Test Protocol for H&ETQP Amine 4

Evaluation of Solvents – Process and Atmospheric Chemistry

Proposed test protocol for use in the evaluation of amine-based solvents

The delivered protocol should not be considered a definitive document. Whilst it has been developed using the best available information at the time of writing, it is expected to be a dynamic document. The protocol should be improved in the future (e.g. during implementation) as new data and information is made available and which has direct relevance.

Table of Contents

Test Protocol Section I: Formation and emission of CO_2 capture process compounds

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Two stage test protocol for emissions from plant

1. Lab-scale study of solvent degradation
2. Emission Measurements at technology providers CO_2 capture plant

Part A: Lab-scale study of solvent degradation

A1. Description

The set-up should consist of an absorber and stripper, with a height in the range of 0.5m to 1m. Both columns should be filled with packing material. The column diameters are determined by packing material diameters. The diameter of the columns is not significantly affect the results obtained. The temperature in absorber, should match maximal absorber and stripper temperatures planned for CCM. For the absorber maximal temperatures are likely to be around 70°C and in stripper 125°C. Temperature in the absorber and stripper could be varied in order to test the sensitivity of solvent degradation to temperature. The absorber should have a reflux unit and there should be a possibility to sample from the reflux.

The exhaust gas can be sourced from a burner or be a mixture of synthetic gases. There should be an option to increase NOx concentration in exhaust gas. It would also be desirable to change CO_2 concentrations and Oxygen content in the gas. Varying these parameters would give a good indication of how the solvent would perform in worst-case scenario conditions. Ideally it would be good if the apparatus could reproduce rich and lean loadings encountered in a CO_2 capture plant. It is however difficult to predict what loadings are achievable in an apparatus with small dimensions. Parameters in the apparatus should be set to reproduce the conditions the solvent will be exposed to at Mongstad CO_2 capture plant.

The apparatus should be built for and operated with low gas and liquid velocities. The aim of this is to have high residence times in the columns. The apparatus design should be well-specified and easy to reproduce. The apparatus could be operated with the gas going once-through or with the gas in a closed loop. In a closed loop it would be easier to maintain water-balance in the apparatus, which would make it easier to quantify degradation in the apparatus. In a closed loop one would however lose control of the ratio between NOx species, CO_2 and oxygen in the experiment.

A once-through set-up is recommended since it gives greater control over the experimental parameters. It is at the same time technically more demanding to run such experiments, and this trade-off must be considered in the implementation of the test protocol. This apparatus can be used to study the entrainment forming potential of the solvent. It cannot be used to quantify/predict entrainment level in a plant, since the apparatus is not designed to reproduce gas and liquid flows in a CO_2 capture plant. It should however give an indication of the relative risk of entrainment presented by a given solvent system.

A proposed apparatus is shown in Figure 9 in Part C of this Section.

A2. Campaign

Any new apparatus should have an initial MEA campaign of 2 weeks duration. The liquid should be sampled and degradation compared against previous data (from apparatus built with same design). For the solvent system to be tested, an 8 week campaign should be conducted. The liquid and gas-phase leaving the absorber would be sampled at 2, 6 and 8 weeks. After this, a one week campaign with a higher NOx concentration would be carried out. Sampling should be completed on the last day of this campaign.

The suggested length of campaign is somewhat arbitrary. Degradation products can be detected in a campaign of shorter duration. There is however the possibility that dominant degradation mechanisms change as degradation products start to accumulate in the liquid. Campaign durations from 1 month to 4 months could be considered.

A3. HSE

The HSE aspects of Part A are discussed in Part C of this document.

A4. Results

These experiments should give a qualitative picture of what degradation products are formed for a given solvent system. This would provide input on what degradation products to look for in emissions from a plant running on the specified solvent. These experiments should also give a relatively good picture of the risk presented by the different solvents. The formation rates of key chemical groups of degradation products, such as nitrosamines, nitramines and alkylamines, can be compared against the rates for MEA (used as a standard reference solvent system in this case). Such a comparison should give a good overview of the relative risks presented by different solvents.

If the data on the formation rates of different degradation products is combined with data on the volatility of different degradation products and a model of a water-wash unit, a prediction can also be made of the emission profile of the solvent system at CCM. In addition, study of the liquids behaviour in the column can also be used to determine the risk of solvent forming aerosols.

Part B: Emission measurements at technology providers CO_2 capture plant

B1. Description

The goal should be to measure the emissions at CO_2 capture plants operating under representative conditions. In all plants, the sampling should be conducted with identical equipment and techniques. If necessary, a pipe could be mounted on top of the absorber to facilitate isokinetic sampling. It must be ensured that the plant is operating under representative conditions at the time of sampling. Verification of this is not a trivial matter, especially not without full insight into the technology providers plans for plant operation.

The parameters to monitor in order to validate that a plant is operating at representative conditions are as follows:

- The plant should be close to 90% capture
- Gas velocities should be close to plant specifications
- Solvent should have been in the plant for at least 1 month
- The plant should be at close to neutral water-balance
- The plant should be close to the specified energy consumption
- The plant should have been operating on exhaust gas continuously for at least 8 hours

The operation of the water-wash at the time of sampling and in the preceding week should be documented. The rates at which freshwater are added to the water-wash should form part of this documentation.

B2. HSE

The measurement of emissions from a CO_2 capture plant may involve physical risks for the people conducting the sampling. Access to the top of the absorber may vary significantly from plant to plant and should therefore be considered on an individual plant basis. There is also the need to transport the sampling equipment up to the top of the absorber.

B3. Analysis of the samples

There is still substantial uncertainty regarding the analytical methods for some of the degradation products that may be formed in CO_2 capture plants. It would therefore be advantageous if at least some of the analytical work is carried out by the same research group. This approach would ensure that relative emission numbers between different technology providers are as reliable as possible.

B4. Results

These emission measurements should give a direct picture of the emission profile for the solvent technology. It may, however, be that the existing plant operated by the technology provider differs significantly from the plans for CCM. In this case, the effect these differences may have on the emissions should be considered. It may also be that the CO_2 capture plant runs on an exhaust gas that has more NOx and/or a higher level of impurities than will be encountered at CCM. Again, such differences can significantly affect the emission profile and should be thoroughly considered. An option suggested to overcome or address the above issues could be to run the solvent at a pilot plant with conditions closer to those that will be encountered at CCM.

B5. Background

It should be recognized that solvent degradation in post-combustion CO_2 capture plants is not fully understood. There are also a number of process parameters that may significantly affect solvent degradation. Furthermore, a quantitative picture of how entrainment is affected by different process parameters is not available at present. As a result of these knowledge gaps, there is less confidence in extrapolating results from laboratory-scale apparatus to CCM. Laboratory-scale results should therefore be validated with at least two solvent systems, before being used to draw quantitative conclusions on solvent degradation.

The ability to make a fair comparison between technology providers is a key consideration in a process test protocol such as this. Primarily, this means determining the emission numbers for the selected solvent system, based upon the individual provider’s process design and operation. Since different technology providers are likely to be working with different solvents, each with different degradation rates and volatility, there are also likely to be differences in process design and operation. This means that testing the solvents under identical conditions, while useful, should not be the main method of comparing the solvents.

B6. Preparation work

Prior to conducting the process test protocol for a technology provider’s solvent system, it would be useful to test it for 1-2 known solvent systems. This could, for example, be MEA and Piperazine. Such testing could be especially useful for the laboratory-scale test protocol.

B7. Sampling and analysis

Unfortunately, there is currently substantial uncertainty regarding the sampling and analytical methods for components such as nitrosamines. To our knowledge, methods have also yet to be developed for sampling and chemical analysis of nitramines in emissions from CO_2 capture plants.

This means that if sampling and analysis is conducted by different research groups for different technology providers one may not be confident that the reported emissions are correct in absolute or relative terms. Utilizing the same laboratories for analysing the same components in samples from all technology providers would provide a greater confidence that the relative numbers are correct.

If different research groups are to be used for analytical work, an alternative option would be to send out identical samples to all of the groups, in addition to the samples from the technology providers. If the laboratories report the same analytical results for the identical samples, one would have confidence that the samples from technology providers were also being analysed in a consistent manner.

In addition to sampling the gas leaving the plant, the water-wash and lean amine liquid should also be sampled. The degradation products found in emissions, water-wash and lean amine could be checked for consistency (all volatile and semi-volatile degradation found in the liquid phases would to some extent be extended to appear in the emissions).

Part C: Lab-scale study of solvent degradation and potential emission to air

C1. General

The proposed bench-scale apparatus consists of a combined complete absorber and stripper setup. This setup has the aim of reflecting a realistic system for degradation under process conditions. The apparatus is a cyclic system enabling evaluation of the overall solvent degradation and potential emissions of volatile compounds from an amine absorption based CO_2 capture plant process. Compared with a purely oxidative or thermal experimental setup, this system permits the study of possible influence of the different degradation mechanisms occurring in the process.

The experiments aim to give a realistic picture of the risk presented by the different solvents. The formation rates of key chemical groups of degradation products, such as nitrosamines, nitramines and alkylamines, can be compared against the rates for MEA (used as a standard reference solvent system in this case) under similar conditions. Such a comparison should give a good overview of the relative risks presented by different solvents.

If the data on the formation rates of different degradation products is combined with data on the volatility of different degradation products and a model of a water-wash unit, a prediction can also be made of the emission profile of the solvent system at CCM.

C2. Experimental setup

The apparatus has a total height of approximately 2 meters and a footprint of 80x150 cm. The apparatus can be built into an aluminium framework set on wheels. Instead of using inert materials like glass or teflon, which are often used in bench-scale setups, the apparatus is constructed from 316 stainless steel. The solvent flows counter-currently through a metal contactor with a specified contact area. The experimental setup aims to provide a realistic, qualitative picture of the composition of the complex mixture of degradation products formed with a given solvent system at process conditions. In addition, the setup should provide an overview of the potential emissions to air from the absorber without the presence of emission reducing technologies, thus representing a “worst case” emission profile.

