Development of an improved product based approach for the calculation of NMVOC emissions from solvent use in Germany and uncertainty analysis

Jochen Theloke, University of Stuttgart, Institute of Energy Economics and the Rational Use of Energy, Heßbrühlstr.49a, D-70565 Stuttgart, Germany JT@ier.uni-stuttgart.de

Rainer Friedrich, University of Stuttgart, Institute of Energy Economics and the Rational Use of Energy, Heßbrühlstr.49a, D-70565 Stuttgart, Germany RF@ier.uni-stuttgart.de

ABSTRACT

This paper describes an improved product based approach for the calculation of NMVOC (Non-Methane Volatile Organic Compounds) emissions from solvent use, as it has been developed for Germany, for the calculation of NMVOC emissions disaggregated to source groups and speciated to substance classes. The same method can in principle also be used for all other OECD countries. Furthermore, a method for the quantification of uncertainties is introduced. This product based approach for the calculation of solvent emissions comprises the following steps: First, the use of solvents and solvent based products (e.g. paints, adhesives, degreasing agents) was derived from production statistics and foreign trade statistics. Secondly, the use of these goods in each specific industrial and commercial sector and in households was estimated. The emission factors were then calculated under consideration of application techniques, emission control measures and other pathways of release (e.g. waste, water, recycling). In the year 2000, emissions from solvent use in Germany have been calculated to about 863 Gg, with approximately 25% (223 Gg) emitted by paint application. About 105 Gg of NMVOC emissions originated from domestic solvent use, emissions from washing and cleaning agents as well as body and hair care products included. The printing industry emitted approximately 80 Gg of NMVOC. The remaining emissions originate from a variety of other sources. Annual total emissions from solvent use have an 95%-confidence interval of \pm 30% according to our assessment based on a semiguantitative approach. However, there are substantially greater uncertainties in the analysis of individual source sectors. Furthermore plausibility checks have been conducted between the solvent consumption of the product related approach and a solvent based approach with data from the solvent industry. In addition to that, two evaluation experiments in Augsburg and Paris evalutated the difference between modelled and measured ambient air concentrations of NMVOCs. Finally a methodology for the quantification of uncertainties of emissions from paint application was developed, using Monte Carlo simulation, resulting in a 90%confidence interval of ± 10 % of the modelled emissions from paint application.

INTRODUCTION

Emissions of non-methane volatile organic compounds (NMVOCs) still contribute significantly to current air pollution problems. They are responsible for the formation of photo-oxidants such as groundlevel ozone – in connection with nitrogen oxides (NO_x) – and individual NMVOCs (e.g. benzene) do have adverse health effects on their own account. NMVOCs are partly responsible for the decrease of stratospheric ozone as well as the

reinforcement of the greenhouse effect. The major anthropogenic NMVOC sources are road transport and solvent use. Among these, solvent use emissions currently account for about 50% of all anthropogenic NMVOC emissions in Germany. Figure 1 displays the distribution of NMVOC source groups in Germany¹.





Biogenic sources emitted about the same amount of NMVOC's like road transport. Other NMVOC emissions are mainly caused by production processes, combustion in industry and public power plants and from small combustion and households.

In the frame of the international reporting requirements (e.g. for the Kyoto protocol², UNECE Gothenborg protocol³, EC legislation⁴, etc.) is it more and more necessary to apply a methodology for calculating emissions using consistent approaches as they are required there.

Furthermore, the examination of potential abatement strategies needs information on the sources and a substance-related compilation of the inputs of organic solvents and solvent containing products as well as the accurate determination of the emissions caused by these products.

A first calculation of emissions from solvent use for the old federal states of Germany for the year 1986 was presented by Bräutigam and Kruse⁵. For more recent years rough estimates were carried out on the basis of this study until lately. Solvent use emissions were assessed by Obermeier⁶ for the federal state of Baden-Wuerttemberg for the year 1990. More general results for a federal state (North Rhine-Westphalia) about the solvent emissions from small trade and private households were introduced in ⁷. With emerging new knowledge on NMVOC sources and emission factors and because of the reunification and the resulting expansion of the examination area it was necessary to develop new methods for the

determination of NMVOC emissions from solvent use in Germany, as it is described in this paper.

