
| (180) | 250 | (750) | 1000 | Czech 2004 | |
| 200 | 260 | - | - | | EU 2006 |
| (75) | 100 | - | - | Norway 2003 | |
| (75) | 100 | (225) | 300 | Poland 2005 | |
| 6000 ppm or 7960 $mg/m^3$ IDLH (Immediately dangerous to life and health) | | | | | USA NIOSH |

The principle applied to pregnant workers in Finland is 10% of the OEL value ($OEL_{8h}$ and/or $OEL_{15\ min}$) (Taskinen, Lindbohm et al. 2006), which entitles workers to special maternity leave. This provides an 8-hour exposure value of 20 ppm for methanol and a 15-minute exposure value of 33 ppm.

Other reference values can be found as specified by CalEPA and OEHHA and in a literary reference Vyskocil (2000) and they are collected in table 7.

Table 7. Other reference values

| reference value | concentration | reference |
|---|---|---|
| chronic inhalation reference exposure level (no health effects under this level) | 10 mg/m$^3$ | California Environmental Protection Agency (CalEPA)1999 http://www.epa.gov/ttn/atw/hlthef/methanol.html |
| chronic toxicity, inhalation reference exposure level | 4 mg/m$^3$ | California Office of Environmental Health Hazard Assessment (OEHHA) 2006 http://www.oehha.ca.gov/air/chronic_rels/pdf/67561.pdf |
| acute toxicity, inhalation reference exposure level | 28 mg/m$^3$ | California Office of Environmental Health Hazard Assessment (OEHHA) 2006 http://www.oehha.ca.gov/air/acute_rels/pdf/67561a.pdf |
| reference concentration RfC (ambient air concentration) acute (1h) inhalation exposure | 104,8 mg/m$^3$ | (Vyskocil and Viau 2000) |
| reference concentration RfC, chronic inhalation exposure | 0,38 mg/m$^3$ | (Vyskocil and Viau 2000) |

### 5.1.3 REFERENCE VALUES FOR BIOMONITORING

Table 8. Reference values for biomonitoring

| Unit | Guideline value | Provider of guideline value |
|---|---|---|
| Methanol in the urine | 15 mg/l (end of shift) or 470 µmol/l BEI (Biological Exposure Indices) | ACGIH 2005 |
| Methanol in the urine | 30 mg/l (end of shift) BAT (biological tolerance value) | Germany |
| Methanol in the urine | Finland has no reference value for methanol in the urine. The proposed reference limit for non-exposed population is 170 µmol/l and 200 µmol/l during pregnancy. | Finland FIOH |
| Formic acid in the urine | The reference limit for non-exposed population is 70 mmol/mol of creatine. The biomonitoring action limit is 200 mmol/mol of creatine. The limit for formic acid during pregnancy is 90 mmol/mol of creatine. | Finland FIOH |

Monitoring measurements are not necessary if the methanol concentration in the urine is less than 170 µmol/l and if there are no essential changes in production or protection. The situation is the same with regard to formic acid if 70 mmol/mol of creatine is not exceeded.

## *5.2 PRINCIPLES AND SETTING OF DNEL VALUES*

In conjunction with registration of a substance, the registrant (for example, the importer) shall develop REACH exposure scenarios that compare exposure to the DNEL value (derived no effect level) when assessing the hazard to human and to the PNEC value (predicted no effect concentration) when assessing hazards to the environmental. The following examines derivation of a DNEL value according to the REACH guidelines.

The DNEL value comes from the words derived-no-effect-level and refers to the dosage that is expected to no longer have any effect in humans. When setting the value, existing information is used about toxic effects in humans and animal testing as well as assessment factors to account for uncertainty arising from limited information. As this study concentrates on determining exposure and creating exposure scenarios for methanol, a comprehensive description of hazardous properties is not being performed. Instead, the focus is placed on describing the most important information about the toxicity of methanol on the basis of the summary reports, and this will be used to set the preliminary DNEL values in this study. The DNEL for methanol that is actually used in registration is set by the methanol registrant (or a consortium formed by them) in the registration phase. The same general risk assessment principles and REACH guidelines as those used to set DNEL values in this study will be used in the registration phase; however, depending on which studies are selected as key studies and which assessment coefficients the registrants decide to use, the final DNEL values may deviate from those presented here.

The size of the DNEL value is greatly affected by which studies are selected as critical for use in assessing DNEL values and, on the other hand, what kind of assessment or uncertainty factors are used. Larger assessment factors can be used to be certain of remaining on the safe side, but in many cases the use smaller assessment factors is completely justified, in which case a higher limit value is selected. DNEL (like other limit values) is not an absolute line between risk and non-risk but a value below which the performer of the assessment has been at least relatively certain that the level is safe. When setting the limit values and considering the size of the assessment factors, information about the substance's critical effect and dose-response relationship should be taken into consideration, as should any uncertainties related to the existing data. If there are significant uncertainties related to the existing information about effects and their dose-response relationships, the assessment factors can be increased to account for this uncertainty.

Depending on the substance and its uses, it may be necessary to set one of more DNEL values in order to take the exposed populations and different types of exposure. In general, separate DNEL values are set for workers and the other exposed (via the environment) population. In addition, it is often necessary to set DNEL values for workers for both acute and long-term exposure. Similarly, it may also be necessary to set DNEL values for different routes of exposure (dermal exposure, inhalation exposure).

According to the latest guidelines, OEL values (indicative occupational exposure limits (IOELVs) set in accordance with Council Directive 98/24/EC of 7 April 1998 can also be used when considering a worker's inhalation exposure unless there is new scientific proof that the value in question does not provide workers with sufficient protection (RIP_3.2-2_SEG_5_19_COM_note_DNEL_and_OEL.doc 2007). For methanol, the EU has set this value at 260 mg/m$^3$ for an eight-hour period of exposure. The EU has not set a value for acute exposure.

In this project, preliminary DNEL values have been set for the following cases:

- Acute worker exposure (skin and inhalation)
- Long-term worker exposure (skin and inhalation)
- Acute consumer exposure (skin and inhalation)
- Long-term consumer exposure (inhalation)

Consumers are also indirectly exposed to methanol through food, including fruit juices or alcoholic beverages containing methanol, and the sweetener aspartame is also converted into 10% methanol in the digestive tract. These affect the background concentrations of human blood, but examination of this kind of exposure is not part of the exposure scenarios described in this project. Otherwise oral exposure to methanol is associated with methanol abuse and accidents, and examination of abuse is not within the scope of these exposure scenarios either. This is why no oral DNEL has been set for methanol. A summary of the DNEL values is presented in table 9. Justification for the values is presented in sections 5.2.3-5.2.6.

Table 9. Preliminary DNELs developed in this project

| Way of exposure | Worker | Consumer |
|---|---|---|
| Acute (15 min) inhalation exposure (systemic effects) | DNEL=270 mg/m3 | DNEL=232 mg/m3 |
| Acute dermal exposure (when exposure occurs only via the skin) | DNEL=1,2 mg/kg (max 15 min exposure, total dermal exposure per day DNEL=9,6 mg/kg) | DNEL=1,2 mg/kg (acute max 15 min exposure) |
| Acute total exposure (inhalation + skin) | DNEL=1,2 mg/kg | DNEL=1,2 mg/kg |
| Acute local exposure (iho/hengitystiet) | * | * |
| Acute oral exposure | No relevant. Is connected to misuse. | No relevant. Is connected to misuse. |
| Long-term inhalation exposure (systemic effects) | DNEL= 67,5 mg/m3 (4 h/d) | DNEL= 27 mg/m3 4 h/d exposure (windscreen fluid scenario); chronic environment exposure DNEL= 4,5 mg/m3 |
| Long-term dermal exposure | DNEL= 9,6 mg/kg | No relevant |
| Long-term total exposure (mg/kg/d) | DNEL= 9,6 mg/kg | no developed here because no need for this endpoint in our scenarios |
| Long-term oral exposure | No relevant. Is connected to misuse. | No relevant. Is connected to misuse. |
| Long-term local exposure | * | * |

* Critical effect is caused by absorption through skin or inhalation to the blood circulation. Therefore no DNEL value is set for local effects (skin/inhalation)

The toxicity of methanol and its dose-response relationships have been examined in the HTP documentation for methanol (Ketsu 2006) , IPCS's Environmental Health Criteria document (WHO 1997) and the NTP-CERHR expert panel report (NTP-CERHR 2003) as well as an opinion by an expert group from the Dutch Expert Committee on Occupational Standards (DECO) on the reproductive toxicity of methanol (DECOS 2006) and the OECD's SIDS report (OECD 2004), in which the information described is utilised when setting the DNEL value used in this study.

### 5.2.1 METHANOL TOXICITY LABEL

Methanol is completely absorbed by the system. The methanol toxicity label must be marked with the differences between human and rodents commonly used as test animals that are observed under exposure to higher concentrations of methanol.

According to studies by Horton and partners (Horton, Higuchi et al. 1992), blood methanol concentrations always rise linearly in the same manner in rats, monkeys and humans when they are exposed to methanol concentration levels of 1200 ppm (1500 mg/m3) over a 6-hour period. At higher dose levels, blood methanol concentrations in rats and mice rise exponentially while the increase in humans continues in a linear manner. Thus, rodents can be more sensitive to toxic effects resulting from the actual methanol at doses higher than this dose level. On the other hand, high exposure levels in humans causes formate, a metabolic product of methanol, to accumulate in the system, which in turn leads to other symptoms typical of methanol poisoning. Accumulation of formate in primates has been observed to take place at methanol exposure of > 500 mg/kg of body weight (OECD 2004). In Horton's studies on inhalation exposure (Horton, Higuchi et al. 1992), monkeys did not show measurable accumulation of methanol or formate even when monkeys were exposed to 2000 ppm 6h/day, 5 days/week for 1-2 weeks. Studies on humans show that no increase in formate concentrations occurs at concentrations of 200 ppm (Lee, Terzo et al. 1992; Franzblau, Lee et al. 1993; D'Alessandro A and CE 1994).

There is little information available about toxicokinetics at smaller inhalation exposure levels. Horton's (Horton, Higuchi et al. 1992) study showed no significant increase in blood methanol levels in monkeys when they were exposed to concentrations of 50 ppm for 6 hours. There is little information concerning human inhalation exposure at small concentrations. At an exposure level of 260 mg/m3 (200 ppm), blood methanol concentrations in test subjects more or less quadrupled, rising from 1.8-1.9 mg/l to approximately 8 mg/l (Lee, Terzo et al. 1992). There are no studies on the effect of smaller exposure levels on blood methanol concentrations in humans.

Average formic acid excretion (U-Form) in unexposed workers is 55 mmol/mol of creatine. The reference limit for non-exposed population has been set at 70 mmol/mol of creatine, which also takes into account the variations in formic acid concentrations of unexposed workers, so that only 5% of the measured results provide a false positive result. The biomonitoring action limit for formic acid in the urine is 200 mmol/mol of creatine measured after 16 hours of exposure, which is equivalent to 8 hours of inhalation exposure to the OEL concentration of 270 $mg/m^3$ for methanol (200 ppm) (Liesivuori and Savolainen 1987).

Blood methanol concentrations in the normal population vary depending on, for example, the food eaten, but generally range between 0.32-2.61 mg/l (Sedivec, Mraz et al. 1981). Methanol intake from normal sources (food, drink) is usually much less than 10 mg/kilogram of body weight (WHO 1997). According to a study by Davoli (Davoli, Cappellini et al. 1986), administration of a single oral dose of aspartame totalling 500 mg, equivalent to a 50 g dose of methanol(< 1 mg/kilogram of body weight), to a test subject raised the blood methanol level by an average of 1 mg/l.

Methanol is absorbed through the skin. On average, methanol absorption through the skin has been reported to be 0.135±0,062 mg/cm2*min (Batterman and Franzblau 1997) or 0.192 mg/cm2*min (Dutkiewicz, Konczalik et al. 1980). Dutkiewick ym., 1980 estimates than the exposure of one hand to methanol for 2 minutes causes 170 mg of systemic methanol exposure, which is equivalent to 8 hours of inhalation exposure at a concentration of 50 $mg/m^3$ (38 ppm). According to Battermani & Franzblau (1997), placing a hand in 100 % methanol for 15 minutes causes methanol exposure similar to that found after 8 hours of inhalation exposure at 400 ppm, leading to blood methanol concentrations of 11 mg/L.

### 5.2.2 CRITICAL TOXIC EFFECTS OF METHANOL

Based on empirical data from human exposure, the critical toxic effect of methanol is its acute toxic effects and effects on the central nervous system, which are primarily non-specific, reversible central nervous system symptoms. The majority of data comes from poisoning cases in which methanol has been ingested orally, but the literature also reports acute cases of poisoning caused by large doses of skin/inhalation exposure (Downie, Khattab et al. 1992). Even long-term inhalation exposure to lower concentrations, such as 800-3000 ppm, can cause methanol poisoning (IPCS International Programme on Chemical Safety 2001). On the other hand, long-term exposure without acute toxic symptoms has not been shown to cause any permanent effects in the target organs, although isolated case studies have suspected a connection between methanol exposure and Parkinsonism (Filkelstein and Vardi 2002) or pyramidal tract syndrome (Hageman, Hoek et al. 2003).

Animal testing shows evidence of methanol's possible foetal toxicity.

The acute toxicity of methanol (loss of vision, metabolic acidosis, loss of consciousness and death) at high doses is based on the formation of formic acid and its degradation product formate in the system after methanol exposure. Humans and other primates (such as monkeys) are much poorer at processing formate than rodents, for example, due to the fact humans are much more sensitive to the acute toxic effects of methanol than rodents. Exposure to methanol leads to the accumulation of formate in the system and the above-mentioned serious toxic effects appear in humans at clearly lower concentrations than in rodents. This difference should be taken into account when drawing conclusions about methanol toxicity based on data from animal testing.

Work-related exposure and exposure testing performed under test conditions show that headache and mucous membrane irritation occur in workers exposed to concentrations over 200 ppm, a level at which the earliest effects are also proven by EEG registration (Mutray, Kurten et al. 2001; Ernstgård, Shibata et al. 2005; Ketsu 2006). Serious toxic effects, such as vision impairment, are linked to the formation of formate in the system and only appear at higher levels of exposure, after the accumulation of formate has begun (see the section on toxicokinetics). Vision impairment typical of methanol exposure have been reported in workers at exposure levels of >1200 - 8300 ppm (Ketsu 2006) or when serum formic acid concentrations exceed 200 μg/mL" (Barceloux, Bond et al. 2002).

Possible neurological and neuropsychological effects at lower methanol exposure have also been studied in healthy human subjects under experimental conditions (Chuwers, Osterloh et al. 1995; Muttray, Kurten et al. 2001) and (Cook, Bergman et al. 1991).

Muttray et al.(Muttray, Kurten et al. 2001) exposed volunteers to 20 and 200 ppm concentrations of methanol for 4 hours and monitored the symptoms and EEGs. No significant differences in symptoms or EEG were observed between the exposed groups, but the 200 ppm group showed signs of a slight acceleration in brain activity. Chuwers et al. (Chuwers, Osterloh et al. 1995) exposed volunteer human subjects (15 men and 11 women of working age) to methanol concentrations of 200 ppm for 4 hours. The exposure was not considered to cause any findings in visual, neurophysiological or neuropsychological tests, although very slight indicative effects were observed after methanol exposure in the P-300 evoked response test (the brain's electric response to an unusual stimulus) and the Symbol Digit test, which requires attention, concentration, information processing ability, and psychomotor co-ordination. Cook's working group (Cook, Bergman et al. 1991) exposed male volunteers (n=12) to methanol concentrations of 192 ppm for 75 minutes. Clinical studies showed an increase in blood methanol concentration, but the exposure had no effect on formate concentration. Extensive neuropsychological testing did not show significant effects following exposure, but some deterioration was observed in memory and ability to concentrate and in the brain's P-200 evoked response to light flashes and sounds. The effects in both these studies were very slight and indicative. Based on these studies, it can be said that exposure to methanol concentrations of approximately 200 ppm only causes at most very slight effects in healthy humans of working age and is very close to the level that causes no effects in women and men of working age (no-observed adverse effect level, NOAEL level).

One long-term exposure test has been performed on monkeys, in which the monkeys underwent inhalation exposure to 10, 100 and 1000 ppm concentrations for 21 h/day for 29 months (NEDO 1987). The result was histopathological nerve-brain-liver-kidney changes starting at 10 ppm exposure. The changes at 10 ppm exposure were mainly fat granules in the liver. The fact that there was no control group in the study makes it impossible to assess the relevance of the changes at lower exposure levels. The same study was also conducted in rats and mice, where effects were only observed at 1000 ppm doses (rat) or not at all, even at the maximum dose (1000 ppm, mouse) (NEDO 1987).

The possible developmental toxicity of methanol can be considered to be a second critical effect. A recently published summary report from the Dutch Expert Committee on Occupational Standards DECOS (DECOS 2006) proposes that methanol be classified into reproductive category 2 because of its developmental toxicity and marked with risk phrase R61. This recommendation is based on relatively strong evidence of developmental toxicity in rodents. The key study with regard to these effects was a study by Rogers et al. in 1993 in which pregnant mice were exposed to methanol concentrations of 0, 1000, 2000, 5000, 7500, 10000 and 15000 ppm for 7 hours per day during the $6^{th}$ to $15^{th}$ days of gestation. Malformations in the offspring were observed at concentrations starting at 2000 ppm. The no-effect (NAOEL) level was 1000 ppm (Rogers, Mole et al. 1993; Rogers JM, Mole ML et al. 1993).

The differences in methanol metabolism between humans and rodents that were described earlier make it difficult to use these studies as the basis for drawing conclusions regarding the developmental toxicity of methanol in humans: rodents tolerate higher methanol concentrations without the toxic effects of formate accumulation. Based on mechanical studies, this developmental toxicity in rodents is caused by the toxic effects of the methanol itself (not by its metabolic products) on the developing fetus. In mice exposure to 1000 ppm leads to blood methanol concentrations of about 97 mg/L. In humans, exposure to 200 ppm for 4-6 hours causes a blood methanol concentration of approximately 8 mg/L (see above, toxicokinetics).

Burbacher ym. (Burbacher, Shen et al. 1999) exposed female macaque monkeys to methanol (0, 200, 600 and 1800 ppm 2h/day, 7 days/week) prior to and during birth and during pregnancy. The blood methanol concentrations in these female macaques increased by 2, 5 and 15 times compared to the starting level. No maternal toxicity was observed and the methanol did not affect reproductive capability. The possible methanol exposure effects observed in this study were very slight deviations in the neurological development of the offspring during the first months of life and were found in two out of nine tests designed to measure neurological development. Changes were already evident at a dose level of 200 ppm in one of the tests. It was not possible to demonstrate a clear dose-response relationship for these effects, so the results were mainly indicative. In a later report (Burbacher, Grant et al. 2004) on the same study, the researchers reported results that showed that methanol exposure in female macaques affected the length of gestation, in other words, the exposed monkeys gave birth to their offspring earlier than those that were not exposed. The mechanism behind this effect is not clear. Four of the exposed female macaques also showed complications during gestation (uterine bleeding), but it is unclear whether this is due to exposure or simply coincidental. Although it is difficult to draw conclusions from these indicative effects, in combination with the rodent results they do give rise to concern that foetal effects could also be possible in humans and at smaller dose levels that those causing the toxic effects in humans and monkeys resulting from formate accumulation.

It must be noted that methanol is not currently classified as developmentally toxic in the EU. The Dutch Expert Committee on Occupational Safety DECOS (DECOS 2006) has recently issued an opinion in which they propose that methanol be classified into EU Repr. Cat 2 due to its developmental toxicity (T – Toxic, R61 – May cause harm to the unborn child). In GHS, this would correspond to Repr. Cat 1B; Danger, May damage fertility or the unborn child, the indication of danger would be the same as that for vision effects and the acidosis effects.

However, the classification of methanol into a more moderate developmental toxicity category can also be justified. This would mean the following classification in the current EU system: Xn -

Harmful, R63 – Possible risk of harm to the unborn child, and in the GHS system: Warning - Suspected of damaging fertility or the unborn child (Repr. Cat 2, the same indication of danger as above).

### 5.2.3 DNEL LEVEL FOR ACUTE (0-15 MIN) WORKER AND CONSUMER EXPOSURE (INHALATION, SKIN, OVERALL EXPOSURE) TO METHANOL

Acute exposure of workers to methanol is relevant in scenarios where drivers have to dilute methanol to make a working solution of windshield washing fluid, and in renovation work and the manufacturing of pharmaceuticals. The same scenario also occurs with consumers using windshield washing fluids, where this is considered to only apply to adults and (children are forbidden from handling windshield washing fluids containing methanol). Thus, the same systemic DNEL dose is applied to consumers and workers, but, according to the RIP guidance, the default average weight for consumers is 60 kg in comparison to 70 kg for workers.

The starting point for setting DNEL is studies by Cook et al. and Chuwers et al. (Cook, Bergman et al. 1991; Chuwers, Osterloh et al. 1995) in which very slight, sub-clinical central nervous system effects were observed at concentrations of approximately 200 ppm during exposure lasting 75-240 minutes. It is also known that concentrations >200 ppm may cause headache in workers (Ketsu 2006). Serious symptoms of methanol poisoning, such as vision impairment, have been observed in workers subject to exposure > 1200 ppm for an entire working day (Ketsu 2006).

Based on this information, acute exposure (15 min) at concentrations less than 200 ppm (=270 mg/m3) is not expected to have any effects. This is also used as the DNEL value for acute exposure in workers.

If 100% absorption of methanol from the lungs is presumed, this corresponds to a systemic dose of about 1.2 mg/kg of methanol (amount of air inhaled 0.31 $m^3$, 70 kg-person). Therefore, the 15-min systemic methanol dose should not exceed 1.2 mg/kg.

Table 10. Preliminary DNEL values calculated for acute worker exposure.

| | |
|---|---|
| DNEL, inhalation (when exposure only occurs via inhalation) | 200 ppm (= 270 mg/m3) |
| DNEL, dermal exposure (when exposure only occurs via the skin) | 1.2 mg/kg |
| DNEL, overall exposure (inhalation+skin) | 1.2 mg/kg |

The same value of 1.2 mg/kg is applied to consumers for overall exposure, but according to the RIP guidance, the default weight of 60 kg used for consumers is slightly lower than the body weight of a worker. The air concentration corresponding to 1.2 mg/kg of methanol exposure is 232 mg/m3 for 15 minutes of exposure.