Figure 1 shows a simple process flow diagram (PFD) of the apparatus with the main components identified. Possible instrumentation for gas sampling and physiochemical properties are not shown, but are discussed in the text below.

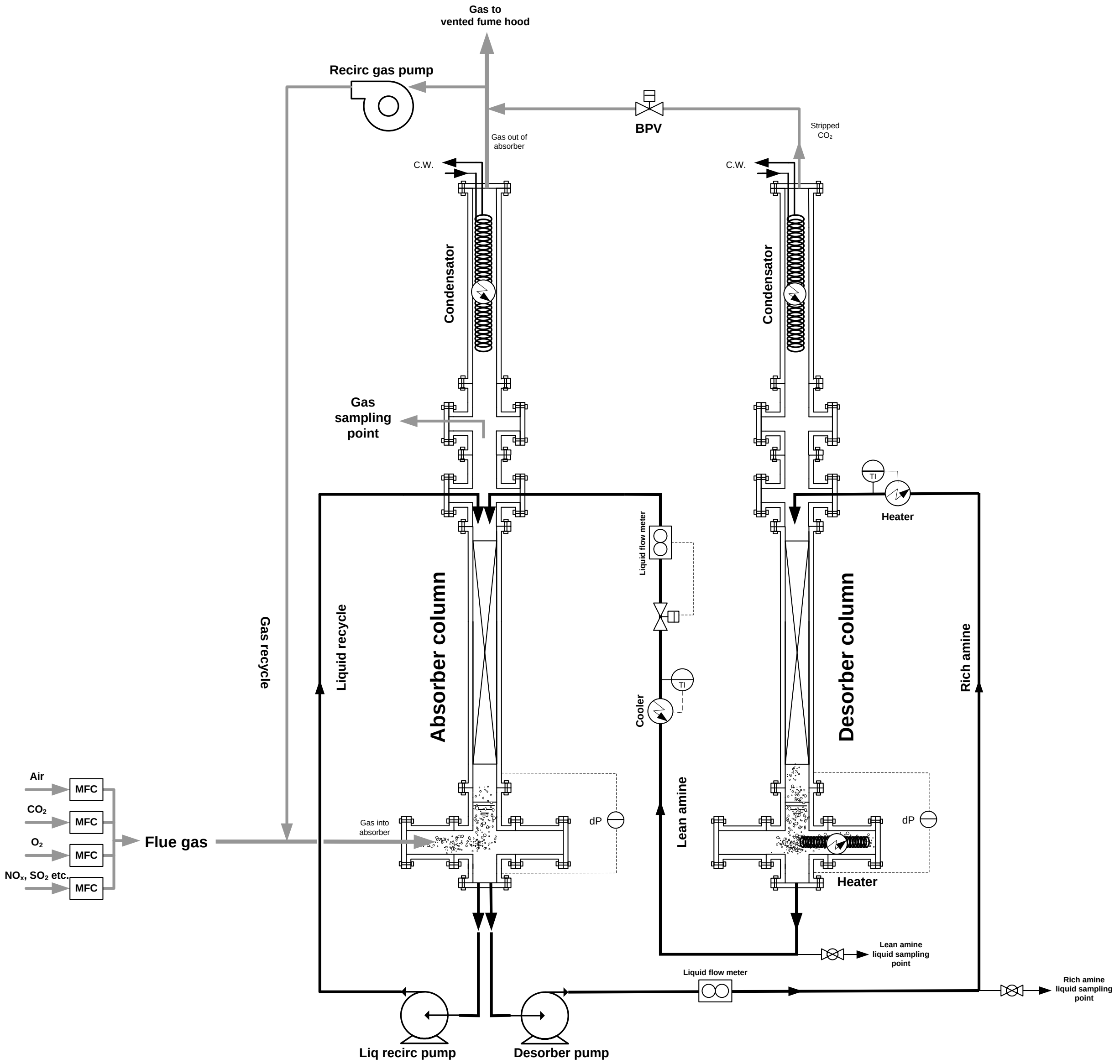


Figure 1: Apparatus for amine degradation under process conditions, including detection of volatile compounds emitted from the absorber.

A structured metal packing with a high specific surface area is used in both columns as the gas-liquid contactor. In order to simplify the manufacture and setup of the system, the two columns could be designed to be virtually identical with a column diameter of 50 mm ID. It is expected that temperatures are controlled within the range 30-70°C in the absorber and within the range 100-130°C in the stripper. These ranges include the maximal absorber and stripper temperatures planned for CCM. The apparatus can be operated either as an open system, a closed system or a combination (once-through, total or partial recycling) as regards the gas side. The liquid solvent is recycled between the absorber and stripper sections. The stripper column sump is equipped with an electric heating element for re-boiling of the amine. Both absorber and stripper have a cooling section located at the top in order to minimize water loss of the discharged gas/vapour.

It is important to obtain high flexibility in the absorption system in order to vary the loading level of rich solvent. The loading level can be controlled by altering several of the operating parameters including; CO_2 partial pressure, temperature and gas/liquid flow rates. The absorber is equipped with liquid and gas recycling in order to obtain realistic loadings of the rich solvent. Flue gas can be partially sparged into the absorber sump to increase mass transfer between gas and liquid.

Both columns have an enlarged sump equipped with flanged access points for easy piping and the possibility of adding online instrumentation for the measurement of temperature, ionic strength, pH, dissolved oxygen and loading of rich amine in the sump. pH and dissolved oxygen in the lean amine should be monitored after solvent cooling and pressure release and not directly in the desorber sump. Both the absorber and the desorber column have a section upstream from the structured packing with flanged access points for allowing sampling of the gas from the column. This sampling and analysis could be performed either manually or by addition of online instrumentation. Online gas analysis of e.g. CO_2 and O_2 can also be installed at other desired points in the gas lines of the apparatus.

The flue gas should be a mixture of synthetic gases which enables control of CO_2 and O_2 partial pressures and the option of adding NO_x or SO_2 etc. in low concentration to the exhaust gas. NO, NO_2 and SO_2 should be added as diluted calibration gas from gas cylinders. It is also possible to oxidize a small part of pure NO to NO_2. A once-through gas feed system will require considerable addition of water to compensate for the loss of humidity in the outlet gas even with an efficient gas cooling. The loss of water is approximately 13 g/m^3 gas if the gas is saturated at 15°C. Compensation of the water loss by humidification of the feed gas requires an additional column upstream of the absorber and thus leads to a more complex set-up. Freshwater addition trigged by a level controller in the absorber sump offers a simpler concept. The main advantage with an open gas system is the easy way to obtain a constant inlet gas composition.

Minor water loss will be obtained with an approximately closed gas loop. Only a small gas flow needs to be withdrawn from the gas loop as feed to the CO_2 and oxygen analyzers connected in series. This gas flow is typically about 1 L/min which corresponds to a water loss of about 20 g/d if the gas is saturated at 15°C. Another advantage with a closed loop is the simple and accurate determination of the material balances for a given component. The flow rate of each component in the feed is approximately equal to the flow rate transferred to the solvent. The main drawback is a more complex gas feed control system to obtain a constant gas feed composition. An open system will require more inert feed gas than a closed loop. However, if a minimum gas velocity is used, the gas consumption should be acceptable.

If the mass balance is important for the tests, it can be calculated with very good accuracy if a closed gas system is chosen. This is shown for component "i" below:

$M_{i,\,feed} = Q_{i,feed} * C_{i,feed}$
$M_{i,absorbed} = Q_{i,absorbed} * C_{i,absorbed} = M_{i,\,feed} - M_{i,\,outlet}$
$M_{i,\,outlet} = Q_{i,outlet} * C_{i,outlet}$

As $Q_{i,outlet} << Q_{i,feed}$ $M_{i,\,outlet} / M_{i,\,feed} \approx 0$.

Hence,
$M_{i,absorbed} \approx M_{i,\,feed}$

With an open system it might be necessary cool the sampling gas leading to partial loss of hydrophilic components.

C3. Sampling and analysis

Sampling and analysis of liquid from the rich and lean solvent is the main indicator of the state of degradation of the solvent. The liquid analysis also predicts potential compounds present in the effluent gas from the absorber. Sampling of gas from the absorber upstream from the condenser is important in order to evaluate the concentrations of volatile amine and degradation products.

The methodology applied for analysis of gas and liquid samples should be the current state-of-the-art, performed by either manual or online sampling. SINTEF currently has in-house research activity on the development of online analysis by mass spectrometry for both gas and liquid samples that could develop into suitable applications required for this system.

Liquid samples could also potentially be sent for bulk toxicity testing.

C4. HSE

In general, a complete HAZOP-study of the apparatus and experimental setups has to be performed prior to finalising the detailed apparatus design. A well functioning safety system with automated alarms is important for such apparatus which will have unmanned operation over extended time periods. For instance, the pressurised stripper section operating at high temperatures should have safety valves preventing build-up of pressure upon failure of components such as the regulating valves etc. The PFD in **Figure 1** can be seen as a principle drawing and the finalised PFD will contain more detailed components not shown here.

The experiments involve NOx and will lead to the formation of carcinogenic compounds in addition to amine vapour. The apparatus should be located in a well-ventilated fume cupboard with all emitted gas discharged in a vented fume hood. A risk assessment should be performed prior to every experiment involving new solvents.

Implementation of test protocol: Section I

The process test protocol should be executable within a 6 month time frame.

Part B of the test protocol consists of an emission measurement campaign. There is some experience with such campaigns and no risk that it cannot be executed in a reasonably short period of time. The main risk is that the results produced are ambiguous or uncertain. If for example no nitrosamines are found in one campaign, there might be a question if there was some failure in analysis or sampling.

It is therefore important that attention is given to consistency in execution of Part B at different plants. Part A is also useful, in that one can have a reasonable idea of the emission profile of a technology provider prior to doing the emission campaign. Part A involves the building of an experimental apparatus. Provided that sufficient preparatory work has been done this should not take a lot of time. A prototype of the apparatus should have been built and tested prior to running the test protocol. All components needed to build the apparatus should have been ordered prior to starting the test protocol.