With method describe here, NMVOC emissions from solvent use were assessed in Germany for the base years 1994, 1996, 1998 and 2000. The amount of consumption of solvents and solvent containing products were identified with the help of a product based approach. The domestic consumption of different organic solvent substance classes calculated thus were validated and checked by a solvent related approach.

The work described here was carried out for and fincanced $by^{8,9}$ the German Umweltbundesamt.

OBJECTIVES

In this paper, a product based approach for the calculation of NMVOC emissions from solvent use is discussed. NMVOC emissions have been calculated for Germany for the year 2000, disaggregated into source groups and speciated to substance classes. Furthermore a method for the quantification of uncertainties is introduced.

DEFINITIONS AND SYSTEM BOUNDARIES

The definition of solvents and VOC as it is used by the solvent directive (1999/13/EC) of the EU legislation, defines solvents as follows¹⁰:

"Organic solvent shall mean any VOC which is used alone or in combination with other agents, and without undergoing a chemical change, to dissolve raw materials, products or waste materials, or is used as a cleaning agent to dissolve contaminants, or as a dissolver, or as a dispersion medium, or as a viscosity adjuster, or as a surface tension adjuster, or a plasticiser, or as a preservative."

According to the "EU-VOC guideline" ¹⁰ Volatile organic compounds are defined as follows:

"Volatile organic compound shall mean any organic compound having at 293,15 K a vapor pressure of 0,01 kPa or more, or having a corresponding volatility under the particular condition of use. For the purpose of this Directive, the fraction of creosote which exceeds this value of vapor pressure at 293.15 K shall be considered as a VOC."

Based on our results, the main emission sources of NMVOCs from solvent use are the production of solvent containing products and the application of solvents and solvent containing products. It has to be taken into account, though, that some products are used both as solvents and as a chemical reaction component. Toluene, for example, is used as a solvent in varnishes and adhesives and as a reaction component for the production of Toluenediisocyanat (TDI). In a similar way, Methyl Ethyl Ketone is used as a solvent in printing inks and as basic material at the synthesis of Methyl Ethyl Ketone Peroxide. Products which are used as a chemical reaction component do not count as solvents according to the solvent definition.

METHOD

A product based approach was applied for the calculation of solvent emissions. First, the use of solvents and solvent based products (e.g. paints, adhesives, degreasing agents) was derived from production statistics and foreign trade statistics. Secondly, the use of these goods in specific industrial and commercial sectors and households was estimated. The emission

factors are then calculated under consideration of application techniques, emission abatement measures and other pathways (e.g. waste, water, recycling).

For the solvents related approach, data was used as complied by solvent manufacturers about domestic solvent consumption to assess the domestic consumption of different solvents directly, i.e. without the detour via the consumption of solvent containing products. The domestic consumption of solvents was defined as the balance from production, import and export. For the solvent related approach generally accessible statistics offered only a limited basis, thus the applicability of this method depended on obtaining supplementary information mostly from the solvent industry.

The product related approach is described more exactly as follows:

• For the determination of the solvent inputs as well as the resulting NMVOC emissions, economic statistics were processed and evaluated as well as supplementary information obtained from industry associations and most different other institutions by surveys.