Table 11. Preliminary DNEL values calculated for 15 min of acute consumer exposure.

| | |
|---|---|
| DNEL, inhalation (when exposure only occurs via inhalation) | 232 mg/m3 |
| DNEL, dermal exposure (when exposure only occurs via the skin) | 1.2 mg/kg |
| DNEL, overall exposure (inhalation+skin) | 1.2 mg/kg |

### 5.2.4 SETTING THE DNEL VALUE FOR WORK-RELATED LONG-TERM EXPOSURE (INHALATION,SKIN, OVERALL EXPOSURE)

The starting point for setting the DNEL for methanol is controlled studies performed by Chuwers (Chuwers, Osterloh et al. 1995) and Cook (Cook, Bergman et al. 1991) on the neuropsychological effects of low methanol exposure, on the basis of which approximately 200 ppm can be set as the LOAEL level (lowest observable adverse effect level), which is probably very close to the so-called NOAEL level, which does not cause adverse effects in these healthy people aged 20-50.

Because the observed effects were very moderate and sub-clinical, 200 ppm is probably very close to the level that does not cause any effects. In the EU, this level has been set as an indicative limit value for 8 hours of work-related exposure and thus the same occupational hygiene limit value is also applied in Finland. On the other hand, an additional 10x safety margin during pregnancy is also applied in Finland, which means that pregnant workers may not be exposed to methanol concentrations of more than 20 ppm. If the RIP guidance is followed when setting a worker's DNEL value for methanol, assessment factors should be added to the LOAEL level described earlier in order to cover extrapolation from the LOAEL level to the NOAEL level and, if necessary, to also cover possible variation between workers. In this manner it is easy to obtain DNEL levels that are clearly lower than the present occupational hygiene limit values.

Taking into account the relatively new studies published in the late 1990s and early 2000s regarding slight central nervous system disturbances in humans and the indicative effects on gestation/foetal development observed in macaque monkeys at concentrations of 200 ppm, there is reason to try and set a DNEL value that is lower than the LOAEL level of 200 ppm for work-related 8-hour exposure in order to be more certain of being on the safe side. It must be noted that this DNEL would also prevent effects on pregnancy/foetal development.

When setting the DNEL value according to REACH Implementation guidelines, the NOAEL/LOAEL levels should be assessed first followed by the need to cover uncertainties with assessment factors. If the level used as the starting point is LOAEL 200 ppm, which is probably very close to the no effect level, a small assessment factor 2 can be used for LOAEL-NOAEL extrapolation. As the exposure tests were performed on a group of healthy people of different ages and genders that is quite representative of workers, a smaller factor of 2, rather than the normal factor of 5, can be used to cover the variation between workers (RIP3.2.-2_SEG_3_01_HH_DG 2007). The final DNEL for acute central nervous system effects is the LOAEL divided by these assessment factors, meaning that in terms of acute central nervous system effects the DNEL for workers would be 200 ppm/2*2=50 ppm. Because methanol has a short half-life and the effects are slight and reversible, this can be considered to provide protection from effects for exposure lasting the entire working day (< 8 hours). There is no evidence that methanol causes permanent central nervous system effects.

If the developmental toxic effects observed in mice are considered relevant to humans, the NOAEL obtained from mouse studies is 1000 ppm. Mice are probably more sensitive than humans to the developmental toxic effects caused by methanol due to the metabolic difference presented in the toxicokinetics section. Thus, the use of a lower assessment factor than the normal 10x factor for extrapolation from mice to humans can be justified. If a 4x assessment factor is used for extrapolation from mice to humans and a 5x assessment factor for the variation between pregnant women, the DNEL value would be 1000 ppm/4*5=50 ppm, or 67.5 mg/m3 for full-day exposure. This level can with reasonable certainty be considered to provide protection from these possible developmental toxic effects. This level is 4 times less than the lowest level used in Burbacher's (Burbacher, Shen et al. 1999; Burbacher, Grant et al. 2004) macaque monkey studies, at which indicative effects with unclear relevance were observed. Although there is little information regarding the dose-response relationships of blood methanol concentrations at such low exposure levels, this exposure level is unlikely to cause a clear increase in blood methanol concentration in normal people of working age. Based on this, it is reasonably certain that we are on the safe side with regard to the systemic effects of methanol.

Because methanol is nearly completely absorbed from the respiratory tract, 100% absorption is used as the default value when calculating the systemic dose. Based on this, the following parameters can be used to calculate the methanol dose absorbed by the system during a working day if a person is exposed to 50 ppm (67.5 $mg/m^3$) of methanol throughout the working day:

- The worker inhales 10 m3 of air during the working day.
- The worker's average weight is 70 kg.

This provides a systemic methanol dose of 67.5 mg/m3*10 m3 / 70 kg = 9.6 mg/kg, which is used as the overall methanol dose that exposure must not exceed. This is probably slightly over-estimated because not all the inhaled methanol is actually absorbed (some is lost in exhalation, etc.), but this ensures that the value is on the safe side as there are signs that a very large portion of the inhaled methanol is absorbed into the blood circulation (60-80%) (WHO 1997).

If exposure occurs entirely via the skin, this same DNEL value of 9.6 mg/kg/day is applied to the absorbed methanol dose. If exposure occurs via both the skin and inhalation, overall exposure must remain below the DNEL level of 9.6 mg/kg/day.

Table 12. Preliminary DNEL values calculated for long-term worker exposure.

| | |
|---|---|
| DNEL, inhalation (when exposure only occurs via inhalation) | 50 ppm (= 67.5 mg/m3) |
| DNEL, dermal exposure (when exposure only occurs via the skin) | 9.6 mg/kg |
| DNEL, overall exposure (inhalation+skin) | 9.6 mg/kg |

### 5.2.5 SETTING THE DNEL value FOR CONSUMER EXPOSURE WHEN USING WINDSHIELD WASHING FLUID

The same principles are used to set DNEL for consumer exposure as for work-related exposure, but because the distribution of age and health is greater (consumers range from infants to the elderly, including the sick), a larger assessment factor is generally used for consumer exposure in order to cover the variation to cover the variation between people. Thus, the limit values for consumer exposure are usually smaller than those for workers.

The REACH guidance (RIP 3.2-1B 28.7.2005; RIP3.2.-2_SEG_3_01_HH_DG 2007) recommends an assessment factor of 10 to cover the variation between people while the factor for workers is 5. When considering acute central nervous system effects, the effects of methanol at the LOAEL level were very slight and reversible, and these effects were tested by a representative group of people of different ages and genders. For this reason, a smaller assessment factor would be completely justified. On the other hand, it must be noted that there is no research data on children, who may be exposed to methanol via inhalation while sitting in a car where methanol has been used as windshield washing fluid. In view of this, an assessment factor of 5 was selected in order to cover the variation between different people. Furthermore, an assessment factor of 2 is used to cover extrapolation from LOAEL to NOAEL, for a total assessment factor of 20. This provides a preliminary DNEL of 20 ppm, or 27 $mg/m^3$ for repetitive consumer inhalation exposure for a maximum of 4 hours (use of windshield washing fluid). This level would also provide protection from possible developmental toxic effects (see above) in daily inhalation exposure of this length and is not likely to cause an increase in blood methanol concentrations in comparison to normal levels.

It should be noted that if the EU classified methanol into reproductive category 2 as a substance causing developmental toxicity and marked it with risk phrase R61, as recommended by DECOS (DECOS 2006), this would mean that methanol use in products sold to consumers would be completely banned in the EU. It would also mean that methanol could be subject to the authorisation procedure in REACH. On the other hand, a less strict classification (reproduction category 3, R63) is also justified in view of the differences between the toxicokinetics of methanol in rodents and humans.

### 5.2.6 DNEL VALUE FOR CONSUMER ENVIRONMENTAL (24 H/7 DAYS) EXPOSURE

People are also exposed environmentally to methanol through the surrounding community air. There is no reliable human or animal testing information available about the possible long-term effects of methanol. 27mg/m$^3$ was set as the limit value for a maximum of 4 hours of exposure associated with consumer use of windshield washing fluid. For lack of better information, this value divided into 24 hours is applied to continuous exposure, or 27 mg/m$^3$/6=4.5 mg/m$^3$. Thus, the preliminary DNEL value for continuous environmental exposure is 4.5 mg/m$^3$. This exposure is not likely to cause any increase in blood methanol concentration above the endogenic and nutritional background concentrations, and it corresponds to the limit values set for environmental air in the USA.

## *5.3 PRINCIPLES FOR PNEC AND DETERMINATION OF THE VALUES*

PNEC (Predicted No Effect Concentration) refers to the concentration that no longer has any effect in the population. It is set using existing information about the effects in bioassays and assessment factors to cover the uncertainties resulting from limited information.

Examination of this PNEC value means a brief review of the principle for determining PNEC using methanol as an example substance. Only a very limited number of sources have been reviewed for PNEC determination. REACH requires the collection of all existing research data and a detailed evaluation of the key studies. This report presents data on effects that is publicly available from scientific literature, and the quality of individual studies has not been evaluated. In addition to this publicly available information, more unpublished ecotoxicological information about methanol probably exists inside companies, but this study did not have access to such information. The purpose was not to create PNECs that could be used as such in REACH registration and the chemical safety assessment of methanol but to present a short description of PNEC determination through examples.

The public scientific literature contains the following studies about the acute toxicity of methanol to aquatic organisms.

Acute aquatic organism studies

Fish: (Poirier, Knuth et al. 1986) showed a 96 h LC50 value of 15 400 mg/l in *Lepomis macrochirus*, 29 400 mg/l in *Pimephales promelas* 20 100 mg/l in *Oncorhynchus mykiss*, while a study by Call et al, 1983 (Call 1983) showed 96 h LC50 values of 20 100 mg/l (*Salmo Gairdneri*) and 28 100 mg/l (*Pimephales Promelas*). According to these results, methanol is not acutely toxic to freshwater fish.

Shellfish: With regard to invertebrate aquatic organisms, a study by Kuehn et al. (1989) (Kuehn 1989) found a 48 h EC50 value of >10000 mg/l in *Daphnia magna*. A study by Vaishhnav and Lopas (1990) found *a* 48 h LC50 value of 13 240 mg/l in *Daphnia magna* (Vaishnav and Lopas 1985). Rossini & Ronco (1996) reported 48-h $EC_{50}$ 22 200 mg/l for *Daphnia obtusa* (Rossini and Ronco 1996). A recent study by Kaviraj et al. (Kaviraj, Bhunia et al. 2004) tested several shellfish species regarding their acute toxicity, and the most sensitive of these appeared to be the *Moina Micrura* species with a 96 h (a *significantly longer time than in standard tests*) LC50 of 4820 mg/l, the LC50 values for other species were >10000 mg/l. A 96 h LC50 value of 15900 mg/l has been reported for blue mussels. According to these results, methanol would not be acutely toxic to freshwater invertebrates. LC50 values also exist for salt water invertebrates, for example, Portmann & Wilson (1971) (Portmann and Wilson 1971) reported a 48-h $LC_{50}$ of 1975 mg/l for shellfish (*Crangon crangon*).

Green algae: Stratton and Smith reported an EC50 value of 28 440 mg/l (monitoring period 10-14 days, incubation with and without methanol) (Stratton and Smith 1988). This suggests that methanol is not very toxic to algae either.

Bacteria: A study by Thomulka and Lange (1997) found an $EC_{50}$ (24 h) of 39000 ppm for marine bacteria (*Vibrio harveyi*) (Thomulka and Lange 1997).

Chronic aquatic organism studies

There are very few long-term studies available on aquatic organisms. Kaviraj et al. (2004) performed a 90-day long-term study in which the effects of methanol on tilapia (*Oreochromis mossambicus*)
and the plankton population were observed under natural conditions in outdoor enclosures. Effects on growth and reproduction were observed in the fish at a dose level of 47.49 mg/l and over. NOEC was found to be 23,75 mg/l (Kaviraj, Bhunia et al. 2004).

### 5.3.1 IDENTIFICATION OF PNEC

#### 5.3.1.1 PNECaquatic – predicted no effect concentration for aquatic organisms

Identification of the PNEC is based on an assessment of the environmental hazards. An assessment factor of 10-1000 is used if there is little research data available. If plenty of research data is available (10-15 NOEC values from at least 8 taxonomic groups), statistical methods can be used and a lower assessment factor (1-5) applied (European Commission 2003).

This study used an NOEC level of 23.75 mg/l obtained from chronic toxicity tests on fish as the source data for determining PNEC value.

The information available from public literature about the long-term adverse effects of methanol in aquatic organisms is insufficient because information about chronic effects could only be found for one species. Methanol manufacturers may have such information but it was not possible to gain access to it in this study. According to the REACH Technical Guidance Documents, at least in theory, a large assessment factor should be used when setting the PNEC if the information is so deficient. This assessment assumed that the research results required by the amounts of methanol manufactured and imported actually exist, and a decision was made to use an assessment factor of 10 for the lowest chronic NOEC value in use.

Thus, the PNEC is obtained by dividing the NOEC of 24 g by 10, or

$PNEC_{aquatic}$ = 2.4 mg/l

The effects via the air on organisms in the environment often remain unevaluated in REACH because information regarding such effects on, for example, vegetation are rarely available and may not even be required in REACH. Responsibility for assessing the effect of a chemical on the atmosphere lies with the registrant and is subject to the registrant's expertise. If the substance group concerned (volatile) is known to be harmful to vegetation, the matter should be examined in conjunction with the substance in question.

#### 5.3.1.2 Estimated no effect concentration for sediment organisms PNECsediment

There is no research data available concerning the effect of methanol on sediment organisms. This matter has probably never been studied because absorption of the substance into the sediment is slight.

Due to the weak absorption, it would not be necessary to determine PNEC sediment for methanol from the risk assessment point of view either. If the risk in open water is under control (PEC/PNEC < 1), it can be assumed that sediment organisms would not suffer from the effects of the substance because it does not readily accumulate in the sediment.

For many substances, accumulation in the sediment is an important feature in their environmental behaviour. In such cases, information about the effects on sediment organisms and measured information about the substance's absorption factor between water and sediment may also be available. If the K values and the information on effects in sediment are missing, PNEC sediment can still be determined for the substance on the basis of existing basic physico-chemical information and PNECaquatic value as follows using the so-called equilibrium partitioning method (equation 1) (European Commission 2003).

$$PNEC_{sediment} = K_{susp\text{-}water} / RHO_{susp} \times PNEC_{aquatic} \times 1000 \qquad \text{(equation 1)}$$

$K_{susp\text{-}water}$ = substance suspended in water-water partitioning factor (0.15 $m^3/m^3$),
$RHO_{susp}$ = density of the suspended substance (1150 $kg/m^3$)
$PNEC_{aquatic}$ = 2.4 mg/l

$PNEC_{sediment}$ = 1.96 mg/kg (wwt "wet weight")

#### 5.3.1.3 Predicted no effect concentration for soil organisms PNECsoil

There were no research results concerning the effects of methanol on soil organisms. However, the PNECaquatic value can be used to determine the no effect concentration for soil organisms by means of the so-called equilibrium partitioning method (as with sediment) (equation 2).

$PNEC_{soil} = (K_{soil-water} / RHO_{soil}) \times PNEC_{aquatic} \times 1000$ where (equation 2)

$K_{soil-water}$ = soil-water partitioning factor (0.25 $m^3/m^3$ for methanol),
$RHO_{susp}$ = density of the suspended soil (1700 $kg/m^3$)
$PNEC_{aquatic}$ = 2.4 mg/l

$PNEC_{soil}$ = 0.348 mg/kg (wwt)

#### 5.3.1.4 PBT/vPvB assessment

PBT compares the substance properties persistent (P), bioaccumulative (B) and toxic (T) to the criteria in Annex XIII of the REACH Regulation. Annex XIII sets the criteria for identifying persistent, bioaccumulative and toxic substances and for very persistent and very bioaccumulative (vPvB) substances.

The research data available is sufficient to assess that methanol is not a PBT or a vPvB substance. This conclusion is based on the following assessment.
Assessment of persistence:
Methanol is a very biodegradable substance ((Ready biodegradable, pass the OECD 301 test). Based on this, the substance is not persistent in the environment and does not fulfil the P criterion.
Assessment of bioaccumulation:
Methanol has a low log Kow value (< 1). Based on this, it can be concluded that the substance has only a slight tendency to accumulate in organisms and thus does not fulfil the B criterion (BCF > 2000).
Assessment of toxicity:
Methanol s acute and chronic toxicity to aquatic organisms proves that the substance is only slightly toxic and does not meet the conditions for the T criterion (NOEC < 0.01 mg/l). The substance is not classified as CMR or T, R48, or Xn, R48 either. Based on this information, methanol does not fulfil the T criterion.

## 6 EXPOSURE ROUTES

Inhalation exposure is assessed as the most important exposure route for both workers and consumers in the exposure scenarios of this project. Methanol inhalation exposure takes into account both short-term and long-term exposure in nearly all scenarios. The amounts of methanol-based fuel used by consumers are small, but short-term dermal exposure may occur in the fuel-filling phase.

Assessment of human exposure does not need to take oral exposure into account. Eating is not permitted during use of products at workplaces. Consumers 'oral exposure only applies to accidental or intentional intake of products containing methanol, and these situations do not have to be included in the exposure scenarios.

Environmental exposure was only assessed on two scenarios on an example basis.
The effect of methanol sediment has not been taken into account either, because methanol does not accumulate significantly in sediment. The impacts via the air on environmental organisms were not assessed in this project because data regarding the impact of methanol concentrations in the air was not available, nor could the $PNEC_{air}$ concentration be determined.

Table 13. Relevant exposure routes for assessing worker, consumer or environmental exposure in each category. (s. t. = short term exposure ja l. t =long term exposure, x= relevant route, o= the route has been observed in this project, - = not relevant route)

| scenario | Worker/ Consumer exposure assessment | | | | | | Environmental exposure assessment | | |
|---|---|---|---|---|---|---|---|---|---|
| | oral | | skin | | inhalation | | wat er | soil | (air) |
| | l.a. | p.a. | l.a. | p.a. | l.a. | p.a. | p.a. | p.a. | p.a. |
| 1. Loading and unloading of methanol | - | - | xo | xo | xo | xo | x | x | (x) |
| 2. Methanol as raw material in the manufacture of chemical products | - | - | xo | xo | xo | xo | x | x | (x) |
| 3. Methanol as a carbon source in waste water treatment | - | - | - | xo | - | xo | xo | xo | (x) |
| 4. Production of preparations containing methanol:<br>- production of windshield washer fluids | - | - | - | xo | - | xo | x | x | (x) |
| 5. Use of methanol as an industrial solvent in extraction processes | - | - | xo | xo | xo | xo | x | x | (x) |
| 6. Use of methanol as a solvent in different fields of industry | - | - | xo | xo | xo | xo | x | x | (x) |
| 7. Laboratory use of methanol | - | - | xo | xo | xo | xo | x | x | (x) |
| 8. Use of products containing methanol in professional traffic<br>- use of windshield washer fluids | - | - | xo | - | xo | xo | xo | xo | (x) |
| 9. Consumer use of products containing methanol<br>- use of windshield washer fluids | - | - | xo | - | xo | xo | xo | xo | (x) |
| 10. Consumer use of products containing methanol<br>- use of methanol-based fuels | - | - | xo | - | xo | xo | x | x | (x) |

# 7 INITIAL EXPOSURE SCENARIOS

## *7.1 LOADING AND UNLOADING WORK IN METHANOL TRANSPORT*

### 7.1.1 DIFFERENT PHASES OF TRANSPORT, WORKER EXPOSURE AND RISK MANAGEMENT MEASURES

Approximately 150,000 tons of methanol is imported into Finland each year (Tullihallituksen tilastopalvelu 2006). Methanol is transported to Finland by ship or train. Methanol is unloaded from the ships or train cars into storage tanks or tanker vehicles. The tanker vehicles are unloaded into the downstream user's storage tanks. All of the work phases take place either outdoors or under a shelter.

According to the project, there is one measurement result from the unloading phase of a methanol ship, and this dates back about 10 years. At that time, large concentrations of more than 270 $mg/m^3$ were measured during the unloading of a methanol shipment from both breathing zone atmosphere samples and static sampling. The reference value of $OEL_{15\ min}$ (or 330 $mg/m^3$) was exceeded briefly during the removal and reattachment of handles by a maximum of 4x. Different concentrations were measured from harbour watchmen during 4 hours of work, the largest of which exceeded 1000 $mg/m^3$. Respirators were used during the work, and the samples were collected from outside them.

Methanol exposure during the unloading of tank wagons was assessed in the project on the basis of three new and one earlier measurement. The average exposure of operators to methanol when unloading a tank wagon is slight and all-day exposure was a maximum of 19 $mg/m^3$. The most exposing work phases were working on top of the tank wagons and opening hatches, completing the unloading process and sampling. Acute exposure during measurement was a maximum of 290 $mg/m^3$ during the sampling.

Respirators equipped with AX filters and eye protection should be used during sampling and all situations that involve being near an open hatch. Those opening or closing the hatches should always try to remain downwind. Short dermal exposure situations may occur 2-4 times/day when moving the unloading pipes and when taking samples.

During the project, three different methanol exposure assessments were performed for tanker vehicle drivers based on air measurements taken during loading and/or unloading of the tanker vehicle. The highest all-day exposure concentration calculated for the drivers was 24 $mg/m^3$. This assessment does not include the washing phase of the tanker vehicle. During unloading exposure is possible via skin contact, especially when attaching and removing hoses and emptying the suction hoses. A working day can include 2-4 of such situations. Risk management measures in the work should include the use of butyl rubber protective gloves, eye protection and suitable protective clothing. A respirator equipped with an AX filter must be used when working near an open hatch or emptying the suction hoses.

If a powered air purifying respirator mask is used in the loading or unloading of methanol, it must be EX protected.

### 7.1.2 ENVIRONMENTAL EXPOSURE ASSESSMENT

Environmental emissions caused by different phases of transport were assessed via questions about the company's emissions to the air or waste water. Information was available from some larger companies. Only one company provided information about VOC emissions from solvents discharged into the air. The VOC emissions reported by the companies were generally based on a theoretical evaluation. Air emissions mainly come from tanks that are open during transportation or from intermediate storage tanks during storage. Possible emissions to sewers can be caused by the emptying of suction tubes while tanker vehicles are being unloaded. Other situations causing emissions include possible malfunctions and accidents.