It should be noted that if Part A and Part B are executed sequentially, final results from the process test protocol will only be available after 3 months or more. The environmental part of the test protocol cannot wait 3 months before starting up. One option would be for the environmental test protocol to start up with information on parent amines and theoretical assessment of the process degradation products.

Another option is to start the test protocol with the CO_2 capture plant emission measurements (Part B). Part A could be omitted or carried out after Part B. This would have the advantage of quickly providing emission data as input to the environmental test protocol work. The disadvantage is that one would lose input on what components to look for in the emission measurement campaign.

Test Protocol Section II: Environmental fate of emissions

Section II of the protocol will be divided further into three separate sub-Sections. The first, Section II-A, will focus on the process degradation products. The second, Section II-B, will focus on the atmospheric degradation products (Section II-B). The final, Section II-C, will describe an experimental approach for the evaluating the atmospheric fate of both the process and atmospheric degradation products.

Section II has been divided into three sub-sections (II-A, II-B and II-C) for a number of reasons. Although degradation products from the same chemical classes may form in both the process and in the atmosphere it is highly possible that the individual chemicals will differ due to the nature of the two processes. For example thermal degradation in the process may yield a different range of degradation products from the parent amine than photochemical degradation processes occurring in the atmosphere. Furthermore, the conditions inside the process are expected to remain relatively constant and thus the degradation products are expected to remain constant. In contrast, the nature of the atmospheric degradation products is subject to many more and somewhat variable parameters. This means that the atmospheric degradation products may not be formed in such a consistent manner.

There is also much work to be conducted in CallOff 2, and the division of this part of the protocol into sub-sections allows them to be conducted simultaneously. The described approach will make a more efficient use of the available time allocated for completion of CallOff 2. In addition, as new information becomes available from the work in each of the sub-sections it can be input into the other sub-sections where relevant. For example degradation products which are found to be common to both the process and atmospheric routes should be evaluated just once.

A brief summary of the protocols for Sections II-A and II-B, including a simplified flow diagram in each case, are presented below. The rationale behind all of the protocols and detailed procedures for completing them are described fully in the main text below the summary.

Overview of Test Protocol Section II-A: Process degradation products:

This test protocol is designed to handle a generic amine solvent system for use in CO_2 capture. **Figure 1** gives an overview of the testing procedure. A starting point of the protocol is a list of parent amines that are planned for use in capture of CO_2. An initial process will determine the degradation products which are formed for a selected solvent system/parent amine within the operation of the capture process and released in the final emission. The list of process degradation products is expected to include a large number of different chemicals from a variety of different chemical classes. The first step of the protocol is to complete a full theoretical evaluation of all parent amines and their process degradation products. As it would not be feasible to conduct a full experimental characterization for all of the chemicals a short list of the most hazardous will be generated. A decision chart (Figure 3) was designed for this purpose and was termed procedure “Part A” in the test protocol. Once a short list of 10-20 chemicals is identified, the next stage is to perform two theoretical assessments to determine their atmospheric fate. This is shown in the decision chart in “Part B” of the test protocol (Figure 4). For those chemicals predicted to have an atmospheric lifetime of 3 hr to 3 days, an experimental strategy to better determine their real lifetimes will be implemented as described below. Process degradation products identified as having an atmospheric residence time in excess of 3 days will be subjected to environmental fate assessment in a third decision chart described in “Part C” of the protocol (Figure 5). This process will identify which of the chemicals will be most likely to rapidly deposit to terrestrial and aqueous systems and those which are more likely to undergo long range transport and dispersion, leading to deposition at low concentrations far from the point source (CO_2 capture plant). For those compounds which are expected to deposit rapidly in the area surrounding the point source a series of environmental fate parameters will be determined. The aim of this study will be to identify where the chemicals are expected to concentrate in the environment (e.g. soils or groundwaters). Initially, theoretical Quantitative Structure-Activity Relationship (QSAR) approaches to parameterise the reactivity of a given substance should be used (e.g. EPI Suite™). Where predicted values are insufficiently robust experiment approaches should be pursued. These environmental fate data will ultimately provide a decision making tool for selecting appropriate toxicity and ecotoxicity tests and species in “Part D” of the protocol.

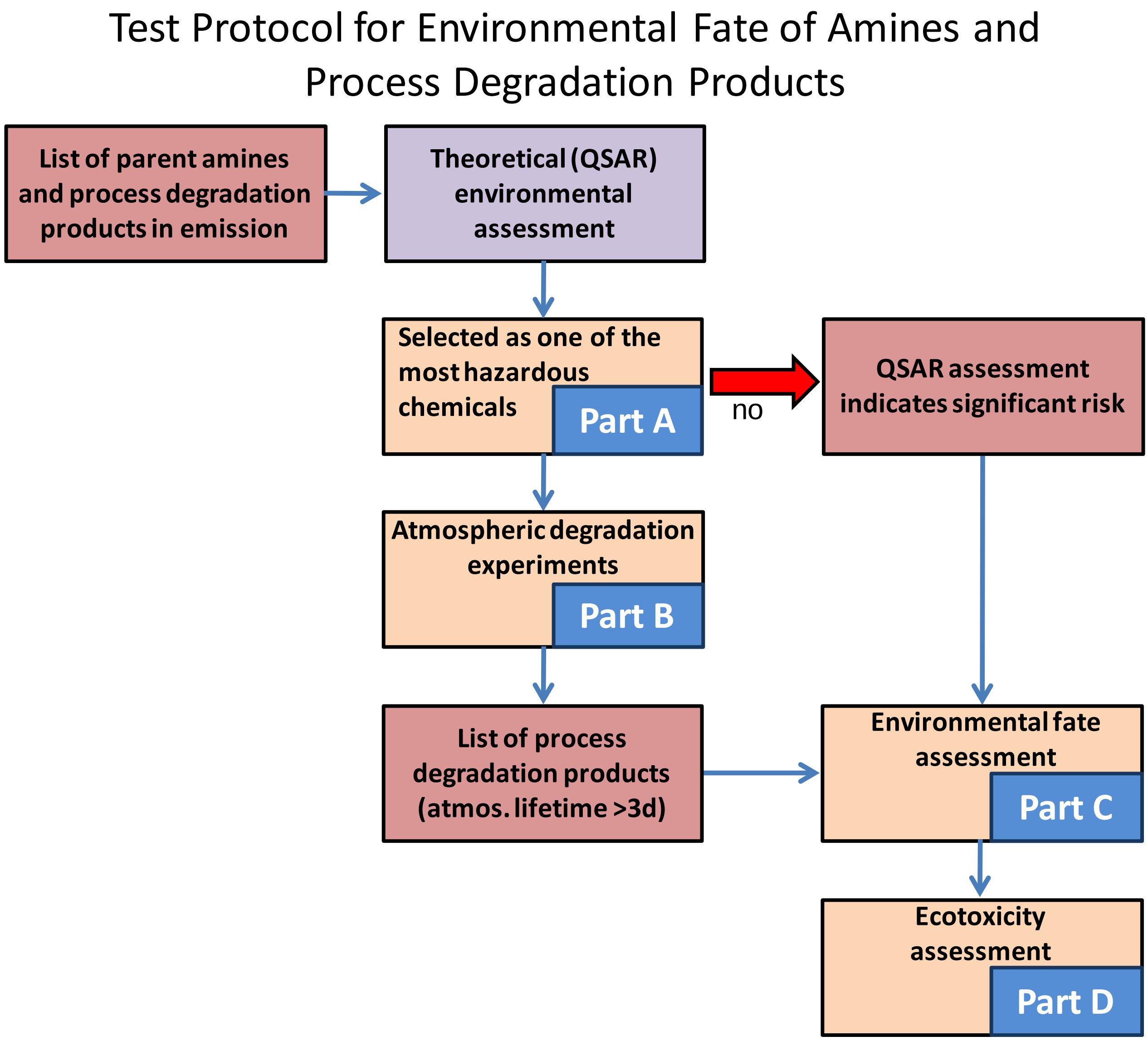


Figure 1: Protocol overview for Test Protocol Section II-A, Process degradation products

Overview of Test Protocol Section II-B: Atmospheric degradation products:

The test protocol is designed to characterise a generic amine for use as solvent in carbon capture. **Figure 2** gives an overview of the testing procedure. The starting point of the protocol is a list of parent amines that are anticipated for use in post-combustion capture of CO_2. The initial decision process will investigate whether meaningful atmospheric chamber experiments can be performed for the amine in question. Volatility of the amine solvents may be in conflict with the feasibility of conducting such atmospheric chamber experiments. A decision table was designed for this purpose and was termed procedure “Part E” in the test protocol. Depending on the results of initial experiments in the photochemical reactor, the next stage would be to perform a series of experiments to determine and constrain the atmospheric fate of the parent amine and the formation of atmospheric degradation products (“Part F” of the test protocol). A strategy for chemical analysis in the experiments is described in detail below. Atmospheric degradation products from the photochemical experiments with a formation yield of more than 0.5% must be included in the list of atmospheric degradation products of the respective amine. Products that form with a lower yield can usually be ignored since their concentration would be insignificant under atmospheric conditions. In a second decision process it will be investigated if experimental tests to determine atmospheric lifetime, aquatic fate and terrestrial fate have to be conducted for the atmospheric degradation products. This decision process is described in “Part G” of the protocol. The last stage of the protocol is to conduct experimental studies of the selected atmospheric degradation products (“Part H” of the test protocol). If no experimental studies are conducted for the parent amine, a list of predicted atmospheric degradation products will be obtained by theoretical calculations, including EPI Suite^{TM} to determine the rate constant of the amine reaction with OH radicals and quantum chemistry calculations to determine viable atmospheric reaction pathways, stable degradation products (lifetime > 1 hour), and potentially toxic degradation products with shorter lifetime (i.e. nitrosamines).