The fundamental way to the determination of solvent use and emissions can be subdivided into the following steps :

- Estimate the domestic use of solvent containing products production and foreign trade statistics (production + import export) as well as by the way of interviews of trade associations.
- Determination of details for the product specific solvent content as well as on the composition of the solvent speciation on the basis of interviews of the appropriate trade associations.
- Determination of the use of solvent borne products on the basis of information of the different trade associations, e.g. The Association of the Varnish Industry (VDL, http://www.lackindustrie.de), Industry Association of Adhesives (IVK, http://www.lackindustrie.de), Industry Association of Adhesives (IVK, http://www.lackindustrie.de), Association of the Chemical Industry (VCI, http://www.lackindustrie.de), Association of the Chemical Industry (VCI, http://www.vci.de), Association of the Mineral Printing Paint Industry (VDMI, http://www.vci.de), association areas as well as other information sources, e.g. environmental consultants as Oekorecherche (http://www.oekorecherche.de) or Oekopol (http://www.oekopol.de), etc., technical literature, personal communications of experts, etc..
- Estimate of the business-related solvent use under consideration of data about business dependent differences regarding solvent content and solvent composition in the respective product types.
- Estimate of solvent emissions with use data found out above under consideration of the stock and the effectiveness of secondary abatement measures as well as the further use of recycled solvents.

Finally, an assignment of the calculated emissions to the corresponding source group related classifications for the respective demands of the required emission inventory was conducted. In Figure 2 the method for the determination of the solvent emissions is displayed including the plausibility check by a solvent related approach. The methodology outlined roughly for the construction of a nationwide solvent use and emission database required the execution of extensive surveys and data analyses.

For example, an essential task was to produce an assignment of goods groups of the production statistics as transparent as possible to the corresponding goods groups of the foreign trade statistics. A position of the foreign trade statistics frequently corresponds to several positions of the production statistics. Where this assignment was not feasible primarily due to nondisclosure cases, other auxiliary data had to be identified. It was, for instance,

impossible to find any meaningful data about pharmaceutical production amounts in tons in the production statistics.



Figure 2: Method for calculation of emissions from solvent use

Amounts of import and export can, however, more or less completely be found for pharmaceutical products as well as their cash values in the foreign trade statistics. In the statistics of the *German Association of the Chemical Industry* (VCI, <u>http://www.vci.de</u>) "Chemiewirtschaft in Zahlen"¹² the production value of the pharmaceutical products is indicated for the respective year. For the production amount or the domestic consumption of pharmaceutical products in Mg, the middle foreign trade value in \in per Mg of an exported or imported pharmaceutical product is put into relation with the production value in \in . Of course this calculation is prone to uncertainties, however it helps to achieve a good estimate of the domestic produced amount of pharmaceutical products

The harmonization of the national production statistics in Europe was primarily carried out with regard to a European harmonization of the production statistics and with the aim of a clear assignment to production and foreign trade statistics. Before this rearrangement, in many cases, the assignment was not clear. Hence this method is applicable for other OECD countries as well.

Such examinations are only conceivable and feasible in larger intervals. For this reason a method was developed with which projections are possible without too much effort, based upon easily available data such as e.g. production statistics or foreign trade statistics etc..

RESULTS

In the year 2000, emissions from solvent use in Germany have been calculated to approx. 863 Gg, with about 25 % (222 Gg) emitted by paint application. Roughly 106 Gg of NMVOC emissions originated from domestic solvent use. Emissions from washing and cleaning agents as well as body and hair care products have a significant share in these domestic application. The printing industry emitted approx. 80 Mg NMVOC in Germany in 2000. The remaining emissions originate from a variety of other sources. In Table 1 the calculated emissions from solvent use in Germany 2000 split into different source groups are presented.

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Table 1: Emissions from solvent use in Germany 2000 dissolved to different source groups

The distribution of the emissions amount and solvent inputs is represented graphically in the following illustrations. In the year 2000, 863 Gg of NMVOC were emitted in Germany from the application of solvents and solvent containing products. Figure 3 shows the distribution of the solvent emissions on the source groups. About 64 % of the solvent emissions caused by the source groups "application of paints and varnishes" and ", "domestic use of solvents ", as well as the "application of other thinners".