### 7.1.3 RISK CHARACTERISATION

This scenario included a risk characterisation for work-related exposure but not an environmental risk characterisation.

Dermal exposure was determined using the EUSES programme. The source data used was dermal exposure that occurred four times per day, for an exposure time of 4 x 15 minutes, limited use (non-dispersive), direct handling, intermittent skin contact, an exposed surface of 0.042 $m^2$, or half of the surface area of both hands, and a layer thickness of 0.01 cm on the skin. The modelling presented here is based on exposure assessments, and the resulting risk relationships are rough assessments that may be over-estimated due to the undeveloped nature of the models. More developed versions of the models or other models will be used in the final exposure scenarios. Exposure assessment based on measurements is closer to the actual exposure level.

Table 14. Preliminary health risk characterisation for the exposure catergory of loading and unloading of methanol

| A) Exposure route and duration | B) Preliminary DNEL | C) Exposure level | D) Comparison, C/B must be <1 |
|---|---|---|---|
| 1) acute exposure 15 min | | | |
| inhalation exposure | 270 mg/m$^3$ dose: 1,2 mg/kg/15 min | 1. Unloading tanker: 1300 mg/m$^3$ (measured outside of the respirator) if protection factor of respirator is 10, the concentration is 130 mg/m$^3$ and dose 0,6 mg/kg/15 min<br>2. Tank truck or tank wagon, measured: 290 mg/m$^3$) if protection factor is 5, the concentration is 58 mg/m$^3$ and dose 0,3 mg/kg/15 min | <1 with respirator<br><br><1 with respirator |
| dermal exposure | 1,2 mg/kg/15 min | 1. Unloading tanker : no enough data for modelling<br>2. Tank truck or tank wagon: EUSES: 3 mg/kg/d, and for 15 minutes: 0,75 mg/kg/15 min | no enough data<br><br><1 |
| total exposure | 1,2 mg/kg/15 min | 1. Unloading tanker (no enough data for modelling)<br>2. Tank truck or tank wagon: 1,05 mg/kg/15 min | no enough data<br><br><1 with respirator |
| 2) long-term 8 h | | | |
| inhalation exposure | 67,5 mg/m3 (8 h/d) dose: 9,6 mg/kg/d | 1. Worker in tanker unloading: measured 1000 mg/m$^3$ outside of the respirator, with protection factor 20, the concentration would be 50 mg/m$^3$ and dose 7,1 mg/kg/d,<br>2. Tank truck or tank wagon: 24 mg/m$^3$ dose: 3,4 mg/kg/d | <1<br><br><1 |
| dermal exposure | 9,6 mg/kg/d | 1. No enough data for modelling<br>2. Tank truck or tank wagon:<br>EUSES: 3,0 mg/kg/d<br>(protective equipments or evaporating excluded) | no enough data<br><br><1 |
| total exposure | 9,6 mg/kg | 1. Worker in tanker unloading: no enough data<br>2. Tanker truck: 6,4 mg/kg/d | no enough data<br><br><1 with respirator |

### 7.1.4 INITIAL EXPOSURE SCENARIO

Loading and unloading work associated with the transportation of products containing methanol was also included in the exposure scenario. Exposure is highest when handling pure methanol, and the risk assessments presented in the scenario are for such situation.

Table 15. Initial exposure category for loading and unloading of methanol. Includes also loading and unloading during transportation of methanol and products containing methanol. Only worker exposure included.

| | |
|---|---|
| 1. Short title | Sector of use: Industry category H transportation and storage<br>Product category: PC 35 Washing and Cleaning products (including solvent based products)<br>Process category: PROC 8 Transfer of substance or preparation (charging/discharging) from/to vessels/large containers at non dedicated facilities.<br>Industrial or professional setting. |
| 2. Descriptionof activities and processes covered | Unloading of methanol from tankers and tank wagons. Loading and unloading during tank truck transportation of methanol and products containing methanol. |
| Conditions of use | |
| 3. Duration and frequency of use | Tanker and tank wagon unloading: whole workshift. Duration of unloading and loading of tank truck varies depending on company from 30 to 120 minutes per day. Frequency also variable. |
| 4.1 Physical form of the substance | liquid solvent, flammable, highly volatile |
| 4.2 Concentration of substance in the product (% substance in the mixture or preparation) | 100 % methanol or lower consentration |
| 4.3 Maximum amount of use per time | Working day: tanker unloading magnitude not known, tank wagon unloading usually several wagons (about 60 $m^3$/wagon), tank truck transportation approximately 30-55 $m^3$ per truck. |
| 5. Other operational conditions<br>Temperature, pressure, volume of the environment/room size | Outdoor temperature, outdoors or open shelters |
| Risk management measures (=Risk Management Measures = RMM), which together with the conditions of use guarantee safe use. | |
| 6.1 Worker exposure RMM<br>(to the final scenario RMM phrases are taken from the library and more data on effiency onprotective equipments are added) | Respiratory protection has to be used: In collecting samples and other sitations where worker has to work above open door of a wagon or vessel and also during emptying methanol pipes. Use atex compatible respirator with AX-filter (powered air purifying system with protection factor 20 in tanker unloading and 5 in tank wagon unloading).<br>Flammable. Smoking prohibited.<br>Use protective clothing, eye/face protection and protective gloves (butylrubber, fluorrubber, teflon, laminated materials) in unloading and loading work. |
| 6.2 RMM in environmental exposure (wastewater, air and soil) | Not included in this scenario, should be assessed. |
| 7. Waste handling and RMM | Possible spills are drained to sewer system. |
| Exposure assessment and the methods how the downstream user can estimate that the conditions of the use described in the exposure scenario are followed | |
| 8. Exposure estimation<br>and reference to its source | For the the final exposure scenario move the data from the final risk characterization table here, now the table is preliminary. |
| 9. Guidance to the downstream user to evaluate whether he works inside the boundaries set by the ES | In the final exposure scenario guidance is given e.g. about the correlation between the amount of use and exposure time to the exposure. |

## *7.2 METHANOL AS A SOURCE SUBSTANCE IN THE MANUFACTURING OF CHEMICAL PRODUCTS*

### 7.2.1 MANUFACTURING OF DIFFERENT PRODUCTS

Approximately 130,000 tons of methanol is used each year in Finland for the manufacturing of chemical products (STTV 2006). The majority of this is used as a raw material and stabiliser in formaldehyde manufacturing. In Finland, the production capacity for formalin, an aqueous solution of formaldehyde, accounts for about 60,000 tons of annual methanol consumption. Some 90% of the formaldehyde manufactured is used for producing phenol, urea, melamine and resorcinol formaldehyde resins for the wood manufacturing, fibreglass and mineral wool industries (Riistama, Laitinen et al. 2005). According to the Product Register of Chemicals, about 3-10% methanol is present in formaldehyde as a stabiliser.

Chlorine dioxide is mainly used for bleaching pulp. Chlorine dioxide is always prepared at the site of use. The pulp industry uses several methods to produce chlorine dioxide in Finland. Common to all of these is the use of sodium chlorate as a raw material. The other production materials depend on the method. The so-called R-8 and SVP-Lite processes use methanol as an auxiliary reducing agent (Riistama, Laitinen et al. 2005; Vainio, Liesivuori et al. 2005).

Formic acid and its ester methyl formate are produced using the methyl formate method, in which carbon monoxide reacts with methanol to form methyl formate, which is then hydrolised with water into formic acid and back to the start of the process as circulating methanol (Riistama, Laitinen et al. 2005). Methyl formate is generally used in foundry resins and many chemical processes. Potassium methylate is an alkali used as an esterisation catalyst and in silane manufacturing. Potassium methylate is also used in various processes in the manufacturing of fragrances, cosmetic products and pigments. It is delivered as a clear liquid methanol solvent.

Sodium borohydride is produced as a solvent and in solid form. Production is based on a reaction between sodium hydride and trimethyl borate. Trimethyl borate is produced separately from boric acid and methanol (Riistama, Laitinen et al. 2005). Sodium borohydride is a effective and selective reducing agent used particularly in the manufacturing of fine chemicals and pharmaceuticals. Trimethyl borate is available as a solvent containing about 30% methanol or as a pure TMB solvent.

Methanol is used in the production of TAME (tertiary amyl methyl ether) and MTBE (methyl tertiary butyl ether), which are oxygenates that improve the burning of fuel and reduce harmful emissions.

Several methods can be used to manufacture biodiesel. Methanol is used when biodiesel is produced from vegetable oil. Esterification is an equilibrium reaction in which the wax substances contained in oil are transesterified with alcohol (usually methanol). The fatty acids in the oil and the methanol form methyl esters (Fatty Acid Methyl Esthers, FAME), or biodiesel, and the glycerol that is separated from the process is produced as a by-product. Rapeseed methyl ester (RME) is produced if rapeseed oil is used as the raw material. There are 20-30 devices functioning on a small scale in Finland, the majority of which are closed systems operating on the gas recovery principle. The estimated methanol use in these machines is about 300 t per year. Open systems have not been examined in this project.

### 7.2.2 DIFFERENT PHASES OF WORK-RELATED EXPOSSURE AND RISK MANAGEMENT

Because all of the manufacturing methods for the above-mentioned chemical products are performed as closed processes, a common exposure scenario can be developed. This scenario specifies the exposure phases that recur in different production phases.

Methanol exposure is highest in maintenance work, which includes various types of pipe maintenance work (such as pump removal, heat exchanger repair, filter changes and leak repair) and in sampling where a sample is taken from a specific place in the methanol pipe system for quality monitoring purposes. Sampling work also includes possible emptying and cleaning of sample dishes. The work phases involved in sampling are often short, in which case air measurement results are compared to the short-term limit value $OEL_{15min}$, which is 330 $mg/m^3$. Measurements taken during pipe maintenance work and sampling over a 10-minute period resulted in 3-38 $mg/m^3$ in outdoor spaces but up to 130 $mg/m^3$ indoors. In order to control risk, a dust mask should be used in work associated with pipe maintenance work and sampling, especially when working indoors. Respiratory protection equipped with an AX filter is suitable for this purpose. If a powered air purifying respirator mask is used, it should be EX protected. Protective gloves (butyl rubber, fluoro rubber, Teflon or laminated plastic materials) protect workers from dermal exposure to methanol.

Other exposing work phases are product packaging and transfer to and from containers. Exposure to methanol while filling barrels was highest when the product s methanol concentration was 100% and the filling line had no efficient local exhaust ventilation system. In such cases, methanol exposure calculated for the entire day was a maximum of about 38 $mg/m^3$. When local exhaust ventilation at the filling line worked properly and the filling work was arranged so that no one needed to work above an open filling point, all-day exposure during the filling of products containing 30-70% methanol was 2-5 $mg/m^3$. The primary risk management measures in filling work are the arrangement of work to reduce exposure and efficient local exhaust ventilation.

Monitoring of the process is often isolated into a separately ventilated space where exposure to the production facilities is minimised. Methanol regeneration is also performed as a closed process and its different work phases include those mentioned above.

Methanol concentrations in the air during biodiesel manufacturing were measured during the use of a small closed esterification system. The raw material was 200 l of rapeseed oil, 40 l of methanol and the required amount of sodium hydroxide. Pressure is used to extract methanol in the premixing phase and the glycerol collection phase that follows the esterification process, and a condenser used to collect it for re-use. Then the rapeseed methyl ester is washed with water to clean it. Methanol concentrations in the air remained under the limit of detection, which means that exposure calculated for the entire day for all workers was less than 1 $mg/m^3$. The device manufacturer reported that methanol concentration in the end product was less than 0.2% of weight.

The FIOH register contained a single measurement report about methanol exposure during waste handling. Methanol concentrations of samples collected into charcoal tubes during the bottling and running of head-space specimen in the laboratory at a waste processing plant were under the limit of detection.

### 7.2.3 ENVIRONMENTAL EXPOSURE

Environmental emissions during the manufacturing of chemical products were assessed via questions about the company's emissions to the air or waste water. Information was available from some larger companies. Small amounts of emissions to the air and waste water occur during maintenance measures. The situations causing the greatest emissions were possible malfunctions and accidents. Recommendations call for waste water to be discharged to a waste water treatment plant equipped with biological denitrification equipment, where any methanol would be utilised as a source of nutrition for microbes.

### 7.2.4 RISK CHARACTERISATION

This scenario included a risk characterisation for work-related exposure but not an environmental risk characterisation. The all-day exposure information obtained via measurements was compared to the preliminary DNEL value of 50 ppm, or 68 $mg/m^3$ calculated in the hazard assessment. Based on the concentrations measured, the higher average concentration for all-day exposure during the manufacturing of chemical products was a maximum of 38 $mg/m^3$. In such cases, the dose would be lower than the DNEL value. The maximum acute exposure measured during maintenance and sampling work performed indoors was 130 $mg/m^3$.

Dermal exposure is possible during maintenance work and sampling and also when transferring material to and from containers or in packaging. Dermal exposure during maintenance work and sampling was determined using the EUSES and EcetocTra programs. The source data used for acute exposure was 5 x 15 minutes exposure time, limited use (non-dispersive), direct handling, skin contact was assumed to be intermittent, an exposed surface of 0.042 $m^2$ , or both hands and part of the arm, and a layer thickness of 0.01 cm on the skin. The ECETOC TRA program was tested using the paper version of the model and the following use scenario selected: use in batch or other process where opportunities for exposure arise. All-day exposure when transferring the substance to/from containers and in packaging was assessed in ECETOC TRA with the following use scenario: dis/charging the substance to/from vessels.

The modelling presented here is based on exposure assessments, and the resulting risk relationships are rough assessments that may be over-estimated due to the undeveloped nature of the models. More developed versions of the models or other models will be used in the final exposure scenarios. Exposure assessment based on measurements is closer to the actual exposure.

Table 16. Preliminary health risk characterisation: use and exposure category of methanol as raw material in the manufacture of chemical products

| A) Exposure type | B) Preliminary DNEL | C) Exposure level | D) Comparison, C/B must be <1 |
|---|---|---|---|
| 1) acute exposure 15 min | | | |
| inhalation exposure | 270 mg/m$^3$ dose: 1,2 mg/kg/15 min | Measured 130 mg/m$^3$ and dose 0,6 mg/kg/15 min | <1 |
| dermal exposure | 1,2 mg/kg/15 min | EUSES: 18,86 mg/kg/day, divided by 5 to dose 5 times 15 min: 3,8 mg/kg/15 min (doesn't consider protection equipments or evaporation)<br>ECETOC TRA: 0,69 mg/kg/day divided by 5 for the dose 5 times 15 min: 0,14 mg/kg/15 min | >1 Need for protection<br><1 |
| total exposure | 1,2 mg/kg/15 min | 0,84-4,4 mg/kg/15 min | EUSES > 1 Ecetoc Tra <1 |
| 2) long-term 8 h | | | |
| inhalation exposure | 67,5 mg/m3 (8 h/d) dose: 9,6 mg/kg/d | Measured 38 mg/m3 and dose 5,4 mg/kg/day | <1 |
| dermal exposure | 9,6 mg/kg/d | EUSES: 18,86 mg/kg/day (doesn't consider protection equipments or evaporation)<br>ECETOC TRA: 6,86 mg/kg/day | >1 need for protection<br><1 |
| total exposure | 9,6 mg/kg/d | 12,3-24,3 mg/kg/day | >1 |

### 7.2.5 INITIAL EXPOSURE SCENARIO

Table 17. Initial use and exposure category of methanol as raw material in the manufacture of chemical products. Only worker exposure included.

| | |
|---|---|
| 1. Short title | Sector of use: Industry category 20.1 Manufacture of basic chemicals<br>Product category: PC 35 Washing and Cleaning products (including solvent based products)<br>Process category: PROC 2 Used in closed, continuous process with occasional controlled exposure (e.g. sampling). Industrial setting. |
| 2. Description of activities and processes covered | Methanol use as raw material in closed continuous chemical processes. Contains also filling barrels with 100 % methanol. |
| Conditions of use | |
| 3. Duration and frequency of use | Usually continuously 8 hours per day and 200 days per year. The frequency of different worktasks variable. |
| 4.1 Physical form of the substance | Liquid solvent, flammable, highly volatile. |
| 4.2 Concentration of substance in the product (% substance in the mixture or preparation) | 100 % methanol or lower consentration |
| 4.3 Maximum amount of use per time | Depends on plant (present the used amounts in the final scenario). In the work of highest exposure (opening process pipelines or sample collecting) the amount varies, generally some litres. |
| 5. Other operational conditions<br>Temperature, pressure, volume of the environment/room size | Processes can happen indoors or outdoors. |
| Risk management measures (=Risk Management Measures = RMM), which together with the conditions of use guarantee safe use. | |
| 6.1 Worker exposure RMM<br>(to the final scenario phrases are taken from the RMM library and more data on the effiency is added) | *In collecting samples and maintenance work*: Use respirator with AX-filter. If powered respirator equipment used, it should be atex compareble. Use of local exhaust ventilation recommended.<br>*In barrel filling line*: The work order and use of local exhaust ventilation should be designed to minimize exposure effiently. Flammable. Smoking prohibited.<br>Use protective clothing, safety glasses and protective gloves (butylrubber, fluorrubber,teflon, laminated plastic materials) in every manufactoring area and worktask. |
| 6.2 RMM in environmental exposure (wastewater, air and soil) | Not included in this scenario |
| 7. Waste handling and RMM | Possible spills are drained to sewer system. |
| Exposure assessment and the methods how the downstream user can estimate that the conditions of the use described in the exposure scenario are followed | |
| 8. Exposure estimation and reference to its source | For the the final exposure scenario move the data from the final risk characterization table 16 here (now the table is preliminary). |
| 9. Guidance to the downstream user to evaluate whether he works inside the boundaries set by the ES | In the final exposure scenario guidance is given e.g. about the correlation between the amount of use and exposure time to the exposure. |

## *7.3 USE OF METHANOL AS AN AUXILIARY SUBSTANCE IN WASTE WATER TREATMENT*

### 7.3.1 USE

Methanol is used in biological waste water treatment plants (activated sludge process or carrier process) as a source of rapidly biodegradable organic carbon in nitrogen removal, otherwise known as the denitrification process. In this process, the denitrifying bacteria denitrify, or reduce, nitrate nitrogen to nitrogen gas. The process requires anaerobic conditions and sufficiently high carbon-nitrogen ratio.

#### 7.3.1.1 Processes

In the activated sludge process, the bacteria that clean the water grow freely in the treatment plant pool water. In the carrier process, the bacteria attach to a suitable growth surface (pieces of plastic or various types of crushed materials, such as Lecasora-type substances). The flow in these biofilters is from bottom to top.

#### 7.3.1.2 Batching method and amount

In activated sludge treatment plants a diluted 10% methanol is discharged through the pipes to the lower part of the secondary treatment tank. Methanol is used to raise the low carbon-nitrogen ratio, usually to 10-50 g/m$^3$ of waste water. In carrier process plants, methanol batching is guided on the basis of continuous nitrate measurements accomplished by measuring nitrate levels in the water entering and leaving the filter.

Finland has 7-10 activated sludge treatment plants that use a total of 3500-4000 t of methanol per year. This amount is expected to increase in the near future.

### 7.3.2 WORK-RELATED EXPOSURE AND RISK MANAGEMENT MEASURES

Methanol moves through closed pipe systems in waste water treatment plants. Work-related exposure was measured during pipe maintenance procedures in one large activated sludge treatment plant, where daily methanol use was 2.5-3 tons. Denitrification at this plant did not involve carriers; instead the methanol was discharged directly to the bottom of the secondary treatment tank. The rotameters and check valves in the pump room methanol pipes are cleaned about once a month at this plant and the work phase lasts for an entire shift. The concentration measured during a 58-minute maintenance job was 770 mg/m3. Assuming that the methanol work lasted approximately 6 hours, methanol exposure calculated for the entire day while performing maintenance measures would be about 580 mg/m$^3$ and about 380 mg/m$^3$ for exposure during 4 hours of the same work. The worker wore protective gloves while working, but had to take them off quite regularly due to the precision required for the work.

The primary risk management measure in this kind of waste water treatment plant would be less frequent performance of the work, which could be achieved if pure water were used to dilute the methanol in the process. In this case, the pump rotameters and check valves would not become dirty so quickly, thus extending the interval between maintenance. Changes in phases involved in the actual maintenance work (such as possible water rinsing or discharging water into the pipe system before the work) could also reduce exposure. Respiratory protection equipped with an AX filter, eye protection and protective gloves suitable for handling methanol (such as butyl rubber gloves) should be used when performing pipe maintenance work. If a powered air purifying respirator mask is used, it should be EX protected.

### 7.3.3 ENVIRONMENTAL EXPOSURE

Methanol is a very biodegradable substance (Ready biodegradable, pass the OECD 301 test). Methanol is a completely water soluble substance for which adsorption into activated sludge and evaporation during the process is slight. The theoretical mass balance STP at the plant is as follows (EUSES 2.0.3):

| | % |
|---|---|
| Degrades (mineralises) | 85.9 |
| Into air | 2 |
| Into water | 12.1 |
| Into sludge | 0.015 |

The substance is added to the anaerobic part of the treatment process, in which case methanol evaporation from the process to the air is even less than theoretically assumed. The aim is for all methanol used as an auxiliary substance in waste water treatment to be consumed as a source of nutrition for microbes instead of being present in the water discharged from the plant.

#### 7.3.3.1 Modelling

An environmental assessment of waste water treatment was performed using EUSES modelling (http://ecb.jrc.it/euses/) and environmental samples. The following value was calculated as a result of modelling: PEC local_aquatic= 0.6 mg/l

#### 7.3.3.2 Measurements

A composite water sample for one day was taken from water entering the sea at the mouth of the waste water plant discharge pipe in June 2006. A total of 71,721 $m^3$ of waste water and 64.3 $g/m^3$ of methanol were fed in on the sampling day. The methanol was fed in under the tank surface as a solvent of about 10%. The air temperature on the sampling day varied between 10-21 °C and relative humidity from 42-97%. The methanol concentration of the composite sample was under the limit of detection, or < 3 mg/l. A default dilution factor of 10, and with the measured concentration as the limit of detection provides a value of PEC local_aquatic= 0.3 mg/l.