The list of theoretically predicted atmospheric degradation products is the basis for the decision to undertake experimental studies in Part G.

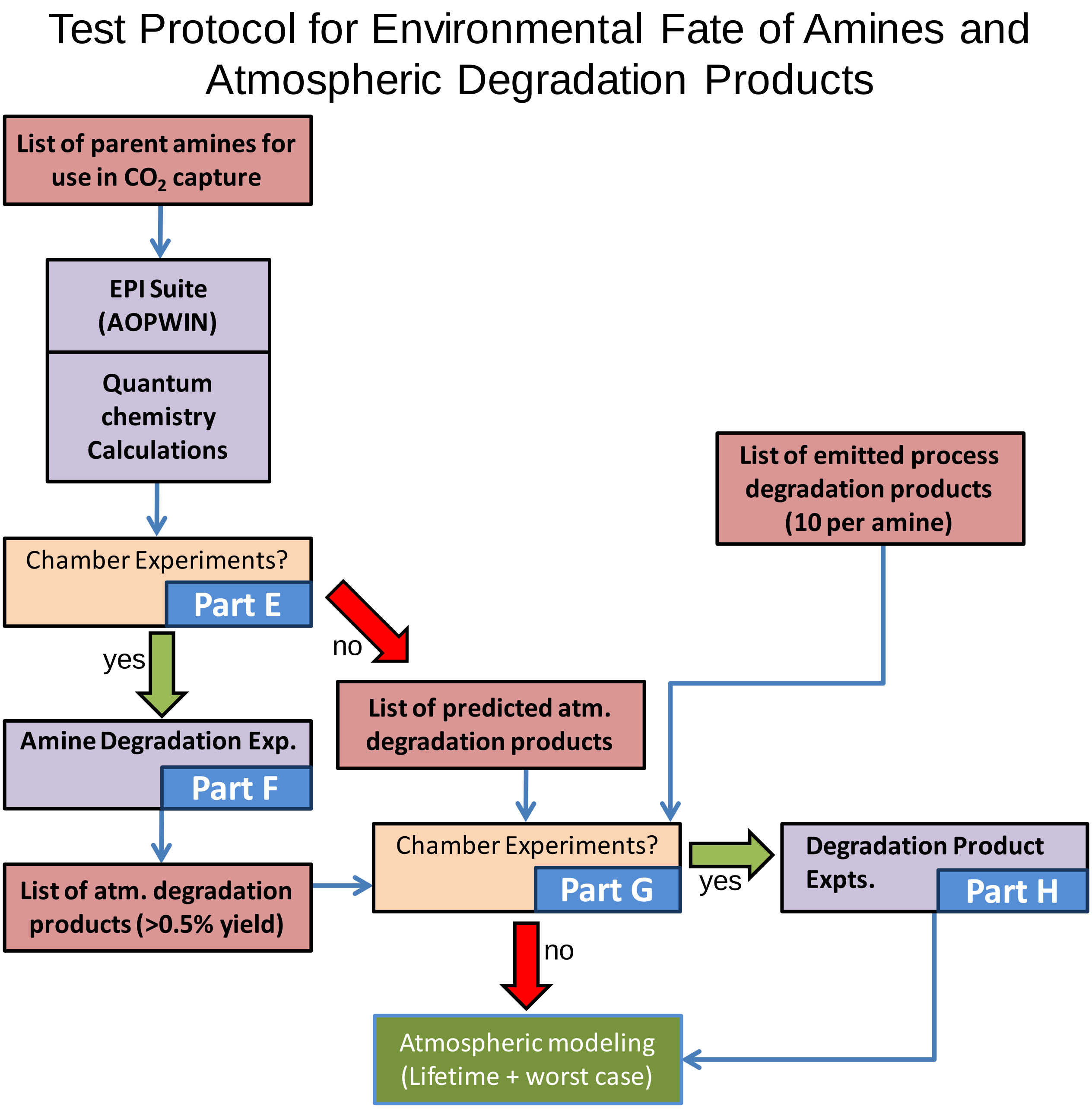


Figure 2: Protocol overview for Test Protocol Section II-B, Atmospheric degradation products

Test Protocol Section II-A: Process degradation products

Summary of the protocol components

- Part A: Selection of compounds that pose a particular risk.
- Part B: Determination of atmospheric lifetimes and secondary degradation products.
- Part C: Assessment of deposition and environmental fate.
- Part D: Toxicity tests to determine safe concentration limits of selected compounds.

Procedure for the test protocol

Part A: Selection of compounds that pose a particular risk

This section refers to Part A shown in the overview diagram in **Figure 1**. A number of chemicals should be selected from this list for further detailed study (**Figure 3**). To do this, model tools and available experimental data for the identified process degradation products will be used to identify approximately 20 compounds that pose the greatest risk in terms of concentration in the emission and toxicity. Existing data indicate that most of the theoretically predicted process degradation products will not be acutely toxic to any organism in the concentration ranges currently assumed for the emission. However, some nitramines, nitrosamines, alkylamines and aldehydes are considered to be significantly genotoxic (e.g. carcinogenic, reproductive impacts etc). In contrast, aliphatic hydrocarbons and most alcohols are considered to be significantly less genotoxic. Alkylamines which form as degradation products in the process and are not parent amines (i.e. generic solvent amines) will be treated in the same manner as other process degradation products.

For compounds that are members of the same chemical family (e.g. alkylamines), further study may be limited to a single representative compound that is predicted to present the greatest risk. This is most likely to be that compound which is present in the highest concentration if similar levels of toxicity are assumed for all family members. However, the availability of the pure chemicals should also be considered. A compound which is not commercially available for purchase and subsequent testing may not be the most sensible choice even if it is identified as the most hazardous. In this case, another member of the chemical family should be selected for testing within the framework of the protocol.

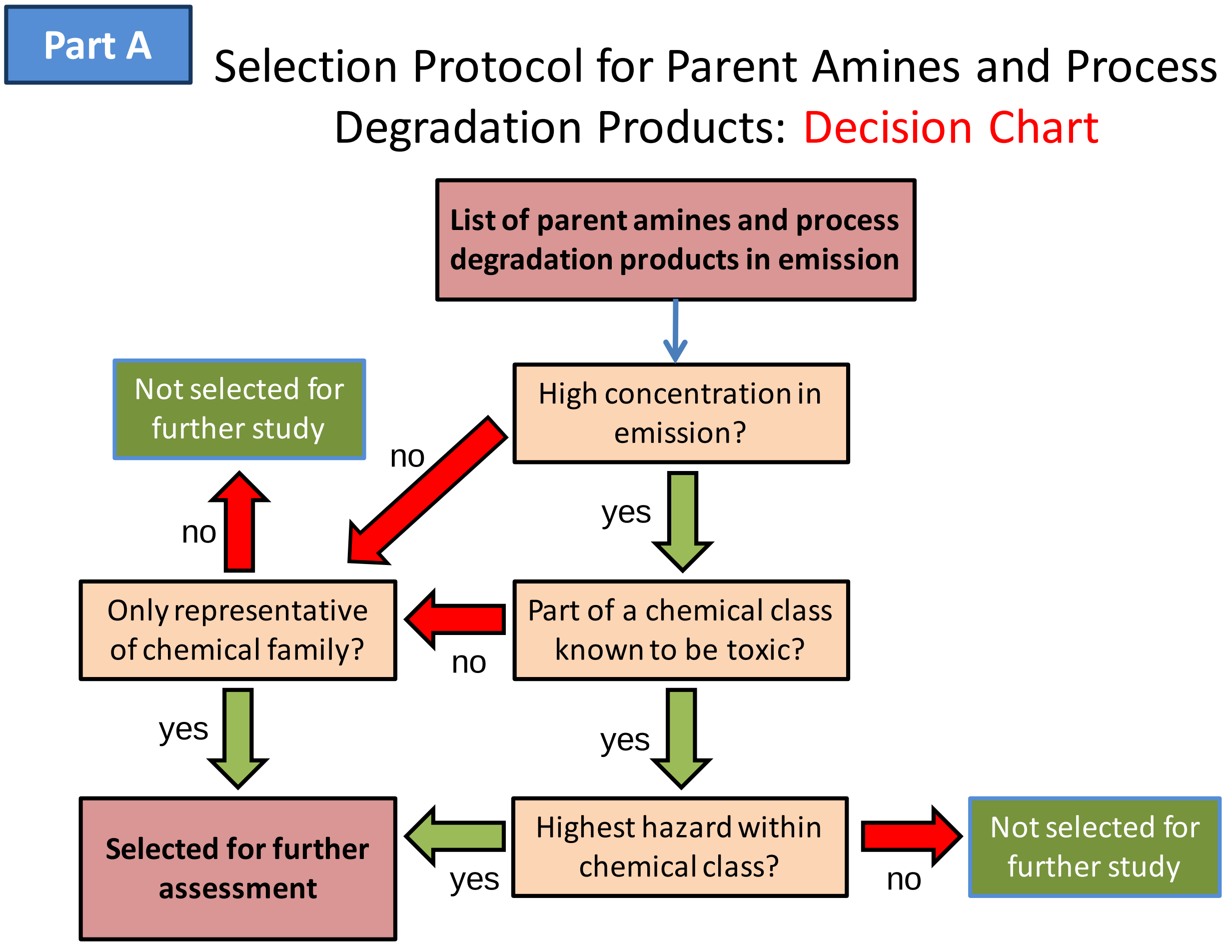


Figure 3: Protocol Part A. Decision chart for selection of parent amine (solvent) and process degradation products for further study

Part B: Determination of atmospheric lifetimes and secondary degradation products

This section refers to Part B shown in the overview diagram in **Figure 1**. A mechanistic consideration of which possible secondary degradation products might be formed from the emitted compounds *in addition* to observed compounds (identified according to Test Protocol Section I) should be carried out. Any additional pathways to form nitrosamines and nitramines and other problematic species should be identified and these compounds added to the list of compounds selected for further study.