Approximately 25% (~222 Gg) of the solvent emissions were caused by paint application. In addition to that, other thinners without specific application which are used partly also in paint application contributed significantly. About 10 % of the emission originated from plants that fall under the jurisdiction of 4. BImSchV¹³. These are required to implement emission control equipment (e.g. thermal incineration) in accordance with the regulations of the German TA Luft¹⁴. More than 50% of the emissions from paint application caused by smaller and middle industry and skilled crafts enterprises which are not required to operate any waste air cleaning plants. When including the areas of wood, building and construction, vehicle refinishing as well as domestic paint application (Do-It-Yourself), more than 90% of the NMVOC emissions from the source group "paint application" originates from small and medium enterprises (SMEs) and skilled crafts enterprises as well as the Do-It Yourself area. 34 Gg NMVOC were emitted from degreasing processes or dry cleaning. The largest portion of the emissions (47 %) is caused by metal degreasing (approx. 15 Gg) here. At the processing and manufacturing of synthetic materials and other products approx. 40 Gg of NMVOC were emitted in 2000. Approximately 45% (approx. 18 Gg) originated from the processing of synthetic materials. Approximately 37% (ca. 340 Gg) of NMVOC emissions from solvent caused by other applications, for example:

- domestic solvent use
- printing industry
- Concrete additives
- Preservation of Wood

Details have to be gathered from Table 1. About 13% of all NMVOC emissions (approx. 105 Gg) come from the use of consumer goods which are used mainly in private households. Personal hygiene products and detergents as well as motor vehicle antifreeze and cooling medium have to be mentioned in particular (see Figure 4).





From the production of printing products approx. 80 Gg NMVOC were emitted in Germany in 2000, with about 40 % (31 Mg) in this area emitted from offset printing processes. A relevant share of emissions stemming from the use of moist media (Isopropanol) and cleaning agents. Approximately 12 Gg of the NMVOC emissions of the printing industry caused by rotogravure printing processes (illustration printing products). The emissions originated primarily from the use of Toluene as a printing ink thinner. Relief printing methods (letterpress and flexography) and screen printing processes were emitted approximately 3 Gg of NMVOC. Nearly 16 Gg were caused by package printing processes and 17.5 Gg were emitted from heatset offset printing.

SPECIATION TO SUBSTANCE CLASSES

To be able to assess the effect of NMVOC emissions, the composition must be known the for the speciation of the emissions to substance classes or individual substances. At first a substance speciation was carried out for every sector from the information available and due to expert interviews. By breaking down emissions to detailed split and summarizing emissions by sectors afterwards, consisting checks with regard to solvent consumption could be conducted. The substance class-related speciation thus developed is prone to high uncertainties due to a fragmentary data basis. After this the NMVOC emissions from solvent use consisted to 21% of Aliphatics, to 26% of Alcohols and to 22 % of Aromatics. Furthermore Esters (10 %), Glycol derivates (9 %), Ketones (6 %), Halogenated Hydrocarbons (2%), Ethers (2 %), Terpenes (1%), as well as small amounts of Organic Acids, Aldehydes, Amines und Amides have to be mentioned Altogether 2% of the NMVOC emissions from solvent use could not be attributed to any substance class.



Figure 5: Speciation of the NMVOC emissions from solvent use to substance classes

PLAUSIBILITY CHECK

The amount of solvent consumption for 1994 speciated by IER to substance classes and partly by individual substances was compared with the solvent consumption according to production statistics of the solvent industry (minus export plus import). The result of this comparison is presented in Table 2.

Table 2 shows that the calculated amounts of solvent consumption are plausible with regard to the total sum and also with regard to the speciation to substance classes. However, table 2 shows as well for the example of the alcohols that further speciation by individual substances bears considerable uncertainties. In the row "sum" only the amounts are summarized which could be compared in table 2. In Table 2 the deviations for substance classes varies between approx. 1.3 percent and 14.4 percent. Comparing the total sum between both approaches, a deviation of about 2 % occurs. But considering the annual consumption of single species , e.g. n-Propanol , the difference is much larger, amounting to several orders of magnitudes.