#### 7.3.3.3 Risk management measures

The treatment process must be sufficiently monitored regarding the amount of substance added in order to avoid an overdose of methanol (optimal carbon/nitrogen level). In an optimal situation, all methanol in the water leaving the treatment plant will have undergone degradation.

### 7.3.4 RISK CHARACTERISATION

#### 7.3.4.1 Environmental risk

The methanol result for the water environment obtained via measurements was under the limit of detection, or less than 3 mg/l, from which the determined PEC local_aquatic= 0.3 mg/l is less than the PNEC concentration.

7.3.4.2 Health risk

Inhalation exposure information for workers obtained via measurements was compared to the preliminary DNEL value for long-term exposure of 68 mg/m³ obtained in the hazard assessment. Because the measurement information was for all-day exposure (about 6 hours of work) of approximately 580 $mg/m^3$, risk management measures are proposed for pipe maintenance work that can help to control exposure.

Dermal exposure is possible during maintenance work. Exposure occurring during maintenance work was determined using the EUSES program. The source data used was 6 hours of exposure time, limited use (non-dispersive), direct handling, intermittent skin contact, an exposed surface of 0.130 m2 , or both hands and part of the arm, and a layer thickness of 0.01 cm on the skin. The following use scenario was selected in the ECETOC TRA model: dis/charging the substance to/from vessels.
(EUSES does not appear to take exposure time into consideration in dermal exposure.)

The modelling presented here is based on exposure assessments, and the resulting risk relationships are rough assessments that may be over-estimated due to the undeveloped nature of the models. More developed versions of the models or other models will be used in the final exposure scenarios. Exposure assessment based on measurements is closer to the actual exposure.

Table 18. Preliminary health risk characterisation for the use of methanol as an auxiliary substance in a waste water treatment plant

| A) Exposure route and duration | B) Preliminary DNEL | C) Exposure level | D) Comparison, C/B must be < 1 |
|---|---|---|---|
| 1) acute exposure 15 min | | | |
| Dermal exposure | 1.2 mg/kg/15 min. | Not relevant | - |
| | | | |
| Total exposure | 1.2 mg/kg/15 min. | Not relevant | - |
| 2) Long-term exposure 8 hours (maintenance work 6 h) | | | |
| Inhalation exposure | 67.5 $mg/m^3$ (8 h/day) Dose: 9.6 mg/kg/d | Measured 580 $mg/m^3$ and dose: 82.9 mg/kg/day if a protection factor of 10 is presumed for the protective device, concentration is: 58 $mg/m^3$ and dose: 8.3 mg/kg | >1 work organisation and need for protective devices<br><br><1 with respiratory protection |
| Dermal exposure | 9.6 mg/kg/d | EUSES: 18.86 mg/kg/day (does not take protective equipment or evaporation into consideration)<br>ECETOC TRA: 6.86 mg/kg/day | >1 Personal protection needed<br><br>< 1 |
| Total exposure | 9.6 mg/kg/d | 89-102 mg/kg/day | >1 Personal protection needed |

### 7.3.5 INITIAL EXPOSURE SCENARIO

Table 19. Use of methanol as an auxiliary substance in waste water treatment, initial exposure scenario

| | |
|---|---|
| 1. Short title | Sector of use: E Water maintenance and waste water treatment<br>Type of preparation: PC 37 Water treatment chemical<br>Use: PROC 2 Closed, continuous process with occasional controlled exposure, industrial use. |
| 2. Description of activities and processes covered | As an auxiliary substance for denitrification at activated sludge treatment plants (supplement). The substance is added directly into the water at the bottom of the water treatment tanks. |
| Conditions of use | |
| 3. Duration and frequency of use | Methanol use in the pipe system is usually continuous, 8 hours/day and 200 days/year. The worst exposure occurs during maintenance work in the pump room lasting all day, 1-12 times/year. |
| 4.1 Physical form of the substance | Liquid solvent, flammable, very volatile |
| 4.2 Concentration of substance in the product (% of substance in the mixture) | Methanol is diluted to 10% before being discharged into the tanks. |
| 4.3 Maximum amount used per time or activity | The amount used depends on the carbon concentration in the waste water, usually 10-50 g/l. The amount flowing from the pipe system during pump room maintenance work varies, generally several litres at a time. |
| 5. Other operational conditions Temperature, pressure, capacity of receiving environment/space (room size x ventilation rate), emission or release factors according to the technology used<br><br>1. Worker exposure<br><br>2. Environmental exposure | 1. Maintenance work is usually performed in the pump room in a relatively small indoor space.<br><br>2. The waste water plant tanks may be located indoors or outdoors. The entire substance amount goes into the process. The theoretical mass balance for methanol in a biological treatment plant is as follows (EUSES 2.0.3):<br>%<br>Degrades (mineralises) 85.9<br>Into air 2<br>Into water 12.1<br>Into sludge 0.015<br><br>The substance is added to the anaerobic part of the treatment process, in which case methanol evaporation from the process to the air is even less than theoretically assumed. The aim is for all methanol used as an auxiliary substance in waste water treatment to be consumed as a source of nutrition for microbes instead of being present in the water discharged from the plant. |
| Risk management measures (=Risk Management Measures = RMM), which together with the conditio ns of use guarantee safe use. | |
| 6.1 Worker exposure RMM<br>(to the final scenario phrases are taken from the RMM library and more data on the effiency is added) | Pure water should be used to dilute methanol in order to extend the pump maintenance interval. Prior to servicing, the methanol in the pumps is rinsed into the sewer using water. Respiratory protection equipped with an AX filter (protection factor of 10), eye protection and protective gloves made of butyl rubber or some other suitable material (fluoro rubber, Teflon, laminated plastic materials) must be used when performing pipe maintenance work. If a powered air purifying respirator mask is used, it should be EX protected.<br>Risk of fire. Smoking forbidden near fuel handling sites. |
| 6.2 RMM in environmental exposure (wastewater, air and soil) | Process adjustment:<br>The treatment process must be sufficiently monitored regarding the amount of substance added in order to avoid an overdose of methanol (optimal carbon/nitrogen level). In an optimal situation, all of the methanol in the water leaving the treatment plant will have degraded. Less than 2% of the substance used evaporates into the air at the treatment plant. |

Continuation of table 19. Use of methanol as an auxiliary substance in waste water treatment, initial exposure scenario

| | |
|---|---|
| 7. Waste handling and RMM | Possible spillage is directed into the sewer. The methanol absorbed into the waste water sludge will degrade microbiologically during normal, sufficiently long-term rotting and storage before downstream use of the sludge (such as use of sludge-soil in landscaping and on fields). |
| Exposure assessment and means for the downstream user to assess compliance with the operational conditions of use in the exposure scenario | |
| 8. Exposure estimation and reference to its source | Health risk<br>In the final scenario, this section will contain the more detailed information about the health risk characterisation that is now found in the preliminary risk characterisation in table 18.<br>Water environment: Methanol concentration in a composite sample taken from water at the mouth of the community waste water treatment plant discharge pipe emptying into the sea was less than the limit of detection, or < 3 mg/l (measurement data). On the sampling day, 71721 $m^3$ of waste water was processed at the plant and 64,3 $g/m^3$ of methanol added. The methanol was added under the tank surface as a solvent of about 10%. The addition of methanol can be optimised based on information obtained from the treatment process.<br>Air: The theoretical average background concentration of methanol caused by the treatment process near the plant (at a distance of about 100m) is 0.7 $\mu g/m^3$ (when methanol use is approximately 60 $g/m^3$ of waste water) (EUSES 2.0.3 modelling). |
| 9. Guidance to the downstream user to evaluate whether he works inside the boundaries set by the ES | In the final exposure scenario guidance is given e.g. about the correlation between the amount of use and exposure time to the exposure. |

## *7.4 MANUFACTURING OF PRODUCTS CONTAINING METHANOL AS A SOLVENT*

### 7.4.1 MANUFACTURE OF WINDSHIELD WASHING FLUIDS

#### 7.4.1.1 Manufacture of windshield washing fluids and work-related exposure

The project examined the windshield washing fluids containing methanol that are available on the market. Finland has approximately 22 manufacturers and importers of products containing methanol and approximately 48 different products in total. There are at least 7 Finnish manufacturers, and 4 or more companies have their products manufactured in Estonia. The products included 27 different brands that contained 27-50% methanol by weight. A total of 14 products contained more than 50% methanol, and 7 products less than 5% methanol. The highest reported methanol concentration in a product was 60% and this applied to 3 products. According to the KETU register, the total amount of use for 36 products was 3,534 tons, from which methanol consumption of 1,620 tons was calculated (KETU 2006). According to the register, 1,761 tons of cleaning and washing agents were used in 2006.

Windshield washing fluids containing methanol are manufactured by diluting methanol with a water-tenside mixture. The dilution is mixed using, for example, a pneumatic appliance or the solution is mixed in a separate mixing tank If a separate mixing tank is used, the solution is also pumped into a container from which it is discharged into retail packages of different sizes. One part of the project involved examining air methanol concentrations at two companies that manufacture windshield washing fluid. The measurements were taken during the mixing and transfer to containers during the manufacture of windshield washing fluid containing about 60% methanol. Average all-day exposure at the company that did not use local exhaust ventilation and workers did not use respiratory protective equipment was 310-600 mg/m³ and the most exposing work phase was transfer to containers, which was done manually. According to a biomonitoring sample (formic acid concentration in the urine less than the reference limit for non-exposed population of 70 mmol/mol), exposure to methanol was slight. In the other company, work was done in a small space equipped with efficient local exhaust ventilation and where the worker used a powered air purifying respirator mask equipped with an AX filter. In this case, the worker's highest average all-day exposure level was 46 mg/m³ measured outside the respiratory protection. According to a biomonitoring sample (formic acid concentration in the urine 38% of the biomonitoring action limit of 200 mmol/mol), exposure to methanol would be slight.

#### 7.4.1.2 Risk management measures

The tanks used in the dilution and mixing phase of windshield washing fluids must have covers and efficient local exhaust ventilation is required at the site of the covers. High concentrations were measured during transfer to containers when a 60% methanol solution was used. If the methanol concentration in a product were reduced to 10%, worker exposure would also decrease during this work phase, but exact exposure would have to be checked by means of measurements. The worker should use respiratory protection equipped with an AX filter and protective gloves made of a material suitable for handling methanol (butyl rubber, fluoro rubber, teflon, laminated plastic materials) during all phases of work. If a powered air purifying respirator mask is used, it should be EX protected.

#### 7.4.1.3 Environmental exposure

Information about emissions to the air or water was not available in the companies. In terms of environmental exposure, the most important route is evaporation of methanol into the air throughout the manufacturing process. Methanol emission to the soil or sewers may also occur during a malfunction or accident situation.

Environmental exposure during the use of windshield washing fluid has been assessed theoretically, by modelling and by measurement in section 7.8.

#### 7.4.1.4 Risk characterisation

Information about workers 'inhalation exposure obtained through measurements was compared to the preliminary DNEL value of 68 mg/m³ for long-term exposure calculated in the hazard assessment. The concentration was exceeded during windshield washing fluid production in a space without efficient ventilation or local exhaust ventilation. In another company where windshield washing fluid was mixed and transferred to containers in a space equipped with local exhaust ventilation, all-day exposure remained below the DNEL value for long-term inhalation exposure.

Dermal exposure is possible in several phases of windshield washing fluid manufacturing. Dermal exposure was determined using the EUSES program and the ECETOC TRA model. The EUSES source data utilised was 6 hours of exposure time, limited use (non-dispersive), direct handling, intermittent skin contact, an exposed surface of 0.042 $m^2$, or half of the surface area of both hands, and a layer thickness of 0.01 cm on the skin. The following use scenario was selected in the ECETOC TRA model: dis/charging the substance to/from vessels. (EUSES does not appear to take exposure time into consideration in dermal exposure.)

The modelling presented here is based on exposure assessments, and the resulting risk relationships are rough assessments that may be over-estimated due to the undeveloped nature of the models. More developed versions of the models or other models will be used in the final exposure scenarios. Exposure assessment based on measurements is closer to the actual exposure level.

Table 20. Health risk characterisation for use of methanol in the manufacture of windshield washing fluids

| A) Exposure route and duration | B) Preliminary DNEL | C) Exposure level | D) Comparison, C/B must be < 1 |
|---|---|---|---|
| 1) acute exposure 15 min | | | |
| Inhalation exposure | 270 mg/m$^3$<br>Dose: 1.2 mg/kg/15 min. | Not relevant | - |
| Dermal exposure | 1.2 mg/kg/15 min. | Not relevant | - |
| Total exposure | 1.2 mg/kg/15 min. | Not relevant | - |
| 2) long-term exposure 8 h | | | |
| Inhalation exposure | 67.5 mg/m$^3$ (8 h/day) Dose: 9.6 mg/kg/d | Highest measured concentration 600 mg/m³<br>and dose: 85,7 mg/kg/vrk<br>When local exhaust ventilation and respiratory protection equipped with an AX filter in use: measured concentration was 46 mg/m$^3$ and dose 6.6 mg/kg/day | > 1 need for local exhaust ventilation and protective equipment<br><br><1 |
| Dermal exposure | 9.6 mg/kg/d | EUSES: 6 mg/kg/day<br>(does not take protective equipment or evaporation into consideration)<br>ECETOC TRA: 6.86 mg/kg/day | <1<br><br><1 |
| Total exposure | 9.6 mg/kg/d | 13.5-92.6 mg/kg/day | >1<br>local exhaust ventilation and respiratory protection and protective gloves |

#### 7.4.1.5 Initial exposure scenario

Table 21. Manufacture of windshield washing fluids, initial exposure scenario. Only worker exposure is taken into account.

| | |
|---|---|
| 1. Short title | Sector of use: 20.4 Manufacturing of cleaning and polishing products<br>Type of preparation: PC 37 Water treatment chemical<br>Use: PROC 5 Mixing or blending in batch processes for formulation of preparations or articles. Industrial use. |
| 2. Description of activities and processes covered | Dilution of methanol into water, mixing and transfer to/from containers in a space equipped with local exhaust ventilation. |
| Conditions of use | |
| 3. Duration and frequency of use | Daily manufacturing during the peak season and continuous work during at this time, for example, 6-8 h. Company-specific variation regarding frequency of use. |
| 4.1 Physical form of the substance | Liquid solvent, flammable, very volatile |
| 4.2 Concentration of substance in the product (% substance in the mixture or preparation) | 100% methanol is diluted into water and tenside. Maximum methanol concentration in the end product is 60%. |
| 4.3 Maximum amount of use per time | Company-specific variation in the amounts used. In Finland, annual use of methanol in windshield washing fluids is about 1,700 t. |
| 5. Other operational conditions<br>Temperature, pressure, volume of the environment/room size | Indoor temperature (about 20 C). |
| Risk management measures (=Risk Management Measures = RMM), which together with the conditio ns of use guarantee safe use. | |
| 6.1 Worker exposure RMM<br>(to the final scenario phrases are taken from the RMM library and more data on the effiency is added) | Indoor work must be performed in a well-ventilated space equipped with local exhaust ventilation and the worker must wear respiratory protection equipped with an AX filter, eye protection and protective gloves made of butyl rubber or some other material (fluoro rubber, Teflon, laminated plastic materials). If a powered air purifying respirator mask is used, it should be EX protected.<br>Risk of fire. Smoking forbidden near fuel handling sites. |
| 6.2 RMM in environmental exposure (wastewater, air and soil) | Not performed in this exposure scenario. |
| 7. Waste handling and RMM | Possible spillage is directed into the sewer. |
| Exposure assessment and the methods how the downstream user can estimate that the conditions of the use described in the exposure scenario are followed | |
| 8. Exposure estimation and reference to its source | In the final scenario, this section will contain the more detailed information about the health risk characterisation that is now found in the phase 1 characterisation in table 20. |
| 9. Guidance to the downstream user to evaluate whether he works inside the boundaries set by the ES | In the final scenario, this section will include instructions regarding issues such as the relationship of amounts used and exposure time to exposure. |

### 7.4.2 MANUFACTURE AND USE OF OTHER PRODUCTS CONTAINING METHANOL

Information about the manufacture of other products containing methanol was not collected separately during the project. Information was only gathered about the Finnish manufacture of a few other products.

Marking dyes for mechanical wood production are manufactured in Finland. The dyes may contain up to 40-60% methanol. In wood production, the marking dyes in the felling machine are sprayed by hand from the cabin through the chain saw flange, and rather small amounts are consumed each time. However, the worker may be exposed to the colour solvent when filling the colour tank and maintaining the equipment. According to an assessment by the Kuopio Regional Institute of

Occupational Health, felling machine operators experience very little exposure to marking dye substances (Kallunki, Kangas et al. 2002).

Camp stove fuel containing methanol is produced in Finland. The product contains < 10% methanol. There is no exposure information available concerning methanol exposure during use, but because the product is meant for outdoor use and the amounts used are very small, exposure is likely to be slight. However, there is the possibility of dermal exposure when pouring the fuel into the stove.

According to FIOH's measurement register, use of gloss additive in zinc coating basins has been measured in the 21st century in one application, where methanol concentration remained below the limit of detection. According to KETU, there is one product currently used in Finland, and it has a methanol concentration of 3-5%.

The majority of other products containing methanol are probably imported into the country. In Finland, products containing methanol are used in the print industry (in inks and dyes, colour solvents and cleaning solvents) and in paint removal products. KETU contained 5 imported or manufactured inkjet toners and solvents with a methanol concentration of 20-50% and about 15 paint removal substances, 5 of which contained 10-30% methanol. The products often contained other solvents that are more dangerous than methanol. The register of measurement reports carried out by FIOH contains solvent reports compiled for silk and offset printing, in which methanol accounted for a few percent of the entire solvent exposure. The combined concentration for all solvent substances present was up to 33% of the OEL value.

The KETU register also includes numerous other preparations containing methanol, and in some of these the methanol comes from formaldehyde residue. The methanol added to a product is used as a solvent in the product. According to the KETU register, the methanol concentration in four chemical industry auxiliary substances containing silane is up to 65%. Silicone oil is reported to contain up to 66% and polymerisation inhibitor up to 75% methanol. Methanol concentration of 5-40% is reported in sealant substances. Primers, paints and surface treatment substances for the automobile industry contain < 3% methanol. Substances used to remove dirt and deposits from the carburetor are reported to contain 2.5-10% methanol. Furthermore, 2% methanol is found in silicone preparations, liquids used in dental work and accelerating agents.

## *7.5 USE OF METHANOL AS AN INDUSTRIAL SOLVENT IN EXTRACTION PROCESSES*

### 7.5.1 DESCRIPTION OF DIFFERENT APPLICATIONS, WORK-RELATED EXPOSURE AND RISK MANAGEMENT MEASURES

The exposure information for this exposure category is based on pharmaceutical industry use, but similar extraction processes can be used in other industries, for example, in the manufacturing of raw materials needed in the cosmetics and foodstuffs industries. According to the literature (Riistama, Laitinen et al. 2005), methanol is used in a closed process to extract sitosterol. No use or exposure information was obtained for this application in the project.

Methanol is used as a solvent and an extraction agent in the manufacture of pharmaceutical substances or preparations. According to the KETU register, about 90 tons of methanol is used annually in the pharmaceuticals industry (STTV 2007), but in practice this figure is at least ten times higher. This difference can be due to the fact that pharmaceutical industry use of methanol may be registered as solvent use rather than pharmaceutical industry use.

The FIOH register contains earlier exposure information about methanol, which has been supplemented with measurements performed during the project. Concentrations that exceed the OEL value (270 mg/m³) have been measured in compression and extraction processes for pharmaceutical raw materials and in post-processing facilities. The risk management measures implemented during these work phases include fresh air hoods operating on pressurised air. If a motorised purifying air respirator mask is used, it should be EX protected. Based on biomonitoring samples, exposure using these risk management measures has been reduced to an acceptable level (U-Form concentration less than the reference limit for non-exposed population, which is 70 mmol/mol).

Solvent use of methanol in the manufacture of pharmaceutical preparations is mainly closed, but methanol exposure during washing of the reactors may still rise above the OEL value set for 15 minutes (330 mg/m³). Use of respiratory protection is recommended for workers and others in the immediate vicinity during sampling, reactor cleaning and centrifuge cleaning. If a motorised air purifying respirator mask is used, it should be EX protected. Based on biomonitoring samples, long-term total exposure during the entire shift would remain under the reference point (U-Form less than 70 mmol/mol).

### 7.5.2 ENVIRONMENTAL EXPOSURE

Methanol use in the manufacture of pharmaceutical substances and preparations causes emissions to the air and the water. The amounts vary by company. Methanol is included in companies 'VOC emissions, which were based on a theoretical assessment. Information was only obtained from a few companies during the project. Assessment of exposure resulting from environmental emissions should be performed separately for each institution using the EUSES modelling program.

### 7.5.3 RISK CHARACTERISATION

Inhalation exposure information for workers obtained via measurements was compared to the preliminary DNEL value of 67.5 $mg/m^3$ for long-term exposure and the preliminary acute exposure value of 270$mg/m^3$ calculated in the hazard assessment. In order to bring all-day exposure under the DNEL value, the recommended risk management measures must be observed during the compression and extraction processes for pharmaceutical raw materials and in the post-processing facilities. The value for acute exposure was exceeded during reactor washing in the manufacture of pharmaceutical preparations, in which case the recommended risk management measures must be observed.

Dermal exposure was determined using the EUSES program and ECETOC TRA model. The EUSES source data utilised for acute exposure was 15 minutes of exposure time, limited use (non-dispersive), direct handling, intermittent skin contact, an exposed surface of 0.13 $m^2$, or the hands and part of the arms, and a layer thickness of 0.01 cm on the skin. Using the paper version of the Ecotoc Tra program, the following use scenario was selected: use in batch or other process where opportunities for exposure arise. (EUSES does not appear to take exposure time into consideration in dermal exposure.)

The modelling presented here is based on exposure assessments, and the resulting risk relationships are rough assessments that may be over-estimated due to the undeveloped nature of the models. More developed versions of the models or other models will be used in the final exposure scenarios. Exposure assessment based on measurements is closer to the actual exposure level.