The atmospheric lifetime in the gas phase of the selected process degradation compounds should be estimated with respect to OH radicals and photolysis (**Figure 4**). The OH reaction rate, *k*(OH), if not available in literature, can be calculated by QSAR (EPI Suite™). UV spectra can be calculated at the B3LYP (6-311G++) theoretical level for an initial evaluation, and the photolysis rates calculated from available solar flux data. Only those compounds which absorb at wavelengths longer than 290 nm will photolyze in the troposphere. The lifetime with respect to OH radicals can be estimated as $1/(k(\mathrm{OH})\times[\mathrm{OH}])$ where [OH], is the tropospheric average concentration of 1.5×10^{6} molecules cm^{-3}. However, this is not a realistic estimate for high latitudes such as Mongstad at 60.8°N, because the solar radiation and hence the radical concentrations are significantly lower. The chemical and temporal evolution of the selected compounds should therefore be evaluated with a zero -dimensional box-model using photolysis data and radical concentrations determined for the Mongstad region.

A chemical reaction model which includes tropospheric background chemistry and the reactions involving the degradation products should be assembled. Such a model can be programmed in the FACSIMILE program package or in KINTECUS, and can build on available chemical reaction schemes such as the Master Chemical Mechanism available from the University of Leeds. This provides a fast and simple way to test the chemical lifetimes and reaction product concentrations for many different compounds at once under variable conditions. Data for the solar radiation can be generated by the NCAR TUV model for the Mongstad site at different times of year and used to obtain realistic photolysis rates and radical concentrations. Local humidity and temperature data can also be included in the model. The solar flux data can be generated for different times of year and the lifetimes should be assessed both for winter when the radiation is at a minimum and for late spring when it is at a maximum. Some compounds may be photochemically destroyed very rapidly in summer but be sufficiently long-lived in winter to be deposited in terrestrial and aqueous environments to a significant degree. This will provide a more accurate estimate of the lifetimes of the compounds at the geographical location in question than an estimate using average tropospheric radical concentrations and photolysis rates. If particle formation rates and/or uptake rates into aerosols have been determined, these can be included as well. The chemical reaction scheme assembled for the box model can be included in a larger scale three-dimensional dispersion model at a later stage.

This information will then be used to provide an estimate of the process degradation product behaviour and life time in the atmosphere. The following three scenarios can be distinguished:

- If the τ_{OH} and τ_{UV} are ≥ 3 days then the compound is considered long-lived, i.e. it will not degrade photochemically in the gas phase. In this case terrestrial and aqueous fate should be considered.

- If τ_{OH} and τ_{UV} ≤ 3 hours then the compound can be considered to be very short lived in the atmosphere and no further action needs to be taken. However, the atmospheric degradation products need to be considered and these chemicals should then form the basis of further assessment within the 'atmospheric degradation products protocol'.

- If τ_{OH} and τ_{UV} fall between these limits then the reaction rates of the compound with OH and other reactants need to be more accurately determined and the chemical fate examined in higher detail.

It should be emphasized that these scenarios will vary with the time of year, as the solar flux and radical concentrations vary significantly throughout the year. Ideally, scenarios for both extremes, summer and winter, would be considered.

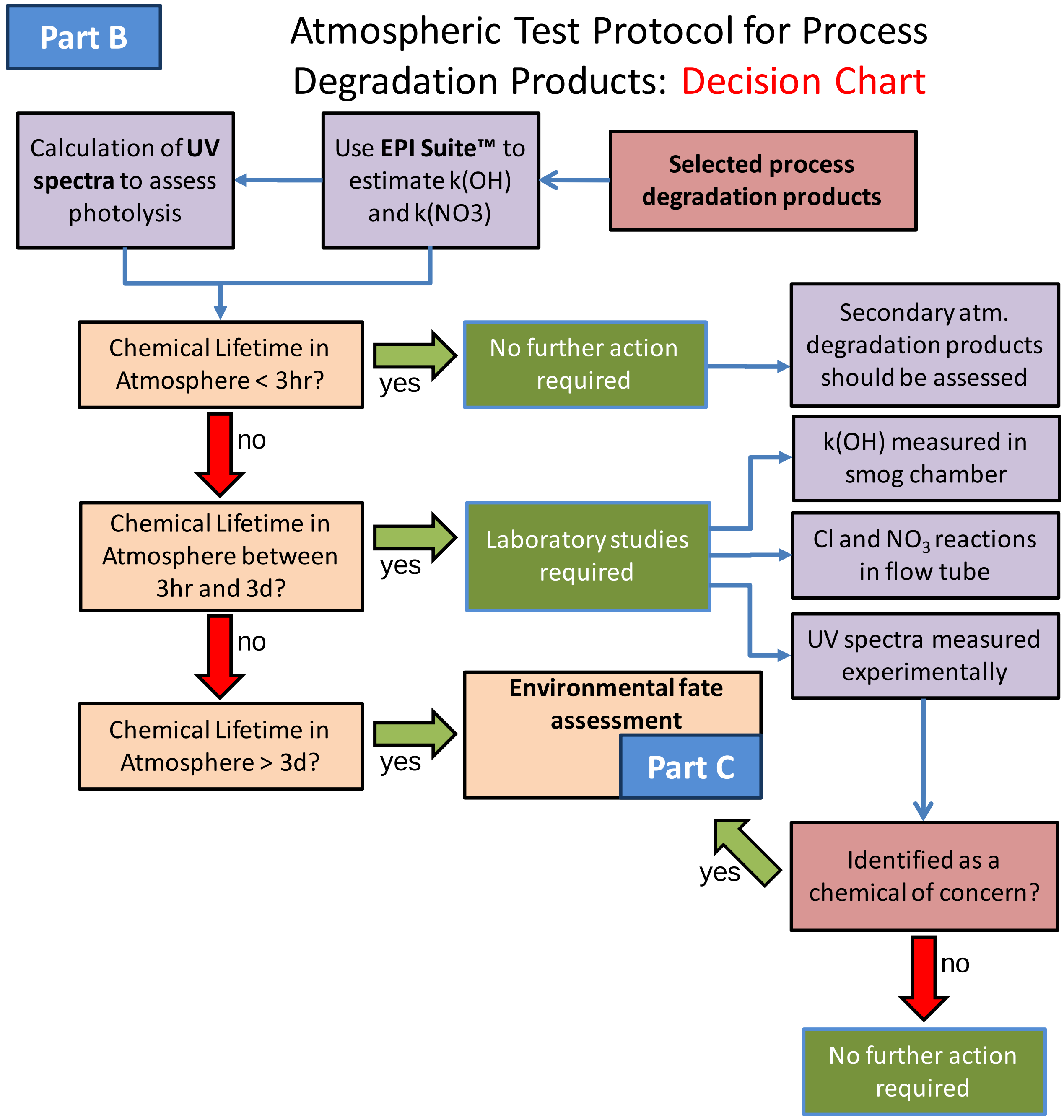


Figure 4: Protocol Part B. Decision chart to determine atmospheric residence times and behaviour for selected process degradation products.

If the compound is determined to have an intermediate lifetime, laboratory experiments are recommended to determine the OH reaction rate. Cl and NO_3 radical reactions are contributing removal processes in the marine boundary layer and at night-time respectively and should be considered. Experiments with Cl and NO_3 radicals using flow tubes should be straight forward if consideration is taken of the formation of salts by reaction between the HCl and HNO_3 products and amines. Measurements of the reaction rate of the selected compounds with radicals can be conducted in a photochemical reaction chamber by the relative rate method. Photochemical reaction chambers of the standard type used in atmospheric chemistry are typically made of polished steel or Pyrex™, have a volume of 1-200 L, and are equipped with FT-IR and GC-MS detection methods. Photochemistry is initiated by photolysis of a radical precursor (e.g. O_3 or Cl_2) by UV lamps. The reaction rate of a compound with a radical is measured relative to a standard for which the reaction rate is very precisely known. An experiment typically takes 1-2 hours and the chamber can be "cleaned" relatively quickly by heating or by photolyzing ozone to allow at least two experiments per day. In addition to the reaction rate, the products of the reaction can be detected throughout the reaction period and if necessary collected from the chamber for further analysis. The potential to form nitrosamines and nitramines can be also studied by allowing the compounds react in the chamber in the presence of NO_x.

For the compounds where the tropospheric photolysis rate needs to be more accurately determined, UV spectra should be measured in the laboratory if possible. Standard UV-vis spectrometers are available to measure the UV spectrum in the region 180-700 nm at a resolution up to 0.05 nm. For both kinetics and UV experiments compounds that have a very low vapour pressure and/or a high affinity to the chamber walls may cause practical difficulties. For these compounds the UV spectra can be calculated at the benchmark theoretical level (CC3) as an alternative to the direct measurement. The reaction rate experiments can be carried out in a flow tube experiment where the reacting gases are flowed through a reaction vessel and thus have a much lower residence time in the reactor. Flowing gases have a lower affinity to the walls of the reactor and this is a well-established technique that should pose no particular difficulties in the laboratory.

In addition to the parent amines (as discussed below), benchmark tests in a large-scale reactor facility should be carried out for a few of the process degradation products that are considered especially important in terms of toxicity and potential to form other compounds and aerosols. There are two reasons for selecting a number of degradation products for testing in a large-scale reaction chamber (e.g. European Photoreactor chamber (EUPHORE) in Valencia, Spain). First, a benchmark test is envisaged for a set of key compounds to be defined at start of protocol implementation. This could be for instance one compound of each chemical class that is predicted to form in the process (e.g. one amide, one nitramine, etc.) in order to evaluate the results obtained in lab-scale reaction chambers. Second, degradation products with low vapour pressure have a tendency to stick to chamber walls and to form particles. This may obscure experiments in a lab-scale facility, but experiments in a large-scale reactor might still yield valuable results due to the small surface-to-volume ratio (close to unity) of the large chambers. Therefore in addition to the key benchmark compounds a second set of semi-volatile compounds will be selected at start of protocol implementation.