Substance classes	Domestic consumption [Mg] (solvent industry)	Domestic consumption [Mg] (own estimate)	Deviation [%]
Aliphatics	300 000	280 000	- 6.7
Aromatics	250 000	286 000	+14.4
Terpenes		10 000	
Halogenated hydrocarbons	35 000	35 000	
Alcohols	360 000	316 000	-12.2
-Ethanol	50 000	85 000	
-Isopropanol	250 000	144 000	
-n-Propanol	40 000	200	
-n/i-Butanol	10 000	56 000	
Glykolderivates	75 000	78 000	+4.0
Esters	75 000	76 000	+1.3
Ketones	60 000	61 000	+1.7
Ethers	30 000	29 000	-3.3
Aldehydes		200	
Organic acids		800	
Phthalates		225 000	
Other VOC's		65 000	
Sum (sum of bold faced substance classes)	1 185 000	1 161 000	-2.0

Table 2:Comparison of the substance speciation of the assessed amounts of solvent
consumption with domestic consumption amounts of the European solvent
industry (for the year 1994)⁸.

UNCERTAINTY ANALYSIS

The uncertainties of calculated emissions from solvent use are quite difficult to quantify. Annual emissions from solvent use typically contain an uncertainty of \pm 30% according to our assessment¹⁵. However, there are substantially greater uncertainties in the analysis of individual source sectors. The reasons are the heterogenic structure of the sources and the quality of available input data. A large variety of sources and emission activities exist with significant uncertainties in the assignment of production , consumption, application and resulting emissions. A chance for the assessment of plausibility is the analysis of surveys, emission declarations, expert surveys (for example from industry associations) and the solvent bilance (see Table 2). The stated annual amounts of solvent use in different industries varies significantly even within the same source group. Another example of input data uncertainties is the wide distribution of solvent content of different paint systems.

Different approaches are possible for the assessment and calculation of uncertainties from NMVOC emissions. First a differentiation has to be made between uncertainty analysis methods and possibilities for verification of the calculated emissions. In uncertainty analysis a further distinction between qualitative, semi quantitative and quantitative methods can be made. As quantitative methods, either error propagation or Monte Carlo simulation can be applied. For verification purposes plausibility checks for example with data from solvent industry on domestic solvent consumption can be used. In addition to that, experiments, for instance for a whole city can be conducted with a comparison between modelled and measured ambient air concentrations. In qualitative and semi quantitative approaches uncertainties are typically classified into five qualitative classes, then bandwiths of the confidence intervals are assigned in percent. The distributions are mostly non-symmetrical. One possibility to calculate quantitative uncertainties is the application of error propagation. Error propagation has the following requirements for application: Firstly, the input parameter must be subject to a Gaussian distribution with a standard deviation in the order of one percent of the mean value.

However, error propagation methods have the following disadvantages:

- Other distributions as Gaussian distributions cannot be properly assessed with the error propagation law.
- The input data required for the calculation of emissions from solvent use are usually not subject to Gaussian distributions and furthermore often correlate.
- Thirdly error ranges of more than 30 % of input data can be treated badly with error propagation. But error ranges of more than 30 % are not unusual for the input data of the solvent emission model.

So we close that error propagation is not a suitable method or quantification of the uncertainties of emissions from solvent use. Figure 6 shows you preliminary and very actual results from a Monte Carlo simulation of our model for emissions from paint application in Germany in 2000. Without uncertainty analysis we had calculated 222 Gg for 2000 from paint application. The average mean of Monte Carlo simulation (10000 iterations) is 231 Gg. The 90%-confidence interval is 231 Gg ± 10 %.