Table 22. Health risk characterisation for use of methanol as an industrial solvent in extraction processes, with pharmaceutical industry use as an example

| A) Exposure route and duration | B) Preliminary DNEL | C) Exposure level | D) Comparison, C/B must be < 1 |
|---|---|---|---|
| 1) acute exposure 15 min | | | |
| Dermal exposure | 1.2 mg/kg/15 min. | ECETOC TRA: 0,69 mg/kg/day (performed once a day) for a dose of 0.69 mg/kg/15 min | <1 |
| Total exposure | 1.2 mg/kg/15 min. | 1.99 mg/kg/15 min. | >1 |
| 2) long-term exposure 8 h | | | |
| Inhalation exposure | 67.5 mg/m$^3$ (8 h/day) Dose: 9.6 mg/kg | Highest <u>measured</u> concentration 335 mg/m$^3$, pressure air hood used, its protection factor could be 20, in which case the concentrations would be 17 mg/m$^3$ and the dose: 2.4 mg/kg/day | >1 work organisation and need for protective devices!<br><1 |
| Dermal exposure | 9.6 mg/kg/d | EUSES: 1.86-18.6 mg/kg/day<br>(does not take protective equipment or evaporation or exposure time into consideration?)<br>ECETOC TRA: 0.69 mg/kg/day | >1<br><1 |
| Total exposure | 9.6 mg/kg/d | 3.1-21mg/kg/day | EUSES >1<br>Ecetoc <1 |

### 7.5.4 INITIAL EXPOSURE SCENARIO

Table 23. Use of methanol as an industrial solvent in extraction processes, initial exposure scenario. Only worker exposure is taken into account.

| | |
|---|---|
| 1. Short title | Sector of use: includes 21 Manufacturing of pharmaceutical substances and products<br>Type of preparation: PC 2 adsorbents<br>Use: PROC 4 Use in batch or other process where opportunity for exposure arises<br>Industrial use |
| 2. Description of activities and processes covered | Methanol is used as an industrial solvent in extraction processes (incl. the pharmaceutical industry) in closed processes. Use in open extraction processes and product manufacturing by compression. Includes sampling and maintenance measures. |
| Conditions of use | |
| 3. Duration and frequency of use | Usually continuous (8 h/day and 200 days/year). |
| 4.1 Physical form of the substance | Liquid solvent, flammable, very volatile |
| 4.2 Concentration of substance in the product (% substance in the mixture or preparation) | 100% methanol |
| 4.3 Maximum amount of use per time | Institute-specific variation |
| 5. Other operational conditions<br>Temperature, pressure, volume of the environment/room size | Indoor temperature (about 20 C). |
| Risk management measures (=Risk Management Measures = RMM), which together with the conditio ns of use guarantee safe use. | |
| 6.1 Worker exposure RMM<br>(to the final scenario phrases are taken from the RMM library and more data on the effiency is added) | In open extraction processes the worker must use a fresh air hood equipped with pressurised air (protection factor of at least 20), full protective clothing and protective gloves.<br>Respiratory protection equipped with an AX filter (protection factor at least 10) and eye protection must be used during reactor maintenance measures, sampling and centrifuge cleaning. If a powered air purifying respirator mask is used, it should be EX protected.<br>Use of protective gloves (butyl rubber, fluoro rubber, teflon, laminated plastic materials) required in all work where skin contact is possible.<br>Risk of fire. Smoking forbidden near the handling site. |
| 6.2 RMM in environmental exposure (wastewater, air and soil) | Not performed in this exposure scenario. |
| 7. Waste handling and RMM | Possible spillage is directed into the sewer. |
| Exposure assessment and the methods how the downstream user can estimate that the conditions of the use described in the exposure scenario are followed | |
| 8. Exposure estimation<br>and reference to its source | In the final scenario, this section will contain the more detailed information about the health risk characterisation that is now found in the phase 1 characterisation in table 22. |
| 9. Guidance to the downstream user to evaluate whether he works inside the boundaries set by the ES | In the final scenario, this section will contain instructions regarding issues such as the relationship of amounts used and exposure time to exposure. |

## *7.6 USE OF METHANOL AS AN INDUSTRIAL SOLVENT*

### 7.6.1 DESCRIPTION OF DIFFERENT APPLICATIONS, WORK-RELATED EXPOSURE AND RISK MANAGEMENT MEASURES

Methanol is used as a solvent in several industrial processes. Based on earlier FIOH service studies, the project collected exposure information about solvent use of methanol in the paper industry, print industry, repair activities and in the electronics industry. In certain situations, methanol is also used as a solvent in the production of formaldehyde-based resins.

The paper industry used methanol to wash rollers. The concentrations were high during the washing, but the washing phases only lasted for 15-30 minutes. The rollers were washed in conjunction with quality changes and in case of malfunction, so washing did not take place during every shift. Methanol concentrations during roller washing were measured in the 1990s, and at that time the largest measured concentrations were as high as 4700 $mg/m^3$, or about 14 times greater than the OEL value for 15 minutes. The rollers had local exhaust ventilation, so not much methanol entered the environment but the worker had to go inside the hood during the washing phase. Methanol is no longer used for washing rollers in the paper industry. Washing involved using a hose to spray methanol into the roller, so the work required the use of respiratory protection, protective gloves, facial protection, a protective apron and boots because the risk of splashing was obvious.

The manufacturing process for urea formaldehyde or phenol formaldehyde resin is a closed process and several measurement results exist for workers ' methanol exposure during manufacturing. According to these measurements, the all-day exposure level in a factory building is a maximum of 4% $OEL_{8h}$, or about 10 $mg/m^3$.

Measurements taken in the print industry are presented in section 7.4.2.

Small methanol concentrations of less than 5 $mg/m^3$ have been measured in repair activities and during removal of filler and paint. This use also involved other solvent substances, in which case the co-exposure caused by the solvents has been more significant than that resulting from a single substance.
In the electronics industry, methanol has been measured during resist removal and solvent use. The concentrations during these measurements all remained under 10 $mg/m^3$.

There is no exposure information available for methanol use in the natural gas network. Use data was obtained from a natural gas supplier. 100% methanol is used in the natural gas network to inhibit hydrate formation in the winter and only when necessary. Hydrate forms in the presence of hydrocarbon when there is a certain pressure and temperature in the pipes. Hydrate is not water soluble and it is a white, crystal-like and hard substance that can even block the pipe. Methanol is primarily used in natural gas pipelines at the reception station for imported methanol if the moisture level in the natural gas entering Finland is too high. The amounts of methanol used vary and, for example, no methanol was used in winter 2006. The highest level of use was in the 1990s, when hundreds of litres of methanol per day could be used and pumping sometimes had to be continued around the clock for several days. Possible methanol exposure at the reception station can only happen during repair or maintenance work, because the methanol supplier transfers the methanol to a closed tank from which it is automatically fed into the pipeline. A second methanol application is natural gas compressor stations, where methanol is used continuously for drying the regulating unit gas. A station-specific system has a 60 litre tank from which methanol is automatically piped. The tank is manually filled by five workers who alternate with each other. When handling methanol, the workers use personal protective equipment (at least protective clothing and gloves).
Because manual filling of methanol involves handling open barrels, protective equipment must be used in this work phase in order to ensure that the risk management measures are sufficient. If a motorised air purifying respirator mask is used, it should be EX protected.

### 7.6.2 ENVIRONMENTAL EXPOSURE

Use of methanol as a solvent substance causes emissions to the air and water. The amounts vary by company. Methanol is included in companies 'VOC emissions, which were based on a theoretical assessment. Information was only obtained from a few institutes during the project. Assessment of exposure resulting from environmental emissions should be performed separately for each company using the EUSES modelling program.

### 7.6.3 RISK CHARACTERISATION

Inhalation exposure information for workers obtained via measurements were compared to the preliminary DNEL value of 68 $mg/m^3$ for long-term exposure and the preliminary acute exposure value of 270 $mg/kg/m^3$ calculated in the hazard assessment. In order to keep all-day exposure below the DNEL value, the recommended risk management measures must be observed during short-term, open handling of the solvent substances (roller washing phases in the paper industry).

Dermal exposure was determined using the EUSES program and the ECETOC TRA model. The EUSES source data utilised for acute exposure was 15 minutes of exposure time, limited use (non-dispersive), direct handling, intermittent skin contact, an exposed surface of 0.13 $m^2$, or the hands and part of the arms, and a layer thickness of 0.01 cm on the skin. (EUSES does not appear to take exposure time into consideration in dermal exposure.)

In the paper version of the ECETOC TRA model, the use scenario selected was roller washing (acute exposure): use for coating/treatment of articles etc. by dipping or pouring. During other work (long-term exposure): use in batch or other process where opportunities for exposure arise.

The modelling presented here is based on exposure assessments, and the resulting risk relationships are rough assessments that may be over-estimated due to the undeveloped nature of the models. More developed versions of the models or other models will be used in the final exposure scenarios. Exposure assessment based on measurements is closer to the actual exposure level.

Table 24. Preliminary health risk characterisation for the exposure category of the use of methanol as a solvent in different fields of industry.

| A) Exposure route and duration | B) Preliminary DNEL | C) Exposure level | D) Comparison, C/B must be < 1 |
|---|---|---|---|
| 1) acute exposure 15 min | | | |
| Inhalation exposure | | Highest measured level 4700 $mg/m^3$ and needed protection factor at least 30 (for example supplied air breathing apparatus) this reduces the level to 157 $mg/m^3$ and dose 0,6 mg/kg/15 min | <1 |
| Dermal exposure | 1.2 mg/kg/15 min. | ECETOC TRA: 6,86 mg/kg/day (done once a day) and the dose would be 6,86 mg/kg/15 min | >1 Need for protection |
| Total exposure | 1.2 mg/kg/15 min. | 7,6 mg/kg/15 min | >1 |
| 2) long-term exposure 8 h | | | |
| Inhalation exposure | 67.5 $mg/m^3$ (8 h/day) Dose: 9.6 mg/kg | Measured in many uses, highest average 10 $mg/m^3$ and dose 1,5 mg/kg/day | <1 |
| Dernmal exposure | 9.6 mg/kg/d | EUSES: 1,86-18,6 mg/kg/day (doesn't consider protection equipments or evaporation)<br>ECETOC TRA: 0,69 mg/kg/day | >1<br><1 |
| Total exposure | 9.6 mg/kg/d | 2,2-20,1 mg/kg/day | EUSES >1<br>ECETOC TRA <1 |

### 7.6.4 INITIAL EXPOSURE SCENARIO

Table 25. Initial use and exposure exposure scenario for the solvent use of methanol in different industrial sectors. Only worker exposure included.

| | |
|---|---|
| 1. Short title | Sector of use: Industry category 20.1 Manufacture of basic chemicals<br>Product category: PC 2adsorbents<br>Process category: PROC 2 Used in closed, continuous process with occasional controlled exposure (e.g. sampling). Industrial setting. |
| 2. Description of activities and processes covered | Methanol used as a solvent in various sectors of industry (paper industry, manufacture of resins, printing, repairing and electronics industry among others). Methanol use as hydrate inhibitor in natural gas pipeline system. |
| Conditions of use | |
| 3. Duration and frequency of use | Usually continuously 8 hours per day and 200 days per year. Work could be done periodically. The frequency of different workstages can vary. |
| 4.1 Physical form of the substance | Liquid solvent, flammable, highly volatile. |
| 4.2 Concentration of substance in the product (% substance in the mixture or preparation) | Maximum 100 % methanol |
| 4.3 Maximum amount of use per time | Varies. In washing of rolls probably 30-50 litres per time. |
| 5. Other operational conditions<br>Temperature, pressure, volume of the environment/room size | Indoor temperature (20 C°). |
| Risk management measures (=Risk Management Measures = RMM), which together with the conditions of use guarantee safe use. | |
| 6.1 Worker exposure RMM<br>(to the final scenario phrases are taken from the RMM library and more data on the effiency is added) | *In shrort-time open use of methanol (for example washing of rolls)*: Use respirator with AX-filter and protection factor 30 (for example supplied air apparatus). Use eye protection, protective gloves, protective apron and boots, because of the danger of spills when spreding methanol with hose. If powered respirator equipment used, it should be atex compareble.<br>Flammable. Smoking prohibited.<br>Use protective gloves (butylrubber, fluorrubber,teflon, laminated plastic materials) in every work where skin contact is possible. |
| 6.2 RMM in environmental exposure (wastewater, air and soil) | Not included in this scenario |
| 7. Waste handling and RMM | Possible spills are drained to sewer system. |
| Exposure assessment and the methods how the downstream user can estimate that the conditions of the use described in the exposure scenario are followed | |
| 8. Exposure estimation<br>and reference to its source | For the the final exposure scenario move the data from the final risk characterization table 24 here (now the table is preliminary). |
| 9. Guidance to the downstream user to evaluate whether he works inside the boundaries set by the ES | In the final exposure scenario guidance is given e.g. about the correlation between the amount of use and exposure time to the exposure. |

## 7.7 LABORATORY USE OF METHANOL

### 7.7.1 DESCRIPTION OF APPLICATIONS, WORK-RELATED EXPOSURE AND RISK MANAGEMENT

Laboratory use of methanol is extensive. FIOH's database of occupational exposure measurements contains eight laboratory applications for methanol: methanol cleaning, preparation of pharmaceuticals in pharmacies, various analyses, use of antifreeze, tissue staining, HPLC analysis, or high pressure liquid chromatography use, use of glue cleaner, and mass spectrometer work. Methanol concentrations were also studied in equipment maintenance and chemical storage. A common factor in laboratory uses was the large proportion of manual work and small, amounts used continually. According to the KETU register, laboratory use of methanol is about 50 tons per year (STTV 2007). There may be thousands of even tens of thousands of people exposed to methanol in laboratory use in Finland. According to Statistics Finland's Classification of Occupations, the country has more than 10,000 laboratory assistants and about 4,500 laboratory technicians (Tilastokeskus 2006).

During different phases of methanol cleaning work performed in reagent manufacturing, a maximum of 18 mg/m$^3$ of methanol was measured from the air, which represents 9% of the $OEL_{8h}$ value determined for eight hours. A maximum of 25 mg/m$^3$ of methanol was measured in the air during the preparation of pharmaceuticals in a pharmacy and during various performed at different laboratories (incl. ochratoxin assay, lignan isolation, PAH analysis, fatty acid assay, vitamin assays). Methanol air concentrations during processing of laboratory waste did not rise above 27 mg/m$^3$ either.

Methanol concentration calculated for all-day exposure during mass spectrometer runs and quality assurance work was less than 1 mg/m$^3$ based on air measurements, when the work was performed inside a fume cupboard and protective equipment included work clothing, protective gloves and safety glasses.

Methanol is used as an eluate in HPLC, otherwise known as high pressure liquid chromatography. A maximum all-day exposure of 12 mg/m$^3$, was measured in the HPLC filtering phase when the work was not performed inside a fume cupboard.

Methanol is also used as antifreeze in refrigeration equipment. Along with ethanol, propanol, xylene and formaldehyde, methanol is used in tissue staining. In a synthesis laboratory, methanol is used as one ingredient in the eluate for column cleaning. Air methanol concentrations in all the methanol applications mentioned above were slight, or less than 2 mg/m$^3$, during the measurement period. The methanol measured from the chemical storage air was also less than 2 mg/m$^3$.

MGG tissue staining is often done automatically and methanol is the primary solvent in the liquid used for staining. Methanol levels of 60 mg/m$^3$ were measured for short 7-minute samples while changing the staining solutions. However, all-day methanol exposure when working at the automated staining machine remained below this level.

Methanol is used to remove glue from ECG lines in a hospital environment, during which short-term air concentrations were 552 mg/m$^3$, which exceeded the 15-minute OEL value of 330 mg/m$^3$ by 1.7 times. Like all other laboratory work involving methanol, this work should also be performed in a fume cupboard in order to reduce exposure. The face velocity in the fume cupboard must be sufficient.

Methanol exposure in laboratory work can not be assessed only on the basis of air concentrations, because dermal exposure is often possible in this type of work. Based on biomonitoring results, some people experience slight methanol exposure in certain work involving methanol (U-Form over the reference limit for non-exposed population but clearly under the biomonitoring action limit), although methanol concentration in the air would be very low. In many laboratory tasks, workers estimated that dermal exposure or splashes on the skin are almost a daily occurrence. The selection of suitable protective gloves is an essential part of risk management. Use of eye protection in methanol work is also appropriate.

However, methanol is only one of many solvents used in laboratories, and the mere monitoring of methanol concentrations does not provide a correct picture of the chemical exposure that occurs in laboratory work. In particular, measurements taken during the handling of waste solvents showed co-exposure effects of solvent substances in excess of the $OEL_{8h}$ levels.

### 7.7.2 ENVIRONMENTAL EXPOSURE

Laboratory use of methanol causes emissions to the air and water. The amounts are application-specific, but are presumed to be small because the amounts used in each laboratory are small.

### 7.7.3 RISK CHARCTERISATION

Based on the measured concentrations, the estimated average concentrations for all-day exposure were, with the exception of glue removal work, less than 27 mg/m$^3$ on average. The concentrations in glue removal work were 550 mg/m$^3$ over a 15-minute period. Glue removal work should be performed in an efficient fume cupboard. In this case, the methanol dose for the entire day would probably remain below the preliminary DNEL value. Short-term, 15-minute concentrations of approximately 60 mg/m$^3$ were measured while solutions were changed in tissue staining work.

The modelling presented here is based on exposure assessments, and the resulting risk relationships are rough assessments that may be over-estimated due to the undeveloped nature of the models. More developed versions of the models or other models will be used in the final exposure scenarios. Exposure assessment based on measurements is closer to the actual exposure level.

Dermal exposure in laboratory work is assessed in the ECETOC TRA model as being so small that it does not need to be taken into account. However, laboratory work is manual in nature, and a more correct exposure assessment could be obtained by taking possible dermal exposure into consideration.

An environmental risk characterisation was not performed in this scenario. The table below presents the health risk characterisation.

Table 26. Preliminary health risk characterisation for the laboratory use of methanol.

| A) Exposure route and duration | B) Preliminary DNEL | C) Exposure level | D) Comparison, C/B must be <1 |
|---|---|---|---|
| 1) acute exposure 15 min | | | |
| inhalation exposure | 270 mg/m$^3$<br>dose: 1,2 mg/kg/15 min | Measured: 553 mg/m3 if fume cupboard is used (efficiency 80 %), reduces the concentration to value 100 mg/m3<br>dose: 0,4 mg/kg/15 min | <1 |
| dermal exposure | 1,2 mg/kg/15 min | Not taken into account according to ECETOC TRA. Necessarily not a correct assumption. | |
| total exposure | 1,2 mg/kg/15 min | 0,4 mg/kg/15 min | <1 |
| 2) long-term 8 h | | | |
| inhalation exposure | 67,5 mg/m3 (8 h/d)<br>dose: 9,6 mg/kg/d | measured: < 27 mg/m$^3$<br>dose: 3,9 mg/kg/day | <1 |
| dermal exposure | 9,6 mg/kg/d | Not taken into account according to ECETOC TRA. Necessarily not a correct assumption. | |
| total exposure | 9,6 mg/kg/d | 3,9 mg/kg/day | <1 |

### 7.7.4 INITIAL EXPOSURE SCENARIO

Table 27. Initial use and exposure category for laboratory use of methanol. Only worker exposure included.

| | |
|---|---|
| 1. Short title | Sector of use: M Professional, scientific and technical activities<br>Product category: PC 21 Laboratory Chemicals<br>Process category: PROC 15 Use a laboratory reagent.<br><br>Non-industrial setting. |
| 2. Description of activities and processes covered | Use of methanol in various laboratory functions: Preparation of reagents, preparation of medical agents in the chemist's shop, various analysis, use as refrigerant, colorant for tissues, HPLC-analysis, use for glue cleaning and ms-tasks. Maintenance of laboratory equipment and waste handling in laboratories. |
| Conditions of use | |
| 3. Duration and frequency of use | Usually continuously 8 hours per day and 200 days per year. Work could be done periodically. The frequency of different workstages can vary. |
| 4.1 Physical form of the substance | Liquid solvent, flammable, highly volatile. |
| 4.2 Concentration of substance in the product (% substance in the mixture or preparation) | Maximum 100 % methanol |
| 4.3 Maximum amount of use per time | Variable use depending on the function. |
| 5. Other operational conditions<br>Temperature, pressure, volume of the environment/room size | Indoor temperature (about 20 C°). |
| Risk management measures (=Risk Management Measures = RMM), which together with the conditions of use guarantee safe use. | |
| 6.1 Worker exposure RMM<br>(to the final scenario phrases are taken from the RMM library and more data on the effiency is added) | Handling of methanol should always be done in fume cupboard.<br>Use protective gloves (butylrubber, fluorrubber,teflon, laminated plastic materials) in every work where skin contact is possible. Use of protective goggles during all methanol tasks.<br>Flammable. Smoking prohibited. |
| 6.2 RMM in environmental exposure (wastewater, air and soil) | Not included in this scenario |
| 7. Waste handling and RMM | Worker exposure to methanol during waste handling in one target was < 27 mg/m$^3$. Total exposure to all solvents was however above the occupational limit values. |
| Exposure assessment and the methods how the downstream user can estimate that the conditions of the use described in the exposure scenario are followed | |
| 8. Exposure estimation and reference to its source | For the the final exposure scenario move the data from the final risk characterization table 26 here (now the table is preliminary). |
| 9. Guidance to the downstream user to evaluate whether he works inside the boundaries set by the ES | In the final exposure scenario guidance is given e.g. about the correlation between the amount of use and exposure time to the exposure. |

## *7.8 USE OF PRODUCTS CONTAINING METHANOL IN PROFESSIONAL TRAFFIC*

### 7.8.1 USE OF WINDSHIELD WASHING FLUIDS CONTAINING METHANOL, WORK-RELATED EXPOSURE AND RISK MANAGEMENT MEASURES

In 2006, there were about 48 windshield washing fluids containing methanol on the market in Finland and 41 of these products contained 23-60% methanol. According to information obtained from a separate statistics service provided by the KETU register, the amount of methanol used in 36 products was 3534 tons in 2004, from which a total methanol use of 1620 tons was calculated (KETU 2004). According to the register, 3780 tons of washing and cleaning agents were used in 2006, with methanol accounting for 1761 tons of this amount. There is no information available concerning the number of users of windshield washing fluids containing methanol. According to the vehicle register, Finland had about 2.9 million vehicles in autumn 2006, and based on information from Statistics Finland's Classification of Occupations, approximately 68,000 professional vehicle drivers in 2006 (Tilastokeskus 2006). The truck fleet comprised 86,700 vehicles in 2006, of which 33,600 were involved in licensed traffic. Finland has about 9,000 taxis.