The large-scale chamber permits studies of the atmospheric degradation of compounds under natural sunlight conditions as opposed to with UV lamps. The chamber has a large volume of 200 m^3 which minimizes wall effects and makes it especially useful for studying compounds with low vapour pressures. The chamber is equipped with a large range of analytical equipment which allows the detection of gas phase compounds and particles in a number of complimentary ways. This makes it ideal for conducting detailed product studies.

The testing of selected benchmark process degradation products is described in Section II-C.

Part C: Assessment of deposition and environmental fate

This section refers to Part C shown in the overview diagram in **Figure 1**.

C1. Deposition to terrestrial and aqueous environments

For process degradation products which are not expected to degrade rapidly in the atmosphere due to reaction with OH radicals or photolysis, deposition to terrestrial and aqueous environments should be assessed (**Figure 5**). Long-lived compounds (>3 days) are by definition less affected by atmospheric transformation and their main atmospheric sink is deposition to the ground. Thus, their environmental fate in soil and water can be very relevant and must be evaluated in detail using QSAR methods and where necessary experimental testing. Terrestrial and aquatic environmental fate testing (described in detail in this Section; II-A, Part C) is indicated for long-lived compounds which are identified through implementation of both Section II-A and Section II-B of the protocol.

An assessment of the compound life time with respect to depositional process is important. Those compounds which are rapidly deposited to terrestrial and aquatic environments will not be expected to be transported large distances and may therefore result in high environmental concentrations near to the point source (CO_2 capture plant). In contrast, those chemicals which do not deposit rapidly can be expected to be transported further away from the point source and undergo atmospheric dispersion. This dispersion is expected to lead to much lower environmental concentrations and therefore such compounds are of significantly lower risk. It is recommended that the following environmental fate processes and related physico-chemical properties are determined for each compound:

- Octanol-air coefficient (K_{oa})
- Henry's Law constant

Both parameters maybe estimated using EPI Suite™ or other computational chemistry approaches. The octanol-air partition coefficient (K_{oa}) is the ratio of a chemical's concentration in octanol to the concentration in air at equilibrium. It is useful for predicting the partitioning behaviour between air and environmental matrices such as soil, vegetation, and aerosol particles. Various models utilize K_{oa} to screen and rank chemicals for environmental persistence and long-range transport. K_{oa} can be estimated using the octanol-water coefficient (K_{ow}) and Henry's law constant for a given chemical.

In addition to determining the K_{oa} and Henry's Law constant it is recommended that relevant chemicals are also assessed using the OECD Persistence and Long-Range Transport Screening Tool and the Average Deposition Flux (given in mg m^{-2} d^{-1}) calculated as described in Section 2.3 of the EU Technical Guidance Document (TGD). The OECD Tool is a screening-level tool for organic chemicals (MS Excel document). A steady-state model consisting of three different environmental compartments (i.e. air, oceanic surface water, soil) is used to calculate overall persistence (POV) and long range transport potential (LRTP) for the comparative assessment of environmental hazard properties. The tool is designed to identify potential POPs (Persistent Organic Pollutants)/PBTs (Persistent, Bioaccumulative, Toxic) according to persistence and long-range transport. The Tool requires estimated degradation half-lives in soil, water and air, and partition coefficients between air and water and between octanol and water as chemical-specific input parameters. From these inputs the Tool calculates metrics of POV and LRTP from a multimedia chemical fate model, and provides a graphical presentation of the results. If no measured values of chemical properties can be found from literature, values can be estimated with EPI Suite™. The Tool provides the following output:

Persistence

- Overall Persistence (POV)

Long Range Transport Potential

- Characteristic Travel Distance (CTD)
- Transport Efficiency (TE)

The EU TGD describes a method for calculating atmospheric deposition. To do this, the predicted environmental concentration in air ($PEC_{localair}$) is calculated as an average concentration at 100 meters from the source. This distance is assumed to be representative for the average size of an industrial site. The concentration in air is used for exposure of humans; therefore, an annual average concentration is calculated. Deposition is calculated as an average for a circle around the source with a radius of 1000 m, which is supposed to represent the local agricultural area. The calculation of deposition flux is dependent on the Henry's Law constant and the fraction of the substance that is associated with the aerosols.

C2. Environmental fate

For those compounds which are persistent in the atmosphere but are expected to undergo relatively rapid deposition to terrestrial and aqueous environments an assessment of their environmental fate should be conducted. This assessment is important for determining into which environmental compartment the compounds will ultimately be transported to and reside. From this information, a relevant and targeted assessment of the chemical's persistence (e.g. resistance to degradative processes) and potential ecotoxicological impacts (e.g. which organisms to study) can be conducted. Initial assessment should look to utilize existing experimental data for the compounds of interest. Where there are gaps in the data for particular chemicals an initial assessment can be conducted using a QSAR-based modelling approach such as EPI Suite™ and PBT Profiler. The PBT Profiler offers a screening tool to identify pollution prevention opportunities for chemicals without experimental data. The persistence, bioaccumulation, and fish chronic toxicity values estimated by the PBT profiler are automatically compared to criteria published by the EPA. Those values that meet or exceed the criteria are flagged for the user on the PBT Profiler results page. When estimations meet or exceed criteria, that material should be evaluated as a potential PBT Chemical.

Ideally, laboratory experiments should be conducted to generate the missing data, and these should definitely be conducted if the QSAR approaches do not return reliable data. This protocol recommends that OECD guidelines for experimentally determining each of the missing parameters are used (provided in list below). It is recommended that the following environmental fate processes and related physico-chemical properties are determined for each compound:

- Water solubility (OECD Test No. 105)
- Octanol-water coefficient (K_{ow}) (OECD Test No. 107)
- Vapour pressure (OECD Test No. 104)
- Bioaccumulation and bioconcentration factors (OECD Tests Nos. 305, 315 and 317)
- Biodegradability (OECD Tests Nos. 301, 302, 306, 307, 308 and 309)
- Soil and sediment adsorption coefficients (K_{oc}) (OECD Test No. 106)
- Aqueous hydrolysis half-life and rate constant (OECD Test No. 111)

Water solubility and K_{ow}: The water solubility and K_{ow} are closely linked parameters which are dependent upon the physico-chemical characteristics of a given chemical. Aqueous solubility plays a major role in defining the movement and ultimate fate of chemicals in the environment. For example, high solubility leads to expeditious distribution in water, i.e., chemicals that rapidly and completely dissolve in water will be transported along with the general flow of water. High solubility is generally associated with a very low affinity for adsorption to solids in water, e.g., soil particles or sediment. High solubility is associated with limited bioconcentration. Higher solubility is generally associated with more rapid (ready) biodegradation.

Water solubility can be effectively calculated for a compound if the K_{ow} is known. K_{ow} is a physical property used extensively to describe a chemical's lipophilic or hydrophobic properties. It is the ratio of a chemical's concentration in the octanol-phase to its concentration in the aqueous phase of a two-phase system at equilibrium. Since measured values range from $<10^{-4}$ to $>10^{8}$ (at least 12 orders of magnitude), the logarithm (Log K) is commonly used to characterize its value. OECD Test No. 105 is the recommended method for determining water solubility and OECD Test No. 107 for determining K_{ow}.

Vapour Pressure: The vapour pressure of a chemical is important with respect to the rate at which it will volatilise or evaporate from the pure phase or from concentrated mixtures. This is directly relevant in the case of process degradation products, which may be washed out of the atmosphere via precipitation and subsequently evaporate back into the atmosphere upon drying. It is also useful in conjunction with other chemical properties, e.g., solubility in water, for estimating partition coefficients between air and water. Vapour pressure is a strong function of molecular size and temperature. OECD Test No. 104 is the recommended method for determining vapour pressure.

Bioaccumulation and bioconcentration: Bioconcentration is the intake of chemical contaminants through an organism's epithelial tissues or gills, and the subsequent concentration of that chemical contaminant within the organism's tissues to a level that exceeds ambient environmental concentrations. Bioaccumulation is the process by which chemical contamination in organisms increases with each step in the food chain. In general, chemicals that have the potential to bioconcentrate also have the potential to bioaccumulate. Bioconcentration in fish can be readily measured in the laboratory and is frequently used to predict the importance of bioaccumulation, which is much more complicated to determine. The potential for bioconcentration in fish is expressed as its bioconcentration factor, or BCF. In addition to bioaccumulation and bioconcentration, biomagnification is the process by which chemical contaminants are concentrated at levels that exceed chemical equilibrium from dietary absorption of the chemical. Biomagnification is considered beyond the scope of this protocol.

The appropriate OECD test should be selected depending on which environmental compartment the chemical being assessed is expected to accumulate in. For example, chemicals expected to partition and remain in aqueous environments should be tested using OECD Test No. 305 (fish bioconcentration). Chemicals expected to partition to sediments and soils should be tested using OECD Tests Nos. 315 (sediment dwelling Oligochaetes) and 317 (soil dwelling Oligochaetes) respectively.

Biodegradation: Hazard assessment or risk in general, and aquatic hazard classification in particular, are normally based on data obtained in standardised tests for ready biodegradability as described in OECD Test No. 301 and generated in the BIOWIN application in EPI Suite™. When the ready biodegradation tests indicate a biodegradability of <60%, inherent biodegradability testing should be conducted (OECD Test No. 302). Since inherent biodegradability can be considered to be a specific property of a chemical, it is not necessary to define limits on test duration or biodegradation rates. Biodegradation >20% may be regarded as evidence of inherent, primary biodegradability, whereas biodegradation above 70% may be regarded as evidence of inherent, ultimate biodegradability.

However, results of tests simulating the biodegradation in water, aquatic sediment and soil may also be more relevant and should therefore be used for these purposes. Degradation of organic chemicals in the environment can significantly influence exposure and, hence, it is a key parameter for estimating the risk of long-term adverse effects on biota. Degradation rates, or half-lives, should preferably be determined in simulation biodegradation tests conducted under conditions that are realistic for the particular environmental compartment of interest (e.g. surface water, sediment or soil). As a result this protocol does not recommend a single biodegradation test, but rather that the user selects the appropriate test for the chemical of interest based upon which environmental compartment it is expected to accumulate/reside in.