Figure 7 and Figure 8 shows the results of two city experiments in Paris¹⁷, France, and Augsburg, Germany (conducted in 1998 in Augsburg and 1999 in Paris)¹⁸, On the x-Axis the relation of modelled to measured concentrations of selected hydrocarbons are displayed vs. the measured and modelled ambient air concentrations of Carbon Monoxide (CO). The results in Figure 7 show a relatively good agreement. The deviations between modelled and measured concentrations deviate at a maximum factor of 2 apart for Propane in the Paris experiment. One of the reasons for the underestimation could be the under representation of Liquid petrol gas heaters in the model. Figure 8 indicates much larger deviations between measured and modelled ambient air concentrations. In Augsburg rather large deviations for some species could be noticed. These originated primarily from solvent use and here in

particular from white spirits (main component: n-Decane). The reasons for these significant differences could not be fully analysed and explained yet, hence verification experiments are necessary.



Figure 7: Results of City experiments in Augsburg (EVA), Germany and Paris, France (ESQUIF)^{16, 17}

Figure 8: Results of City experiments in Augsburg (EVA), Germany and Paris, France (ESQUIF)^{16, 17}



CONCLUSIONS

The product and solvent based method described in this paper for the calculation of NMVOC emissions has proven to be well designed and was successfully applied for the generation of detailed emission inventories for NMVOCs on high spatial and temporal resolution. By using this method, a detailed assessment of NMVOC emissions from solvent use can be conducted for other OECD countries as well, with acceptable input requirements, as the structure of economic statistics are standardized. Furthermore, a substance related split of NMVOC emissions can be conducted based on this methodology. The developed method was applied to calculate the NMVOC emissions from solvent use in Germany 2000. The total sum of emissions from solvent use was approximately 863 Gg in Germany in the year 2000. About 25 % (223 Gg) caused by paint application, about 13 % came from antifreeze for cars, hairsprays, washingup liquids, detergents, after shave, frangrance, perfumes, cooling mediums and fire extinguishers. 80 Gg were emitted from printing processes and 18 Gg from the processing of synthetic materials. 40 Gg originated from degreasing processes and dry cleaning. Almost 42 Gg emitted from the application of concrete additives and 31 Gg from wood preservation. The remaining emissions originate from a variety of different source groups, e.g. the application of glues and adhesives (22 Gg), application of propellants (16 Gg), from solvent use in chemical industry (22 Gg). In addition to that, 225 Gg were emitted through the application of thinners without a detailed attribution to sources (mostly for equipment cleaning). The NMVOC emissions from solvent use were speciated to 21 % Aliphatics, 26% Alcohols, 21% Aromatics, 10% Esters, 9% Glycol derivates, 6% Ketones, 2% Halogenated Hydrocarbons, 2% Ethers and 1% Terpenes as well as small amounts of organic acids, Aldehydes, Amines und Amides. A plausibility check resulted in good agreement between the solvent consumptions for 1994 estimated with the product based approach and the same using the solvent based approach (with data from the European solvent industry as a basis). Fur thermore, the modelled emissions were evaluated by two city experiments in Paris, France and Augsburg, Germany. The comparison between modelled and measured ambient air concentrations of single species was partial in good agreement for some individual species. However, in some cases significant discrepancies were identified. In the case of Augsburg, particularly large differences for some NMVOC species typically from solvent use and here primarily from white spirits (main component : n-decane) were found. The reasons for these differences between measured and modelled ambient air concentrations are yet to be analysed in detail.. Thus, further verification experiments are necessary. Annual emissions from solvent use have an uncertainty bandwith of \pm 30% according to our assessment with a semi quantitative approach. Preliminary and very recent results from a quantitative uncertainty analysis using Monte Carlo simulation (10 000 iterations) for our modelled emissions from paint application in Germany in 2000 show an average mean of 231 Gg. The 90%-confidence interval is 231 Gg ± 23 Gg When not taking into account any uncertainties in previous calculations, approx. 222 Gg from paint application had been calculated for the year 2000.

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KEYWORDS

NMVOC Emissions, Solvent Use, Substance Speciation, Uncertainty Analysis, Plausibility Checks, City Experiments, Product Related Approach, Monte Carlo Simulation