FIOH has previously studied methanol concentrations in the cab air during police car patrols. Although there were some vehicle-specific differences, the majority of air concentrations during the measurements exceeded the OEL level, or 270 mg/m$^3$. In spring 2006, the same concentrations were studied for trucks during short- and long-haul journeys, for buses during urban and long-haul traffic, for vans during parcel delivery and for taxis during customer transport. A total of 34 driver samples were taken. Working solutions of different strengths were in use, and these had a frost resistance ranging between -14 and -25°C. The average concentration of methanol exposure for truck, van and bus drivers was estimated to be less than 27 mg/m$^3$ for the entire day. During long, one-way journeys, truck driver exposure for the entire day was estimated to be an average of 29 mg/m$^3$. The average all-day concentration in taxi traffic is estimated to be a maximum of 57 mg/m$^3$ if exposure is continuous. Dermal exposure is also possible, for example, when adding fluid to the reservoir or diluting a product containing up to 60% methanol into a suitable working solution.

Because the preliminary DNEL determined for consumers is smaller than that for professional drivers, consumer exposure should be reduced. Taxis transport consumers, so a lower DNEL value should be applied to taxis and taxi drivers (and other driver groups in this scenario). Section 8.1 presents the risk management measures for consumer exposure. Respiratory protection is not suitable for risk management and it is not easy to install air filters in all vehicles, so the primary risk management measures when using windshield washing fluids containing methanol should be to reduce the concentration of methanol in the windshield washing fluid. In this case, a maximum value would be proposed for methanol concentration in the working solution. The maximum methanol concentration in the working solutions used in consumer vehicles and taxis would be 10% if 27 mg/m$^3$ were used as the DNEL values for consumers. In addition, dermal exposure should be prevented through the use of protective gloves when diluting the solution or filling the reservoirs.

### 7.8.2 ENVIRONMENTAL EXPOSURE

Environmental exposure during the use of windshield washing fluid has been assessed theoretically, by modelling and by measurement. A local concentration was determined fro methanol (worst case) in the water environment $PEClocal_{water}$ during the use of windshield washing fluid (Kultamaa/Finnish Environmental Institute).

The concentration was calculated manually first, because there are no suitable models. As the calculations provided a concentration that exceeded the PNEC (2.24 mg/l), water samples taken from an intersection area (the intersection of Vihdintie, Mannerheimintie and Hakamäentie at Ruskeasuo) were used to determine methanol concentration.

Theoretical $PEC_{local}$

The methanol concentration in working solutions of windshield washing products containing methanol varied between 12-30%. Measurements showed that windshield washing fluid consumption in a passenger vehicle-sized taxi averaged 0.4 l/h (=litres per hour), 0.9 l/h in vans, and 0.7 l/h in trucks. Consumption of products containing methanol in consumer passenger vehicles ranged between 0.5-2.1 l/h for an average of about 1.5 l/h. According to the KETU register, use of windshield washing fluid containing methanol was 3,534 tons in 2004, and the amount of methanol was 1,620 tons.

The highest realistic local environmental exposure to methanol in windshield washing use is assumed to occur at busy, traffic light-controlled intersections. In this case, vehicles are always waiting for the lights to change or driving through the intersection. Windshield wiper use is assumed to be at the same level as in traffic (windshield washing fluid consumption 0.3 l/h). Traffic density at a busy intersection can be more than 100,000 vehicles per day (> 4000/h) and about half of these vehicles have to stop at the traffic lights. The area of an intersection is presumed to be 100x100, from which runoff water enters a ditch or stream where it is diluted by a factor of at least 10.

If we assume that in theory an average of 25 vehicles are always waiting at the intersection for a green light (=25 vehicle hours), we can assume that windshield washing fluid consumption at this intersection totals 7.5 litres/hour (0.3 l/vehicle/hour). If only half of the vehicles use fluid containing methanol and the average methanol concentration is 25%, methanol emissions in the area are 0.94 l/h (22.5 l of methanol/day = 17.8 kg of methanol/day). The windshield washing fluid is assumed to be diluted into an amount of water that is equivalent to the average daily precipitation for one hectare, which in Finland is 16,400 litres (600 mm/365 days = 1.64 mm). In this case, the average daily concentration of methanol in the runoff water is 17 800 g/16500 l = 1079 mg/l. A dilution factor of 10 is used in the stream and evaporation is assumed to be 0 in the worst case, in other words under certain weather conditions. This provides a $PEC_{local}$ = 108 mg/l.
PEC/PNEC = 108 mg/l/2.24 mg/l = 48

$PEC_{local}$ based on water sample

Four water samples were taken at the intersection of Vihdintie, Mannerheimintie and Hakamäentie at mid-day on 22 March 2007. According to the Finnish Meteorological Institute, the temperature at the Kaisaniemi measurement station was +5.1 C and relative humidity 91%, wind speed was 2.9 m/s and air pressure 1015.1 hPa. There was variable cloudiness but no rain. It had rained on the previous day or night, because the road surface was wet and a road works site had some puddles. The samples were taken from the Mätäoja stream before and after the intersection and from a well at the intersection area and from a pit at the road works site, where surface water from the road is assumed to run off. Methanol concentrations in all of the samples were below the limit of detection, or less than 1 mg/l.

$PEC_{regional}$ in different environments calculated using the EUSES model

Performed with the EUSES 2.0.3 modelling under the direction of Arto Kultamaa (Finnish Environmental Institute). The OVA guidance for methanol was used as the source of the data entered. The minimum molecule weight (40 g/mol) permitted by the model was utilised. Methanol is classified as a readily biodegradable substance, and its biodegrabability exceeds the standard test requirements for ready biodegradability. Using this information, the program assessed the $PEC_{regional}$ value to be 0.003 mg/l for water, 2.45E-06 mg/kwwt for soil, and 1.64E-03 mg/kwwt for sediment.

### 7.8.3 RISK CHARACTERISATION

Because taxi traffic must take the preliminary DNEL value of 27 $mg/m^3$ recommended for consumers into consideration, the proposed maximum methanol concentration of 10% also has to be observed in worker use. The health risk characterisation using current products is presented in section 8.1.4.

The modelling presented here is based on exposure assessments, and the resulting risk relationships are rough assessments that may be over-estimated due to the undeveloped nature of the models. More developed versions of the models or other models will be used in the final exposure scenarios. Exposure assessment based on measurements is closer to the actual exposure level.

Section 7.8.2 presents the environmental exposure assessment for the use of windshield washing fluids performed with EUSES 2.0.3. The local concentration of methanol obtained through modelling exceeded the PNEC value, and thus a water sample was analysed to check the environmental concentration. Based on the environmental sample, concentrations were below the PNEC value of 2.24 mg/l.

### 7.8.4 INITIAL EXPOSURE SCENARIO

Taulukko 15. Initial exposure scenario for use of windshield washer fluids containing methanol in professional traffic.

| | |
|---|---|
| 1. Short title | Sector of use: H Transporting and storage<br>Product category: PC 35 Washing and Cleaning products (including solvent based products)<br>Process category: PROC 11 Spraying outside industrial settings or applications. |
| 2. Description of activities and processes covered | Use of methanol in windscreen washing fluids (profesional drivers in trucks, busses, vans and taxis). Various exposure situations: washing of windscreen and driving lights during driving and filling washing fluid tanks. |
| Conditions of use | |
| 3. Duration and frequency of use | Used in winter weather, snowy or wet driving conditions. Normal car ventilation and fan on operation mode. The frequency varies according to weather conditions and use habit. Duration was set similar to consumer use: passenger in city busses about 3 hours per day, long-distance busses up to 8 hours per day, passenger cars the use varies ( the maximum use was set to 4 hours). |
| 4.1 Physical form of the substance | Liquid solvent, flammable, highly volatile. |
| 4.2 Concentration of substance in the product (% substance in the mixture or preparation) | Methanol content in products lowered for example to level 10 %. |
| 4.3 Maximum amount of use per time | Not possible to set for this use. |
| 5. Other operational conditions<br>Temperature, pressure, volume of the environment/room size | Car indoor temperature (about 20 C°). |
| Risk management measures (=Risk Management Measures = RMM), which together with the conditions of use guarantee safe use. | |
| 6.1 Worker exposure RMM<br>(to the final scenario phrases are taken from the RMM library and more data on the effiency is added) | The methanol consentration of the used washing fluid should be less than 10 %. Safe storage procedures in selling the product and in handling. Only adults are allowed to purchase the product. |
| 6.2 RMM in environmental exposure<br>(wastewater, air and soil) | According to measured environmental sample analyses the methanol concentrations were less than the detection limit 1 mg/l and there were no need for lowering environmental risk. |
| 7. Waste handling and RMM | Methanol containing wastewater should be drained to sewage system. |
| Exposure assessment and the methods how the downstream user can estimate that the conditions of the use described in the exposure scenario are followed | |
| 8. Exposure estimation<br>and reference to its source | For the the final exposure scenario move the data from the final risk characterization table 30 here (now the table is preliminary). |
| 9. Guidance to the downstream user to evaluate whether he works inside the boundaries set by the ES | In the final exposure scenario guidance is given e.g. about the correlation between the amount of use and exposure time to the exposure. |

# 8 ASSESSMENT OF CONSUMER EXPOSURE

Sources of background consumer methanol exposure are collected in section 3.4. Seven Finnish applications that affect methanol exposure were found, two of which are not relevant due to the small concentration of methanol (< 1% and < 0.2% methanol). There is no exposure or measurement information concerning consumer use of glues containing methanol. About 1700 tons per year of methanol is used by consumers in windshield washing fluids and 40-50 tons of methanol-based fuels for various hobby groups. Other applications include use of fuel in camp stoves, where the substances used contain less than 19% methanol and paint removal substances, where according to the KETU register, some products contain 10-30% methanol There is no exposure or measurement information concerning camp stove and paint remover use. Camp stove fuels are intended for outdoor use and the amounts used are very small, so exposure is estimated to be slight. However, there is the possibility of dermal exposure when pouring the fuel into the stove. In addition to methanol, paint removers contain other even more dangerous solvents, for which the co-exposure must be taken into consideration when assessing exposure.

## *8.1 CONSUMER USE OF WINDSHIELD WASHING FLUIDS CONTAINING METHANOL*

### 8.1.1 USE OF WINDSHIELD WASHING FLUIDS CONTAINING METHANOL AND POINTS OF SALE

In 2006, there were approximately 48 windshield washing fluids containing methanol on the market in Finland and 41 of these contained 23-60% methanol. According to information obtained from a separate statistics service provided by the KETU register, the amount of methanol used in 36 products was 3534 tons in 2004, from which a total methanol use of 1620 tons was calculated (KETU 2006). According to the register, 1761 tons of washing and cleaning agents were used in 2006. There is no information available about the number of users of windshield washing fluids containing methanol. According to the vehicle register, there were 2.9 million vehicles in Finland in autumn 2006.

A survey of points of sale was also included in the examination of consumer exposure. According to STTV guidelines, windshield washing fluids containing methanol should be sold in a locked space or one where access to the products can be limited. The guidelines further state that monitoring that only occurs at the cash counter of a retail outlet is insufficient, storage at the store entrance or outdoors is absolutely forbidden, and that toxic chemicals may only be turned over to people over the age of 18. The only exception to the latter condition is fuel, which can be handed over regardless of age. However, engine fuel containing methanol may only be handed over to people under 18 subject to written consent from that person's guardian (STTV 2000). A survey of 13 retail outlets conducted in early winter 2006 in the capital region showed that windshield washing fluids containing methanol were sold in open spaces, either among other goods or near the cash counter. Products were sold in hardware stores, spare parts shops and grocery stores. Gas station chains do not sell products containing methanol in the capital region. Only one outlet had a small sign near the product indicating that sales were forbidden to those under the age of 18. One grocery store clearly had splashes on the floor near the sales location for windshield washing fluid containing methanol. Product labels were compliant with the regulations, but the labels on products containing methanol often used the word odourless to advertise the products, which provides a misleading image of the product safety. The prices of the working solutions of the products surveyed (30) was

0.3-1.0 €/litre for methanol products and 0.7-1.2 €/litre for products not containing methanol (Uuksulainen, Riala et al. 2006).

### 8.1.2 CONSUMER INHALATION EXPOSURE WHEN USING WINDSHIELD WASHER FLUIDS

Consumer methanol exposure in bus passengers and passenger car drivers was studied in 2006. Methanol air concentrations were collected from four different bus trips (10 samples) and five different passenger cars (11 samples). Working solutions of different strengths were used. The buses used a working solution with frost resistance of -24°C and passenger cars used solutions with frost resistance of -8, -14 and -20°C. The so-called reasonable worst case is applied in exposure assessment in the REACH guidance documents. Methanol exposure was a maximum of about 3 $mg/m^3$ in the reasonable worst case for bus passengers during on journey of 1-3 hours in urban traffic. Exposure time was estimated to be 1-8 hours on a long-haul journey, in which case all-day exposure would be a maximum of about 8 $mg/m^3$. In passenger cars, exposure to the solvent substance increased clearly as the amounts used rose (0.4-3.0 l/h). In some car brands, windshield washing fluid consumption was higher because the fluid was simultaneously and automatically directed to washing the lights, and exposure was found to be higher in such cases. In passenger cars, methanol concentrations in the air increased to more than 27 $mg/m^3$ (or 13% of the $OEL_{8h}$ value) after even some two hours of use of a methanol product (frost resistance -20°C). When a methanol solution with frost resistance of -14°C was utilised, the DNEL of 27 $mg/m^3$ was exceeded during 4 hours of use. The highest exposure and reasonable worst case was obtained during copious use of a methanol solution with frost resistance of -20°C, in which case methanol exposure during 4 hours of use would be about 70 $mg/m^3$ (or 26% of the $OEL_{8h}$ value). The results lead to the conclusion that use of 10% methanol solution would probably give a concentration below 27 $mg/m^3$ (= 10% $OEL_{8h}$) when 4 hours of daily use is assumed and the amount used is unlimited.

Table 29. Average exposure of consumers travelling by bus and passenger car to methanol and other solvents used in windshield washing fluids during different periods of use (travel/driving time).

| Vehicle group<br>No. of samples<br>No. of cars | Solvent conc. in washing fluid % | Frost resistance °C | Washing fluid consumption l/h average (range) | Estimated travel/ driving time over 8 h | Estimated methanol exposure during 8 h day ($mg/m^3$) | Estimated methanol exposure during 8 h day (% OEL) |
|---|---|---|---|---|---|---|
| Bus passengers | | | | | | |
| Urban traffic<br>2 vehicles<br>4 samples | MeOH 30% | -24°C | 0.8<br>(0.4-1.2) | 3 h<br>2 h<br>1 h | 3<br><3<br><3 | 1<br><1<br><1 |
| Long-haul traffic<br>2 vehicles<br>6 samples | MeOH 30% | -24°C | 1.0<br>(0.7-1.2) | 8 h<br>6 h<br>4 h<br>2 h | 8<br>6<br>6<br>3 | 3<br>2<br>2<br>1 |
| Passenger cars (assumed maximum exposure duration 4 h) | | | | | | |
| 3 samples<br>3 vehicles | MeOH 24% | -20°C | 2.1<br>(1.2-3.0) | 4 h<br>2 h | 70<br>35 | 26<br>13 |
| 6 samples<br>3 vehicles | MeOH 19% | -14°C | 1.9<br>(0.5-2.7) | 4 h<br>2 h | 38<br>19 | 14<br>7 |
| 2 samples<br>2 vehicles | MeOH 12% | -8°C | 0.5<br>(0.2-0.7) | 4 h<br>2 h | 16<br>8 | 6<br>3 |
| 4 samples<br>3 vehicles | EtOH 25%<br>IPA 8% | -20°C | 1.9<br>(0.6-4.0) | 4 h<br>2 h | | 4<br>2 |
| 2 samples<br>1 vehicle | EtOH 55%<br>MEK 2% | -40°C | 3.5<br>(2.4-4.5) | 4 h<br>2 h | | 8<br>4 |
| 1 sample<br>1 vehicle | EtOH 22%<br>MEK 1% | -15°C | 0.6 | 4 h<br>2 h | | 1<br>0.5 |

MeOH=methanol, IPA = isopropyl alcohol, MEK = methyl ethyl ketone

### 8.1.3 MODELLING OF CONSUMER DERMAL EXPOSURE WHEN USING WINDSHIELD WASHING FLUIDS

Exposure during the dilution of windshield washing fluid was assessed using ConsExpo 4.1 and the EUSES program. According to the RIP 3.2-2 guidance of 2007 (RIP 3.2-2 SEG 5 09a rTGD-Part D-Occupational Oct 2007) instantaneous release and a ventilation factor of 0 l/h must be selected when modelling inhalation exposure with ConsExpo 4.1. The following source data was also used: 10 uses/year, body weight 60 kg (consumer), methanol concentration 0.2 kg/l (weight fraction compound 20%), 5 minutes of exposure time, room volume 48 $m^3$, 1 dl was selected as the amount of use (this was assumed to be the amount of 3 l of diluted fluid that evaporates), uptaken fraction 100%, amount inhaled by consumer 20 $m^3$/day (ConcExpo basic default), surface area of dermal exposure 420 $cm^2$ (one hand) and the amount in contact with the hands 0.5 dl.

ConsExpo calculates the internal dose. In REACH, consumer exposure is assessed as external dose with the exception of special cases (piercings, tattoos, administration of pharmaceuticals) where internal doses are used. When calculating the internal dose, ConsExpo uses skin permeability constants, and the model provides a value based on five different formulas (0.000328 -0.023 cm/hr for methanol).

The ConsExpo model provided a value of 417 $mg/m^3$ for inhalation exposure during a 5-minute dilution phase, from which the calculated daily dose was 1.45 $mg/m^3$ and the annual dose 0.0396

$mg/m^3$. ConsExpo provides an internal dose of 0.0132 mg/kg/day, which is the same as the external dose because 100% was selected as the uptaken fraction.

Dermal exposure to methanol in the dilution phase would be 23.8 $mg/cm^2$ (calculated: 50 $cm^3$ x 200g/$cm^3$/420 $cm^2$) and the amount of methanol in contact with the skin during dilution would be 167 mg/kg (calculated: 50 $cm^3$ x 200 mg/$cm^3$/60kg). Manually calculated from this figure, the average external dose of dermal exposure per day is 167 mg/kg x 10 /365 = 4.6 mg/kg/day.

The consumer section of the EUSES 2.0.3 model requires less source data than the ConsExpo 4.1 model (for example, the ventilation factor is not requested). The EUSES model calculates the amount of the substance in contact with the skin according to the surface area of the exposed skin and the layer thickness of the substance (default value), and does not use the amount of substance in contact with the skin in its assessment. When the same source data was used as for ConsExpo 4.1, the inhalation exposure was also assessed at 417 $mg/m^3$. The inhalation dose calculated from that figure was 0.0138 mg/kg/day. The EUSES program provided a dose of 0.4 mg/kg/day for dermal exposure, from which manual calculation of the short-term single dose would be 0.4 mg/kg/day x 365/10 = 14.6 mg/kg. This is ten times smaller than the dose calculated using ConsExpo.

The programs use different principles when calculating the external dose. The principle of the EUSES model, in which assessment of the amount of substance in contact with the skin is based on the surface area of skin in contact with the substance and the layer thickness of the substance seems better than an assessment based only on the amount of substance (ConsExpo model).

The results provided by the models are presented in risk characterisation table 30 below.

### 8.1.4 HEALTH RISK CHARACTERISATION

The modelling presented here is based on exposure assessments, and the resulting risk relationships are rough assessments that may be over-estimated due to the undeveloped nature of the models. More developed versions of the models or other models will be used in the final exposure scenarios. Exposure assessment based on measurements is closer to the actual exposure level.

A risk characterisation was performed for uses of the products included in the exposure measurements. The highest exposure and reasonable worst case in passenger cars, assuming a maximum exposure time of 4 h, was obtained during plentiful use of a methanol solution with frost resistance of -20°C, in which case methanol exposure would be about 70 $mg/m^3$. Exposure for bus passengers was calculated for eight hours and exposure in this case would be less than 8 $mg/m^3$.

Table 30. Preliminary health risk characterisation for consumer use of methanol containing windscreen washer fluid (product containing 24 % of methanol).

| A) Exposure route and duration | B) Preliminary DNEL | C) Exposure level | D) Comparison, C/B must be <1 |
|---|---|---|---|
| 1) acute exposure 15 min | | | |
| inhalation exposure | 232 mg/m$^3$<br>dose: 1,2 mg/kg/15 min | (417 mg/m$^3$ (EUSES) x 5 min (time for one dilution)) / 15 min = 139 mg/m$^3$<br>dose: 0,72 mg/kg/15 min | <1 |
| dermal exposure | 1,2 mg/kg/15 min | 0,4 mg/kg/d (EUSES),<br>dose: 14,6 mg/kg/dilution | >1 hand protection needed |
| total exposure | 1,2 mg/kg/15 min | 15,32 mg/kg/15 min | >1 |
| 2) long-term 24 h | | | |
| inhalation exposure | DNEL= 27 mg/m$^3$ (4 h/d) 4,5 mg/m$^3$ (24 h) dose:1,5 mg/kg/d | measured:<br>avegage (4 h): 70 mg/m$^3$ (passanger car)<br>average (24h): 12 mg/m$^3$<br>dose: 4 mg/kg/day | >1 (methanol content should be lowered) |
| dermal exposure | no needed here | no dermal exposure during driving | - |
| total exposure | not defined here | not defined here | - |

Because the risk characterisation exceeded preliminary DNEL levels for both long-term and acute exposure, product composition was changed to reduce exposure as other risk management measures cannot be recommended for consumers. Maximum amounts of use cannot be set for consumers either. For example 10% methanol concentration is recommended for products sold as windshield washing fluid. In that case, the dilution phase would not be required and acute exposure would not have to be taken into consideration, meaning that consumer inhalation exposure during four hours of use would probably remain below 27 mg/m$^3$. This is based on the extrapolation of own measurement information (see table 29) and cannot be ascertained through models because the use situation for windshield washing fluid is a special situation (use outside a vehicle and driver exposure via the incoming air) that the models are unable to take into consideration.