It recommended that the general testing strategy outlined by OECD is followed. This consists of first examining the aerobic biodegradability of the target chemical in a screening test for ready biodegradability (OECD Test No. 301) which pertains to freshwater conditions. In the case of a negative result in a test for ready biodegradability, biodegradation of the chemical may be examined by inherent biodegradation (OECD Test No. 302) or an appropriate simulation test to obtain data to be used for assessing the biodegradation rate in a specific environmental compartment. These tests simulate the degradation in a specific environment by use of indigenous biomass, media, relevant solids (i.e. soil, sediment or other surfaces) to allow sorption of the chemical, and a typical temperature which represents the particular environment. The available standardised tests include biodegradability in seawater (OECD Test No. 306), aerobic and anaerobic transformation in soil (OECD Test No. 307), aerobic and anaerobic transformation in aquatic sediment systems (OECD Test No. 308) and aerobic mineralisation in surface water (OECD Test No. 309).

Soil and sediment adsorption: The soil adsorption coefficient (K_{oc}) of organic compounds provides an indication of the extent to which a chemical partitions between solid and solution phases in soil, or between water and sediment in aquatic ecosystems. Adsorption/desorption studies therefore provide information on the mobility of chemicals and their distribution in the soil, water and air compartments of our biosphere. The values can be used in the prediction or estimation of the availability of a chemical for degradation, transformation and uptake by organisms; leaching through the soil profile; and run-off from land surfaces into natural waters.

Estimated values of K_{oc} are often used in environmental fate assessment because measurement of Koc is expensive. K_{oc} can be defined as "the ratio of the amount of chemical adsorbed per unit weight of organic carbon (oc) in the soil or sediment to the concentration of the chemical in solution at equilibrium" (Lyman, 1990); it is represented by the following equation (Lyman, 1990):

$$K_{oc} = (\mu\text{g adsorbed/g organic carbon}) / (\mu\text{g/mL solution})$$

The goal is to obtain a sorption value which can be used to predict partitioning under a variety of environmental conditions; to this end, equilibrium adsorption coefficients for a chemical on various soils are determined as a function of soil characteristics (organic carbon, clay content, soil texture, and pH). OECD Test No. 106 is the recommended method for determining adsorption.

Aqueous hydrolysis: Chemicals can enter surface waters by a number of routes, including atmospheric deposition and may be transformed/degraded in aquatic systems by chemical (e.g. abiotic hydrolysis) processes. Theoretical and experimental determination of aqueous hydrolysis constants and half-lives should been completed over a range of pH values normally found in the environment (pH 4 – 9). In addition to determining the rate of hydrolysis of the test substance as a function of pH, the identity or nature and rates of formation and decline of hydrolysis products to which organisms may be exposed should also be considered. OECD Test No. 111 is the recommended method for determining aqueous hydrolysis. However, it should be noted that this method is generally applicable to chemical substances for which an analytical method with sufficient accuracy and sensitivity is available.

Part C

Environmental Fate Test Protocol for Process Degradation Products: Decision Flow Chart

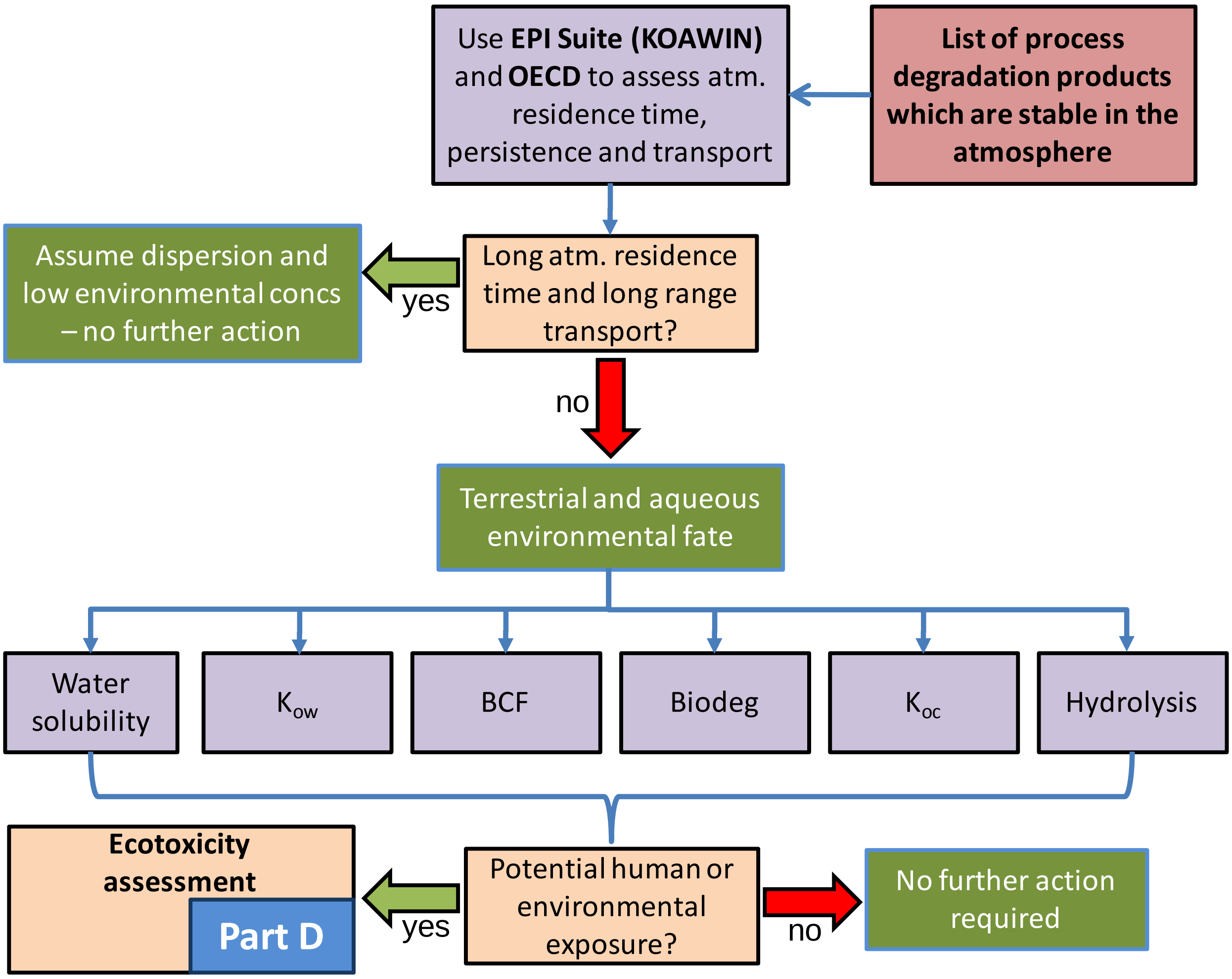


Figure 5: Protocol Part C. Decision chart to determine atmospheric residence times, transport and environmental impacts for the selected process degradation products

C3. When to use QSAR models or generate experimental data

Based on the 6 month time scale allocated for CallOff 2 the user of this protocol should prioritise the use of QSAR models for assessment of deposition and environmental fate processes for individual chemicals. However, the selection of the QSAR models and/or experimental methods to determine required environmental fate data should be determined by the protocol user on a ‘case by case’ basis for each solvent system and the chemicals of study/concern. It is impossible to predict at this point what data will be required and how reliable the use of the QSAR approaches for different chemicals will be. Therefore the user of the protocol should have experience of using QSAR models and assessing the reliability and accuracy of the values produced. The reliability of QSAR data will vary from chemical to chemical and is largely dependent upon the input data into the QSAR for the chemical group in question. For some types of chemical (e.g. polycyclic aromatic hydrocarbons) QSAR are data are considered very reliable as there is a significant amount of input data into the models for this class of chemical.

For other chemical classes, the database is severely limited and therefore the reliability of the QSAR data will be low. In the case that the QSAR data for a specific compound is considered insufficiently accurate or reliable the user of the protocol must generate the required data using experimental methods. Use of the protocol requires sensible decision making during its implementation.

Part D: Toxicity tests to determine safe concentration limits of selected compounds

This section refers to Part D shown in the overview diagram in **Figure 1**. Once the environmental sink (compartment the compounds will ultimately accumulate) is identified for each of the compounds, appropriate toxicity tests may be conducted. Toxicity testing should focus on selecting the appropriate organism(s) from the environmental compartment identified as being most at risk from the chemical of interest. As the types and number of toxicity tests are beyond the scope of this project they will not be discussed herein and will not form part of this protocol. This is a focus within another TQP project. However, it is recommended that the toxicity tests should aim to identify a safe environmental concentration limit for the chemical of interest. It is also suggested that toxicity testing should include assessment of organisms representing at least three trophic levels from the appropriate environmental compartment.

Implementation of test protocol Section II-A

The test protocol should be executable within a 6 month time frame.

The initial QSAR evaluation of the parent amines and their associated process degradation products can be expected to be completed relatively quickly. A time frame of 3-4 weeks is suggested as sufficient to achieve this evaluation and interpret the data. However, consideration must be given to the number of chemicals included in the study as this will affect the time taken to complete this work.

Part A of the protocol focuses on the selection of parent amines and process degradation products (a short list of 10-20 chemicals) for more detailed experimental study. Completion of Part is dependent upon the availability of reliable emission data specifying the full range of chemicals present in the emission and their individual concentrations. This information must at least be available for the short list of chemicals to be generated. Providing the required data is available the completion of Part A of the protocol is expected to take 2-3 weeks.