### 8.1.5 ENVIRONMENTAL RISK CHARACTERISATION

The environmental exposure assessment for the use of windshield washing fluids performed with EUSES 2.0.3 is presented in section 7.8. The local concentration of methanol obtained through modelling exceeded the PNEC value, and thus a water sample was analysed to check the environmental concentration. Based on the environmental sample, concentrations were below the PNEC value of 2.24 mg/l.

### 8.1.6 INITIAL EXPOSURE SCENARIO

Table 31. Initial exposure scenario for consumer use of methanol containing windscreen washer fluid.

| | |
|---|---|
| 1. Short title | Sector of use: Z Public domain<br>Product category: PC 35 Washing and Cleaning products (including solvent based products)<br>Process category: PROC 11 Spraying outside industrial settings or applications. |
| 2. Description of activities and processes covered | Consumer use of methanol in windscreen washing fluids (passengers in busses and passenger cars and drivers of private cars. Various exposure situations: washing of windscreen and driving lights during driving and filling washing fluid tanks.) |
| Conditions of use | |
| 3. Duration and frequency of use | Used in winter weather, snowy or wet driving conditions. Normal car ventilation and fan on operation mode. The frequency varies according to weather conditions and use habit. Duration: passenger in city busses about 3 hours per day, long-distance busses up to 8 hours per day, passenger cars the use varies (the maximum use was set to 4 hours). |
| 4.1 Physical form of the substance | Liquid solvent, flammable, highly volatile. |
| 4.2 Concentration of substance in the product (% substance in the mixture or preparation) | Methanol content in products lowered for example to level 10 %. |
| 4.3 Maximum amount of use per time | Not possible to set for this use. |
| 5. Other operational conditions<br>Temperature, pressure, volume of the environment/room size | Car indoor temperature (about 20 C°). |
| Risk management measures (=Risk Management Measures = RMM), which together with the conditions of use guarantee safe use. | |
| 6.1 Worker exposure RMM<br>(to the final scenario phrases are taken from the RMM library and more data on the effiency is added) | The methanol consentration of the used washing fluid should be less than 10 %. Safe storage procedures in selling the product and in handling. Only adults are allowed to purchase the product. |
| 6.2 RMM in environmental exposure<br>(wastewater, air and soil) | According to measured environmental sample analyses the methanol concentrations were less than the detection limit 1 mg/l and there were no need for lowering environmental risk. |
| 7. Waste handling and RMM | Methanol containing wastewater should be drained to sewage system. |
| Exposure assessment and the methods how the downstream user can estimate that the conditions of the use described in the exposure scenario are followed | |
| 8. Exposure estimation<br>and reference to its source | For the the final exposure scenario move the data from the final risk characterization table 30 here (now the table is preliminary). Inhalation exposure is evaluated by measured data, because no model is appropriate in this special use. |
| 9. Guidance to the downstream user to evaluate whether he works inside the boundaries set by the ES | In the final exposure scenario guidance is given e.g. about the correlation between the amount of use and exposure time to the exposure. |

### 8.1.7 COMPARISON WITH USE OF OTHER WINDSHIELD WASHING FLUIDS

Table 29 also presents the results of exposure measurements for other windshield washing fluids. Ethanol-based windshield washing fluids were studied as comparative products in five consumer vehicles. One of the fluids contained isopropanol and the other a small amount of methyl ethyl ketone. Seven samples were taken and the working solutions had a frost resistance of -15, -20 and -40°C. The co-exposures of the solvent substances during use of the products containing ethanol and isopropanol with a frost resistance of -20°C would be a maximum of 4% of the OEL value over four hours of use. The co-exposure of the solvent substances when using a product containing ethanol and a small amount of methyl ethyl ketone would be a maximum of about 8% of the OEL value during plentiful use of an undiluted solution (frost resistance -40 °C) over a period of four hours. However, an undiluted solution is not generally used, and the working solution is usually diluted so that frost resistance is -20°C. With less use and a diluted solution with frost resistance of -15°C, concentrations of the corresponding ethanol and methyl ethyl ketone solution would be about 1% of the OEL value during four hours of use. According to these results, co-exposure of the solvent substances during use would clearly be several times smaller than when using methanol products (Uuksulainen, Riala et al. 2006). Because the OEL value for ethanol is seven times higher and that for isopropanol two times higher than that of methanol, we can assume that future DNEL values for these substances will also be higher than for methanol. We estimate that use of these substances in windshield washing fluids will not pose any health risk to consumers.

## *8.2 USE OF METHANOL-BASED FUELS*

### 8.2.1 USE OF SPECIAL METHANOL-BASED FUELS

Use of methanol-based fuels was surveyed by searching for applications using internet search engines and by asking combustion engine hobby groups and individuals about their use. The study concerning the use of methanol-based fuels was reported upon in the interim project report (Uuksulainen, Riala et al. 2006).

Methanol is used as 100% fuel in three speedway 500 cc motorcycle classes (speedway, ice speedway and dirt track), three drag racing classes (Pro Modified, Top Methanol Dragster, Top Methanol Funny Car) and five tractor pulling classes. In addition, the fuel for one motorcycle drag racing class (Super Twin Top Fuel) contains 10% methanol. Methanol is also used in two miniature car classes (TP-10 and M-8), where the fuel contains 60-80% methanol. The fuel used in five different model plane classes contains 70-75% methanol. The estimated number of individuals using methanol in all situations involving recreational combustion engines is about 1100-1300, and annual methanol consumption 30-49 tons. Persons under the age of 18 include at least speedway drivers and model plane hobbyists. The age distribution among miniature car hobbyists starts at seven.

There are 130-300 speedway drivers and they use 9300-31800 litres, or 7-25 tons of methanol annually, depending on the amount of practice. Methanol is purchased from suppliers at competitions and through other channels. There are currently 6 drag racing cars and 12 tractor pulling vehicles in Finland. Because a team includes several mechanics in addition to the driver, there are approximately 80 people involved and they use about 6000 litres, or 5 tons, of methanol in competitions each year. Fuel is purchased from specialist car supply outlets.

Miniature cars that are powered by combustion engines consume 2500-3000 litres, or 2-3 tons, of methanol each year. There are about 80-120 hobbyists, and they mainly purchase their fuel from internet online shops. The fuel sold by online shops is primarily imported from the USA or Germany. In September 2006, 10 suppliers offering a total of 51 products were found on the internet. Four other products could also be found in the KETU register (STTV's Product Register of Chemicals). Only one online seller's products were registered in the KETU register in September 2006.

The amounts of methanol used by model plane operators are based on an environmental report from the Finnish Aeronautical Association in 2002 (Borg 2002), which in turn is based on 1998 estimates of the number of model plane operators. The number of hobbyists is 800 and the number of flights each year about 25, with consumption standing at about one litre of methanol each time. Based on this information we can conclude that annual consumption is 20,000 litres, or 16 tons, of methanol. Fuel is mainly purchased from online shops. In September 2006, two online shops offering nine different products were found on the internet. These products were not in the KETU register at that time.

### 8.2.2 CONSUMER EXPOSURE WHEN USING METHANOL-BASED FUELS AND RISK MANAGEMENT MEASURES

Use of methanol-based fuels was studied in speedway races, drag racing, miniature car driving and model plane flying. A total of 11 air samples were taken from the breathing zone atmosphere. A total of 7 biomonitoring samples were taken, 2 from speedway drivers and 5 from drag racing hobbyists.

The highest exposure via the air in combustion engine uses occurred during drag racing, where 40 litres of methanol was used over a 4-hour period. However, concentrations assessed for the whole day would only have been about 6 $mg/m^3$. About 6 litres of methanol was used per motorcycle in speedway races. Concentrations assessed for the whole day would have remained below 1 $mg/m^3$ in speedway use. Daily amounts used in miniature car driving and model plane flying were one litre or less, and the methanol air concentrations resulting from such use remained below the limit of detection.

Biomonitoring samples showed that the average formic acid concentration in the urine for drag racing or speedway hobbyists was less than the reference limit for non-exposed population, and only one sample exceeded the reference limit. The concentration in this sample was 26% of the reference limit. According to current interpretations, the result shows that exposure to methanol or formic acid is slight.

Dermal exposure cannot be excluded and because fuel use involves nearly pure methanol, protective gloves should be used when filling the tanks. Use of protective gloves is also justified because this consumer application can be considered a borderline case between professional and consumer use.

### 8.2.3 ENVIRONMENTAL EXPOSURE

Environmental exposure when using methanol-based fuels is probably very slight due to the relatively small amounts used. It is also likely that all environmental emissions are air emissions due to the volatility of methanol. More detailed modelling of environmental exposure was not performed in this project.

### 8.2.4 HEALTH RISK CHARACTERISATION

The modelling presented here is based on exposure assessments, and the resulting risk relationships are rough assessments that may be over-estimated due to the undeveloped nature of the models. More developed versions of the models or other models will be used in the final exposure scenarios. Exposure assessment based on measurements is closer to the actual exposure level.

The exposure information gained through measurements was compared to the preliminary DNEL value of 27 mg/m³ determined according to long-term, 4-hour consumer inhalation exposure. All the concentrations measured were below this level.

Dermal exposure was assessed using the consumer section of the EUSES model. The following source data was used: 10 uses/year, body weight 60 kg (consumer), methanol concentration 0.79 kg/l (weight fraction compound 20 %), 5 minutes of exposure time, room volume 500 $m^3$ (maximum was set), 1 dl was selected as the amount of use (this was assumed to be the amount of the fluid used that evaporates), uptaken fraction 100%, amount inhaled by consumer 20 $m^3$/day (ConcExpo basic default), surface area of dermal exposure 420 $cm^2$ (one hand) and amount in contact with the hands 0.1 dl.

When modelling dermal exposure, it is assumed that methanol spillage on the skin will be equivalent to the surface area of one hand. This is assumed to be the worst case with regard to dermal exposure. In view of the properties of methanol, use of gloves when filling the methanol tanks manually is justified.

Table 32. Preliminary health risk characterisation for consumer use of methanol-based fuels.

| A) Exposure route and duration | B) Preliminary DNEL | C) Exposure level | D) Comparison, C/B must be < 1 |
|---|---|---|---|
| 1) Acute exposure15 min (tank filling 5 min) | | | |
| Inhalation exposure | 232 mg/$m^3$<br>Dose: 1.2 mg/kg/15 min (consumer = 60 kg) | (200 mg/$m^3$ (EUSES)x5 min.)/15 min.<br>= 67 mg/$m^3$<br>Dose: 0.35 mg/kg/15min. | <1 |
| Dermal exposure | 1.2 mg/kg/15 min. | 1.58 mg/kg/day (EUSES), from which the acute dose is calculated (x 365/10)= 57.7 mg/kg/filling | >1 Protective gloves needed |
| Total exposure | 1.2 mg/kg/15 min. | 58 mg/kg/15 min. | >1 |
| 2) Long-term exposure 24 h (methanol-based fuel use, max. 4 h during the entire day) | | | |
| Inhalation exposure | 27 mg/$m^3$ (4h) (consumer)<br>4.5 mg/$m^3$ (24 h)<br>Dose: 1.5 mg/kg/day | Measured:<br>$ka_{4h}$= 6 mg/$m^3$ (drag racing use)<br>$ka_{24h}$= 1 mg/$m^3$<br>Dose: 0.33 mg/kg/day | <1 |
| Dermal exposure | Not needed here | No dermal exposure during use | - |
| Total exposure | Not determined | Not determined | - |

### 8.2.5 INITIAL EXPOSURE SCENARIO

Table 33. Initial exposure scenario for consumer use of methanol-based fuels. Does not include an environmental assessment.

| | |
|---|---|
| 1. Short title | Sector of use: Z Consumer use<br>Type of preparation: PC 13 Fuels<br>Use: PROC 16 Using material as fuel sources, limited exposure to unburned product to be expected. Consumer use |
| 2. Description of use/process | Motor sports (speedway, drag racing), recreational use, miniature car driving and model plane flying where the fuel is methanol. |
| Operational conditions | |
| 3. Duration and frequency of use | 1-4 hours/day, 5-40 times/year depending on the activity |
| 4.1 Physical form of the substance | Liquid solvent, flammable, very volatile |
| 4.2 Concentration in the product (% of substance in the mixture) | Methanol concentration in the fuel used is 60-100%, other substances include nitromethane. |
| 4.3 Maximum amount used per time or activity | 0.5-20 litres/time depending on the activity. Greatest amounts used in drag racing. |
| 5. Other operational conditions<br>Temperature, pressure, capacity of receiving environment/space (room size x ventilation rate), emission or release factors according to the technology used | Outdoor temperature, outdoor facilities or well-ventilated shelters. |
| Risk Management Measures (RMM) that, in combination with the operational conditions of use, ensure safe use of the product | |
| 6.1 Risk management measures related to consumer exposure (efficiency must be described, specified effect via different exposure routes (oral, skin and inhalation) | (The final scenario will include statements from the RMM library and provide information about the efficiency of protective equipment).<br>Risk of fire. Smoking forbidden near the fuel handling site.<br>Use of protective gloves (buryl rubber, fluoro rubber, Teflon, laminated plastic materials) when handling the fuel.<br>Flammability and toxicity of the product must be taken into consideration in sales and storage. Safe sales and storage space. STTV (Valvira) guidelines must be observed. |
| 6.2 Risk management measures related to environmental exposure (to waste water, air, soil) | Not performed in this exposure scenario. |
| 7. Risk management measures related to waste handling | Waste water containing methanol must be discharged into the sewer. |
| Exposure assessment and means for the downstream user to assess compliance with the operational conditions of use in the exposure scenario | |
| 8. Exposure estimation<br>and reference to its source | For the the final exposure scenario move the data from the final risk characterization table 32 here (now the table is preliminary). |
| 9. Guidance to the downstream user to evaluate whether he works inside the boundaries set by the ES | In the final exposure scenario guidance is given e.g. about the correlation between the amount of use and exposure time to the exposure. |

# 9 BIOMONITORING IN EXPOSURE ASSESSMENT

The results of occupational hygienic and biomonitoring measurements are summarised in table 34. The highest measured air concentrations were in production of windshield washing fluids and the second highest in the pharmaceutical industry. The general ventilation was the only technical measure for reduction of exposure in the first workplace in production of windshield washing fluids. In the second workplace also local hoods and personal protective equipment were in use. In the pharmaceutical industry the duration of the workphases was very short and local hoods were in use. The exposures in production of windshield washing fluids and pharmaceutical industry for the entire day or a shorter period (15 minutes) exceeded the preliminary DNEL -values set in this project.

Methanol concentrations in laboratory work and consumer uses were below DNEL -values. In the laboratories the most effective technical measures were used and all workphases were performed in fume cupboards. The consumers used methanol in outdoors shelters where methanol quickly evaporated to atmosphere without entering their breathing zone.

Due to above mentioned facts the comparison of the workers' inhalation exposure with their total exposure was very challenging, because occupational hygienic samples was not taken inside personal protective equipments. The amount of material was also relatively small. Furthermore, exposure was focused on certain parts of the day at different workplaces and temporal variation in exposure was large.

Table 34. Workers' urinary excretions of formic acid (U-Formia) and methanol (U-MeOH) and methanol concentrations in the air of workplace.
l.t.= long-term, s.t.= short term, inh.= inhalation exposure (*creatinine)

| | Object and work | Task | Exposure time h or min/day | Exposure calculated for the entire day $mg/m^3$ | U-Form (pre sift-next morning) | U-MeOH (pre sift-end of shift) | Notes |
|---|---|---|---|---|---|---|---|
| | | | | | mmol/mol * | µmol/l | |
| | | | | $DNEL_{l.t.inh}$ = 67.5<br>$DNEL_{l.t.inh}$ = 270* | Unexposed 70<br>Reference level 200 | Proposal unexposed 170 | |
| 1 | Consumer 1. Drag racing hobbyists | Speedway driver<br>Speedway driver | Max.<br>12 h/day | 0.3<br>0.3 | 50-27<br><20-34 | - | Concentration dilutes and evaporates quickly outdoors or under a shelter |
| 2 | Consumer 2. Speedway driving hobbyists | Refueller /mechanic<br>Assistant<br>Driver<br>Assistant<br>Mechanic | Max.<br>4 h/day | 5<br>5<br>5<br>2<br>4 | <9-23<br><17-21<br>30-62<br><23-20<br>18-26 | - | Concentration dilutes and evaporates quickly outdoors or under a shelter |
| 3 | Manufacture of windshield washing fluid | Container filling and mixing<br>Transfer to/from containers<br>and other work<br>All-day exposure | 0.5 -1 h<br>2-3 h<br>0.5-1h<br>2-3 h | 111-219<br>170-420<br>313-600 | 37-62[1] | - | Only general ventilation in the space, [1] provided too late, 1 pm? |
| 4 | Manufacture of windshield washing fluid | Transfer to/from containers outside the production room<br>Max.<br>all-day exposure | 1-2 h<br>5-7 | 22-43<br>3<br>25-46 | 90-86 | No result obtained | Powered air purifying respirator mask AX, local exhaust ventilation in use |
| 5 | Pharmaceutical industry solvent | Sampling from reactor<br>Reactor rinsing<br>Reactor emptying<br>Sampling from distillery | 5 min<br>5 min<br>34 min<br>6 min | 13*<br>300*<br><3<br>4* | 38-35<br>38-35 | 7-10<br>32-4 | All work phases are short |
| 6 | Pharmaceutical industry solvent | Use of extraction | Daily, max. 6 h/day | 127-502 | 50-55<br>42-50<br>49-30 | 14-75<br>7-29<br>9-19 | Air fed hood |
| 7 | Laboratory use (MS runs) | Pipetting of methanol solution and production of solutions | 1-3 h/day | <3 | 22-11<br>19-39<br>67-64<br>30-23<br>49-56 | 60-12<br>4-9<br>7-140<br>11-50<br>19-15 | Work in a fume cupboard |
| 8 | Laboratory use | Laboratory use Rotational evaporation | Max. 1-2 h/week | <3 | 21-60<br>117-93 | 5-6<br>19-40 | Work in a fume cupboard |
| 9 | Laboratory use | HPLC laboratory<br>Chromosome laboratory | 1-2 h/week<br>0.5-1 h/week every other month | 12<br>< 3 | 18-20<br>21-20<br>21-38<br>29-36<br>76-18<br>85-105<br>110-100 | 13-31<br>130-88<br>36-54<br>6-14<br>30-33<br>8-8<br>17-9 | General ventilation<br>Work in a fume cupboard |
| | Total samples | | | 48 | 56 (28 different people) | 38 (19 different people) | |

The average urinary formic acid excretions in four exposure groups are shown in figure 10. The highest average urinary excretions were found in production of windshield washing fluids and the second highest in the pharmaceutical industry where also the highest air concentration in occupational hygienic measurements was found. On the contrary the urinary formic acids concentration was far below biological action limit value for formic acid, but the reference limit value for non-exposed population was exceeded in the manufacture of windshield washing. The lowest average excretion of formic acid was measured in laboratory and consumer use, where also the lowest methanol concentration in workplace air was measured. All urinary excretions of formic acid were below reference limit for non-exposed workers except in few cases in laboratory use. This might be indication of possible dermal exposure to methanol in the laboratory use.

The average urinary excretion of methanol in two exposure groups is shown in figure 11. The data was quite limited and only applied from the pharmaceutical industry and laboratory use. The measured concentrations showed that background concentrations increased more in the pharmaceutical industry than in laboratory use. However, average methanol excretions were all below the reference limit for non-exposed population. Urinary methanol seems to be useful method if it is possible to collect urine samples before and immediately after the work shift. Comparison of these samples might give information about exposure to methanol at lower level than formic acid excretions does.

Biomonitoring is essential in exposure assessment when dermal exposure is possible. Biomonitoring can also offer the tool to test the sufficiency of protective gloves. On the other hand, biomonitoring can help to determine the sufficiency of overall risk management in situations where respiratory protection was also used due to the high methanol concentration in the air.

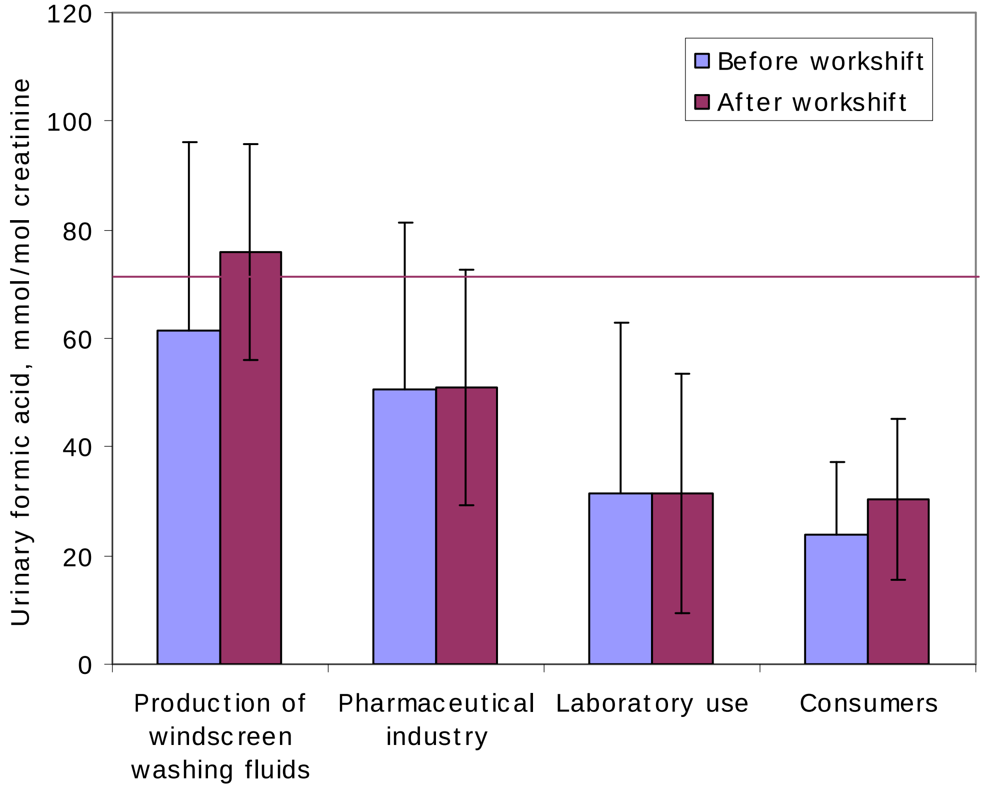


Figure 10. Average excretion of formic acid before workshift and 16 hours after end of exposure in different sectors

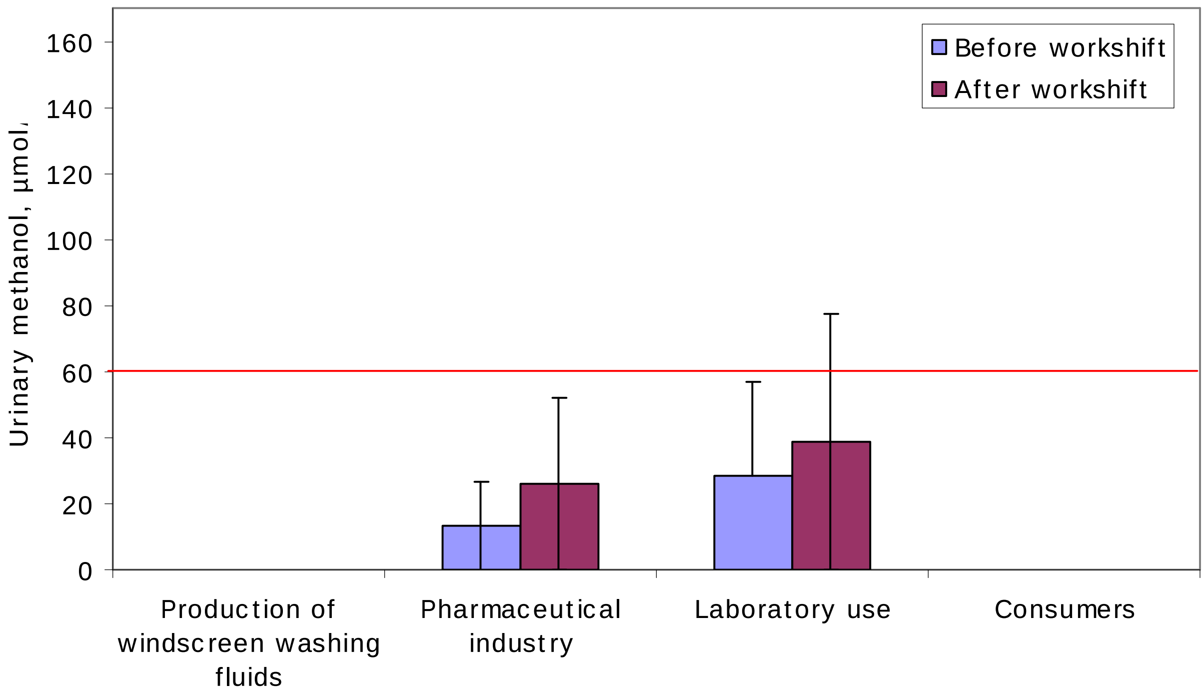


Figure 11. Average methanol excretion before and immediately after workshift in different sectors

# 10 CONCLUSIONS AND RECOMMENDATIONS

This project was successful in determining the main Finnish uses of methanol. Collection of the application and exposure data proved to be quite demanding, and it was gathered from many different sources. In this project, the questionnaires for downstream users proposed in the REACH Regulation to determine use of the substance, applications and exposure were only performed for the project's new measurement targets. It is advisable to schedule sufficient time to collect the application information needed in the actual registration process and other information about the downstream user. In this case, each registering body creates an exposure scenario only for those applications utilising the methanol it imports into the EU area or manufactures in the EU area. The applications were grouped into 10 different exposure scenarios or exposure categories. Since the REACH Regulation provides leeway in the grouping of applications, methanol applications could also be grouped in different ways than that used in this project. One possibility could be the specification of the most exposing work phases into a separate exposure scenario. These could include the grouping of maintenance work in different industry sectors or open industrial use of methanol into a separate category.

The exposure levels were measured on the basis of the reasonable worst case. Because it is difficult to measure dermal exposure to methanol, assessment of dermal exposure was done using modelling. The results provided by modelling are likely to over- and, in part, under-assessments the risk. The models are currently under development, and preliminary assessments of exposure levels will be done via modelling in the future. However, when compiling the final exposure scenarios, measurement of exposure is also likely to be necessary in many cases. The RIP guideline documents specify measurement as the primary method for assessing exposure. The usability of biomonitoring in exposure assessment was examined in several applications. On the basis of the limited material of this project, we decided that biomonitoring was beneficial in this methanol study with regard to ensuring a sufficient level of protection level and assessing dermal exposure.

In view of the REACH regulation guidelines, preliminary DNEL and PNEC values were set in the hazard assessment of methanol. It is notable that in actual registration, the REACH Regulation requires the collection of all existing research information and assessment of the details of key studies. The SIEF Forum (Substance Information Exchange Forum) for companies registering methanol may include hazard property information that is not generally available, and for that reason the final DNEL (or PNEC) assessment may differ from what is presented here.

The aim of the project was to practice creating exposure scenarios, and the risk management methods presented in the report may differ from the final exposure scenarios created by the registering body. However, when registering methanol similar risk management measures may be presented in many applications, depending on what kind of limit values (DNEL/PNEC) and scenario-specific exposure levels are decided upon in the registering body. In many applications, workers' exposure exceeded the OEL values currently in use, meaning that the proposed risk management measures are justified, particularly for workers Applications in which the OEL values were exceeded were manufacturing of windshield washer fluids, maintenance work at waste water treatment plants and short-duration methanol loading and unloading work. Exposure in several industrial applications (short-duration service procedures at reactors, use of extraction solvents or use of roller washing solvent) was also significant and exceeded the current OEL values in some cases.

In the exposure scenarios, we proposed risk management measures that can reduce exposure to a level that is unlikely to pose a health hazard. As risk management measures we recommended the use of personal protective equipment when loading and unloading methanol. New work arrangements and the use of personal protective equipment can reduce methanol exposure in maintenance work at waste water treatment plants. In the manufacturing of windshield washer fluids, the work should be carried out in a well-ventilated space fitted with an efficient local exhaust ventilation system, and the worker must also use personal protective equipment. Working arrangements, efficient local exhaust ventilation system, and personal protective equipment would be necessary in industrial extraction and solvent use of methanol and in maintenance work and barrel fillings in chemical products manufacturing. According to our estimate, the processing of methanol in laboratories should always be carried out inside a fume cupboard.

The scenarios must take into account the possible overlapping of different scenarios. The applications of worker and consumer exposure overlapped in the use of methanol in windshield washer fluids in taxis. In this case, consumer limit values and consumer risk management measures were applied in taxis and other professional traffic. Consumer exposure to methanol in windshield washer fluids was assessed as excessive. As the risk management measures recommended to consumers are mainly product-specific, lowering the methanol content of windshield washer fluids sold to consumers can reduce exposure. Consumers' use of methanol-based fuels was considered to be a more specific consumer application, a borderline case between professional and consumer use, in which case we proposed the use of protective gloves in the exposure scenario to ensure safe use.

Exposure scenarios were not created for all applications, because the required information was not available. These applications included manufacturing of products containing methanol as a solvent (excluding production of windshield washer fluids) and the use of products containing methanol in industry and at workplaces. Products containing methanol often contain other substances that must also require registration. The manufacturer of such a product can compile its own exposure scenario for the product users that outlines the hazards of all the substances contained in the product.

The input of many experts is needed when developing exposure scenarios. FIOH had access to toxicologists and experts in occupational medicine and nervous system diseases for hazard assessment, occupational hygienists, chemists and measurement hygienists for collecting and assessing exposure data. When assessing environmental hazard, we received assistance from the Finnish Environmental Institute. When creating the final exposure scenario, expertise in occupational safety and protective equipment is also needed to ensure that risk management measures can be reasonably and sufficiently focused with regard to the extent of the risks.

Implementation of the project was challenging, because the guidelines for the REACH regulation were under preparation throughout the project and we always tried to apply the draft guidelines of the latest RIP (Reach Implementation Project). The guidelines were still unfinished at the end of the project.

In principle, REACH addresses individual substances and does not take into account the interactions of different exposure agents. However, separate exposure scenarios can be done for the substances, in which case the additive nature of hazards should be taken into consideration, at least according to the current drafts. In contrast, if the overall exposure of the application comprises exposure from several different substances, this cannot be taken into account in REACH. For example, in laboratory work the exposure caused by individual substances in the waste solvent treatment phase may be limited, but the overall exposure to solvent substances significant. In such cases, the existing legislation (Government Decree 715/2001 on Chemical Agents at Work and Ministry of Health and Social Affairs Decree 795/2007 on Concentrations Known to be Hazardous), which cover all preparations and substances. Thus REACH will supplement the existing legislation.

# 11 APPENDICES

APPENDIX 1a. Applications and occurrences of methanol in work-related exposure. Compiled on the basis of the FIOH measurement register data and information collected in the project. A total of 55 applications or occurrences were found for work-related exposure, 33 of which were included in the exposure scenarios of this project (=I).

| | Application | Sector | Intended use/ methanol source | Amounts of methanol t, number of exposed |
|---|---|---|---|---|
| 1. | Loading, unloading and transfer to/from containers (4 applications (=I) included in the scenario) | | | Approx. 150,000 t imported in 2002-2005, hundreds exposed |
| 1.1 M | o | import harbours: loading from ships | | |
| 1.3 M | n | loading to tanker vehicles and unloading 3 n | | |
| 1.2 M | o+n | import by rail: unloading of train tank 1o + 2n | | |
| 1.4 M | n | Transfer of methanol to barrels | | |
| 2. | Manufacturing of chemical products (10 applications (=I) included in the scenario) | | | Approx. 130,000 t (KETU 2006),hundreds exposed |
| 2.1 M | o | Manufacturing of formaldehyde | raw material in reactions and stabilisation substance | 60,000 t (Riistama, Laitinen et al. 2005) |
| 2.2 M | o | Manufacturing of chlorine dioxide (always done at the use site, see paper industry pulp manufacturing | raw material | |
| 2.3 M | no | Manufacturing of antislime agent (biocides) | raw material an/or from methanol formaldehyde | |
| 2.4 M | n | Manufacturing of formic acid | raw material | |
| 2.5 M | no | Manufacturing of methyl formate | raw material | |
| 2.6 M | n | Manufacturing of potassium methylate and sodium methylate | raw material | |
| 2.7 M | n | Manufacturing of sodium boron hydride | raw material | |
| 2.8 M | n | Manufacturing of trimethyl boron | raw material | |
| 2.9 M | n | Manufacturing of biodiesel n | raw material for the esterisation process | Approx. 300 t/year, 20-40 exposed |
| 2.10 M | +n | Manufacturing of petrol additives: MTBE, TAME | raw material | |
| 2.11 | o | Manufacturing of fertilisers | methanol from formalin | |
| 2.12 | n | Manufacturing of waste water treatment chemical | methanol from formalin | |
| 3. | Use of methanol as a process chemical (1 application (=I) included in the scenario) | | | 3,500-4,000 t /a, dozens exposed |
| 3.1 M | n | Waste water purification plants | as a carbon producer, nutrients for microbes | |
| 4. | As a solvent in manufacturing of products containing methanol (1 application (=I) included in the scenario) | | | Manufacturing of windshield washing fluids, approx. 1,700 t |
| 4.1 | no | Manufacturing of paints and dyes as well as paint removers | solvent | |
| 4.2 | o | Manufacturing of glues<br>4.2.1 resorcinol<br>4.2.3 urea and melamine resins<br>4.2.3 phenoformaldehyde resins | methanol from formaldehyde | |
| 4.3 M | n | manufacturing of windshield washer fluids | solvent | 1,700 t (KETU 2006), dozens exposed |
| 4.4 | no | Manufacturing of fuels containing methanol | as a fuel | |

n = study of a new application done in the project, o = old applications from the FIOH register or companies

no = no exposure data

APPENDIX 1b. Applications and occurences of methanol in work-related exposure. Compiled on the basis of the FIOH measurement register data and information collected in the project. A total of 55 applications or occurrences were found for work-related exposure, 33 of which were included in the exposure scenarios of this project (=I).

| | Application | Sector | Intended use/ methanol source | Amounts of methanol t, estimated number of exposed |
|---|---|---|---|---|
| 5. | Use of methanol as a solvent in industry (excluding laboratory use) (8 applications (=I) included in the scenario) | | | 30,000 t (KETU 2006) hundreds exposed? |
| 5.1 M | o+ n | Pharmaceutical industry: Manufacturing of pharmaceutical substances or preparations | as a solvent, in extraction | thousands of tons? |
| 5.2 M | o | Manufacturing of resin | as a solvent | |
| 5.3 M | o | Paper industry: paper impregnation many o | roller washing | |
| 5.4 M | o | Printing industry: manufacturing of textiles (silkscreen printers) other printing industry | as a solvent in printing dyes | |
| 5.5 M | no | Production of sitosterol | as an extraction solvent | |
| 5.6 M | o | Repair activities | putty removal, paint removal | |
| 5.7 M | o | Electronics industry, instrument manufacturing | resist removal, as a solvent in gel | |
| 5.8 M | no | Natural gas network | inhibitor of hydrate formation | |
| 6. | Use of products containing methanol in industry and at workplaces (no scenario created for these uses) | | | |
| 6.1 | o | paper industry and pulp manufacturing | methanol from chlorine dioxide or antislime agent | |
| 6.2 | o | paper impregnation | methanol from resin formaldehyde | |
| 6.3 | o | Manufacturing of plywood, chipboard, fibreboard and other wood panels | methanol from resin formaldehyde | |
| 6.4 | o | Coating plant | methanol from resin formaldehyde | |
| 6.5 | o | Manufacturing of grinding products | methanol from resin formaldehyde | |
| 6.6 | o | Mineral and fibreglass industry | methanol from resin formaldehyde | |
| 6.7 | o | Foundries | methanol from resin formaldehyde | |
| 6.8 | o | Textile industry: silkscreen printers and other printing industry | in printing dyes and solvents methanol | |
| 6.9 | o | Manufacturing of rollers | glue methanol from formaldehyde | |
| 6.10 | o | Use of gloss additive in the zinc coating basin | methanol in the gloss additive one product 3-5 % MeOH in KETU | |
| 6.11 | no | Use of foundry resins | methanol from methyl formate | |
| 6.12 | no | Manufacturing of silane | methanol from potassium or sodium methylate | |
| 6.13 | no | Manufacturing of pigments, perfumes and cosmetic products | methanol from potassium or sodium methylate | |
| 6.14 | no | As an auxiliary substance in welding | methanol from trimethyl borate | |
| 6.15 | no | Use of marking dyes and paint removers | methanol in marking dyes and paint removers | |

n = study of a new application done in the project, o = old applications from the FIOH register or companies

no = no exposure data

APPENDIX 1c. Applications and occurrences of methanol in work-related exposure. Compiled on the basis of the FIOH measurement register data and information collected in the project. A total of 55 applications or occurrences were found in work-related exposure, 33 of which were included in the exposure scenarios of this project (=I).

| | Application | Sector | Intended use/ methanol source | Amounts of methanol t, estimated number of exposed |
|---|---|---|---|---|
| 7. | Laboratory work<br>8 different applications (8 applications (=I) included in the scenario) | | | Approx. 50 t (KETU 2006)<br>thousands exposed? |
| 7.1 M | o | Manufacturing of reagent, methanol cleaning | raw material | |
| 7.2 M | o | Preparation of pharmaceuticals in pharmacies | solvent | |
| 7.3 M | o | Various analyses: incl. ochratoxin assay, lignan isolation, PAH analysis, fatty acid assay, vitamin assays | solvent | |
| 7.4 M | o | Use of antifreeze | solvent, antifreeze protection | |
| 7.5 M | o+n | Tissue staining | solvent | |
| 7.6 M | o | HLPC analysis, or high pressure liquid chromatography use | solvent | |
| 7.7 M | o | Use of glue cleaner | solvent | |
| 7.8 M | n | Mass spectrometer work | solvent | |
| 8. | Use of products containing methanol in professional traffic (1 application (=I) included in the scenario) | | | All windshield washer fluid use 1,700 t (KETU 2006)<br>tens of thousands exposed |
| 8.1 M | o+n | Use of windshield washer fluids | in windshield washer fluid | |
| 8.2 | no | Use of biodiesel | < 0,2 % MeOH, | |
| 9. | Treatment of waste containing methanol (included in different scenarios) | | | |
| 9.1 | o | Bottling and analysis of head-space specimen | disposal of solvent | |

n = study of a new application done in the project, o = old applications from the FIOH register or companies

no = no exposure data

APPENDIX 1d. Applications and occurrences of methanol in consumer exposure. Compiled on the basis of the FIOH measurement register data and information collected in the project. 7 applications causing consumer exposure were found, 2 of which have been taken into account in the methanol exposure scenarios (=I).

| | Application | Sector | Intended use / methanol source | Amounts of methanol t, |
|---|---|---|---|---|
| 10. | Consumer exposure to methanol (4 applications to methanol registration) | | | |
| 10.1 M | n | Dilution and use of windshield washer fluids n | as a solvent in washer fluids, max. 60% weight in the purchased product, usually < 25% MeOH in the diluted product | All windshield washer fluid use 1,700 t (KETU 2006) hundreds of thousands exposed? |
| 10.2 M | n | Manufacturing of methanol-based fuels (in Finland only mixed by some individuals for recreational use) and use in different activities n | 60-100% in fuel (speedway, drag racing, model car racing, flying of model airplanes) | 39-49 t, 1,100-1,300 exposed |
| 10.3 | no | Use of fuels (camp stoves) | < 10 % MeOH in fuel | |
| 10.4 | no | Use of paint removers | max. 20% MeOH in products | |
| 10.5 | no | Use of glues containing methanol | methanol from formaldehyde | |
| 10.6 | no | Methanol from fuel MTBE | < 1 % MeOH in MTBE | |
| 10.7 | no | Use of biodiesel | < 0.2% MeOH, | |

n = study of a new application done in the project, o = old applications from the FIOH register or companies

no = no exposure data

APPENDIX 2

DESCRIPTION OF CHEMICAL USE AND EXPOSURE FOR EXPOSURE SCENARIOS

| Name of chemical: | |
|---|---|
| Contact information for target company: | Contact person and contact information<br><br>Name of person filling in the form |

| Description of work and/or process |
|---|
| |

| Departments, process phases, work phases under assessment |
|---|
| |

| Use of chemical being examined in different company sites | | | | | | |
|---|---|---|---|---|---|---|
| Product | % of chem. in the product | Other harmful constituents | Chemical use/year | Frequency of use | Use: | Note: (chem. temperature etc.) |
| | | | | | ☐ closed process<br>☐ partly open process<br>☐ tanks<br>☐ spraying<br>☐ manual<br>☐ other: | |

## Work space, number of workers and ventilation

| Where the work being assessed is performed and extent of facilities | Machines and equipment used | Number of workers in the entire company |
|---|---|---|
| | | |

| Worker titles and number of people in the sites of use | Work tasks and their duration/day | Need for protective equipment | Ventilation at the site: |
|---|---|---|---|
| | | ☐ respiratory protection<br>☐protective gloves<br>☐eye protection<br>☐protective clothing<br>☐other: | ☐ general ventilation<br>☐ local exhaust ventilation<br>☐ encapsulation/ partitioning<br>☐ other: |
| Worker titles and number of people in the sites of use | Work tasks and their duration/day | Need fro protective equipment<br>☐ respiratory protection<br>☐protective gloves<br>☐eye protection<br>☐protective clothing<br>☐other: | Ventilation at the site:<br>☐ general ventilation<br>☐ local exhaust ventilation<br>☐ encapsulation/ partitioning<br>☐ other: |
| Worker titles and number of people in the sites of use | Work tasks and their duration/day | Need fro protective equipment<br>☐ respiratory protection<br>☐protective gloves<br>☐eye protection<br>☐protective clothing<br>☐other: | Ventilation at the site:<br>☐ general ventilation<br>☐ local exhaust ventilation<br>☐ encapsulation/ partitioning<br>☐ other: |

| Earlier risk evaluations performed at the site (site, date, essential results) |
|---|
| |
| Earlier occupational hygiene studies performed at the site (site, date, essential results) |
| |
| Observed or known health hazards (occupational diseases, eczema) irritation symptoms, etc.) |
| |

APPENDIX 2 continues

Other chemical and work environment risk factors

| Are the following risk factors present? | present | not present | no information | more information |
|---|---|---|---|---|
| solvents | ☐ | ☐ | ☐ | |
| other dangerous chemicals | ☐ | ☐ | ☐ | |
| dust | ☐ | ☐ | ☐ | |
| fibres | ☐ | ☐ | ☐ | |
| gases | ☐ | ☐ | ☐ | |
| vapours, fumes and smoke | ☐ | ☐ | ☐ | |
| other: | ☐ | ☐ | ☐ | |
| Noise | ☐ | ☐ | ☐ | |

| Product names of the products used |
|---|
| |

| Safety data sheet and package labelling | | | |
|---|---|---|---|
| | yes | no | more information |
| Safety data sheets at the site of work (or on the intranet) | ☐ | ☐ | |
| Lists of chemicals | ☐ | ☐ | |
| Package labelling in order | ☐ | ☐ | |

| Protective equipment used? | used | not needed | no information | more information needed about type |
|---|---|---|---|---|
| respiratory protection | ☐ | ☐ | ☐ | |
| hand protection | ☐ | ☐ | ☐ | |
| eye protection | ☐ | ☐ | ☐ | |
| different work clothing | ☐ | ☐ | ☐ | |
| safety shoes | ☐ | ☐ | ☐ | |
| hearing protection | ☐ | ☐ | ☐ | |
| other: | | | | |

| Requirements of ATEX Directive in work spaces (more information http://www.ttl.fi/Atex ) |
|---|
| |

| Emissions of chemical under examination department | permitted t/v | estimate of total amount t/v | measured t/v |
|---|---|---|---|
| Into air | | | |
| Into waste water | | | |
| Waste | | | |
| Hazardous waste | | | |

Control of environmental emissions

| | |
|---|---|
| Waste water: amount $m^3$/day, type and size of treatment plant (average flow and capacity) | |
| Emissions into the air: No. of emission sources, concentration in emissions, cleaning | |
| | |

Please fill in the form carefully and return it to the following address:

Finnish Institute of Occupational Health
Work Environment Development
Chemical Agents
Arinatie 3A, FIN-00370 HELSINKI
Finland

E-mail: firstname.lastname@ttl.fi
Fax: +358 9 506 1087
Tel: +358 30 4741

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