Once a short list of 10-20 chemicals is identified, Part B of the protocol focuses on evaluating the atmospheric fate of the short listed parent amines and their process degradation products selected in Part A. Evaluation of atmospheric fate is completed through the use of two theoretical approaches to determine their atmospheric fate. The initial QSAR screening approach to generate data is expected to be relatively quick to complete. It is suggested a time frame of 2-3 weeks is sufficient. The resulting data will provide an indication of the atmospheric life time for each of the studied chemicals and whether terrestrial and aquatic environmental fate should be investigated in Part C. For those compounds highlighted as having a theoretical atmospheric life time of between 3 hr and 3 days laboratory studies are required to confirm the fate of the chemicals experimentally. These laboratory based experiments are expected to take 3-4 months to complete.

Process degradation products identified as having an atmospheric residence time in excess of 3 days are subjected to environmental fate assessment in Part C of the protocol. The initial phase of Part C will be to identify which of the test chemicals will be most likely to rapidly deposit to terrestrial and aqueous systems and those which are more likely to undergo long range transport and dispersion, leading to deposition at low concentrations far from the point source (CO_2 capture plant). This phase is based on the use of QSAR models and is expected to take approximately 2 weeks. Those compounds identified as depositing rapidly in the area surrounding the point source will be further studied for a series of environmental fate parameters to determine if they are expected to concentrate in the environment (e.g. soils or groundwaters) and be exposed to humans or other organisms. Initially, QSAR approaches will be used to provide this evaluation and this task is expected to take one month (depending upon the number of chemicals to be assessed). Where predicted values are insufficiently robust experiment approaches should be pursued, the scope of which must be determined by the protocol user based on available time and resources.

The environmental fate data generated in Part C will ultimately provide a decision making tool for selecting appropriate toxicity and ecotoxicity tests and species in “Part D” of the protocol.

Test Protocol Section II-B: Atmospheric degradation products

Summary of the protocol components

Part E: Selection of parent amines for atmospheric fate studies;
Part F: Determination of atmospheric degradation products from parent amines;
Part G: Determination of atmospheric lifetimes, aquatic fate, and terrestrial fate of atmospheric degradation products;

Background information

Atmospheric degradation products are defined in this protocol as the reaction products of the parent amines with atmospheric hydroxyl radicals (OH), chlorine (Cl) and nitrate radicals (NO_3) under atmospheric conditions (temperature, pressure, etc.).

The most important gas-phase production mechanisms:
The atmospheric degradation products from the reaction of amines with nitrate radicals might be the same as in the reaction with OH, but additional products like organic nitrates may form. In the marine boundary layer halogen chemistry can be important, but was not included in the test protocol. In this protocol reactions of parent amines with OH and with NO_3 radicals are considered the most important gas-phase production mechanisms of atmospheric degradation products.

The most important gas-phase destruction mechanisms:
In this protocol the reaction with OH and NO_3 radicals are considered the most important gas-phase destruction mechanisms of atmospheric degradation products. Photolysis of nitrosamine is important for the destruction of this compound class in the atmosphere. The photolysis rates of individual nitrosamines should be studied in experiments. Other atmospheric degradation products or even the parent amines might undergo photolysis to a certain extent. Photolysis rates of solvent amines and atmospheric reaction products other than nitrosamines are expected to be less important. Reactions of atmospheric degradation products with halogen atoms are expected to be less important.

The following processes are not covered by this test protocol:
- Halogen chemistry of amines and atm. degradation products,
- Photolysis rates of solvent amines, and
- Photolysis rates of atmospheric reaction products other than nitrosamines.

The most important gas-liquid partitioning
Partitioning to the condensed and liquid phase of aerosols and clouds can be important for the atmospheric fate of amines. There is a high uncertainty about these processes but previous experience in atmospheric chamber experiments showed that 1) high yields of particulate mass are formed and that 2) amine loss to humid surfaces is high (Nielsen et al., 2010). The gas phase/particle partitioning of semi-volatile atmospheric degradation products such as nitrosamines and nitramines is of special interest to understand their atmospheric fate and for exposure estimates. Heterogeneous reactions on liquid aerosols that lead to the formation of nitrosamines have been proposed in the literature and can be quantified. In contrast, surface-catalyzed reactions on particle surfaces are poorly understood in general and thus it is currently not possible to include these in the test protocol. Uptake of amines and degradation products into aerosol and cloud droplets may be relevant to understand the environmental fate of amines, but have not been included in the test protocol. In the liquid phase, dissolved amines may react with aqueous OH radicals, ozone, or H_2O_2. The aqueous phase chemistry of amines with free radicals in droplets has not been studied until now.

In this protocol the heterogeneous formation of nitrosamines on surfaces is considered the most important process involving gas-liquid partitioning. Also important is the gas phase/particle partitioning of nitrosamines and nitramines. The following processes are not covered by this test protocol:

- Heterogeneous reactions on particle surfaces other than nitrosamine formation,
- Liquid uptake of amines and degradation products, and
- Aqueous phase chemistry of amines.

Terrestrial and aquatic fate:
Terrestrial and aquatic fate studies are a part of the test protocol and will be done with predictive QSAR methods (i.e. EPI Suite^{TM}). *Experimental tests of terrestrial and aquatic fate are not included in the test protocol but have to be considered under certain circumstances*. Abiotic and biotic degradation processes should be studied in soil and water.

Experiment facilities used to complete the evaluation

- Experiments in photochemical reactor;
- Laboratory experiments, UV spectroscopy and kinetics;

Experiments in large photochemical reactor:
Experiments in a large-scale photochemical reactor are conducted in the frame of the test protocol. There are only few outdoor chambers to study atmospheric chemistry in Europe. A large facility is required because in a large reactor volume (e.g. 200 m^3) the influence of surface reactions is minimized as the surface-to-volume ratio is close to or below unity. Previous gas-phase photochemical experiments with amines (Nielsen et al., 2010) have been conducted in the European Photoreactor EUPHORE in Valencia, Spain (http://euphore.es/).

The walls of the reaction chamber are usually made of fully fluorinated FPE (“Teflon”) foil. Fully fluorinated FEP is considered to be chemically inert. However, even at low relative humidity one monolayer of water molecules can attach to the wall surfaces and form a liquid phase. In this liquid phase gas-phase compounds may become dissolved. At elevated humidity the surface water film may represent a separate reaction medium and heterogeneous reactions involving the chamber gas phase and the surface film may take place. Surface-catalyzed reactions may also occur on dry reactor walls.

The chamber injection system should receive special attention. First, it has to be generally ensured that no contaminants are injected simultaneously with the reactant gases. Second, connection lines have to be cleaned regularly and should be as short as possible. Third, the injected amount of reactant gases has to be known with high accuracy and both injected amount and length of injection period have to be documented in a log of the experiment.

Laboratory experiments:

Experiments in indoor reactors (indoor smog chambers) equipped with appropriate light sources ("blacklights") which reproduce the spectrum of the sunlight are acceptable, if the spectral distribution and intensity of the photolysis source is well-documented and re-adjusted on a day-to-day basis. In addition, calibrated spectrometers in the visible-ultraviolet range will be used to determine the absorption cross sections of target compounds. The photolysis quantum yield as a function of wavelength will be confirmed using quantum chemistry. This information will be used in atmospheric models to derive photolysis rates for a wide variety of atmospheric scenarios. In addition photochemical reactors (chambers and flow tubes) will be used to determine reaction rates and product yields for radical reactions.

Computer models used to complete the evaluation

- SAR and QSAR models;
- Toxicology and fate database;
- Atmospheric box modeling;
- Atmospheric dispersion modeling.

SAR and QSAR models:

Structure-activity relationships (SAR) and quantitative structure-activity relationships (QSAR), collectively referred to as (Q)SARs, are theoretical models that can be used to predict the physicochemical, biological and environmental fate properties of molecules. EPISuite^{TM} (http://www.epa.gov/oppt/exposure/pubs/episuite.htm) developed by the U.S. EPA's Office of Pollution Prevention Toxics and Syracuse Research Corporation is used in this test protocol. Biological properties are typical toxicological endpoints such as LD50, EC50 etc. Predictions based structure-activity relationships are used in the test protocol for example to estimate rate constants ("Atkinson SAR") and toxicological endpoints. The toxicological evaluation, whether e.g. a certain LD50 value corresponds to a harmful compound that constitutes a potential risk to environment and health, is used in the test protocol. The toxicological evaluation itself is not part of the protocol.

Toxicology and fate database:

It is recommended to establish a (web-based, secured access) database system for the atmospheric and process degradation products. All relevant information on molecular properties, toxicological endpoints, abiotic degradation, and biotic degradation should be collected in one database. Input to the database is from SAR and QSAR models, quantum chemical models, or from review of existing literature sources. The level of uncertainty should also be indicated for each entry.

Atmospheric box models:

Numerical box models that include treatments of gas-phase chemistry and aerosol processes are used in the interpretation of results obtained from experiments inside the photochemical reactor. It is important that chamber-typical processes such as wall losses are taken into account and properly represented in the box model. The chemistry solver FACSIMILE (AEA Technology, Oxfordshire, UK) is designed to efficiently solve the differential equations involved in modelling the kinetics of chemical systems. However, FACSIMILE-based atmospheric chemistry box models such as the widely applied MCM model (see http://mcm.leeds.ac.uk/MCM/tutorial_intro.htt) do not take into account aerosol processes. At NILU the flexible aerosol model MAFOR (Karl et al., 2010a,b) has been developed which couples gas-phase chemistry and aerosol processes. Currently, the chemistry of MEA is included in MAFOR and experiments in the photochemical reactor EUPHORE have been modelled (Nielsen et al., 2010). New amine chemistry-specific compounds, reactions and aerosol components can be easily included. FACSIMILE-based atmospheric chemistry box models are recommended for estimation of real-atmosphere chemical lifetimes of degradation products.

Atmospheric dispersion models:

In case the test protocol recommends experimental investigation of a degradation product but it is not possible to acquire the chemical either from commercial production or from lab-scale synthesis, a “worst case” scenario should be simulated using an advanced atmospheric dispersion model. Since the geographic location and the local meteorology have a large influence on both the atmospheric dispersion of a pollutant and the local exposure of the population and the environment, this aspect has to be dealt with in the applied dispersion model.

Atmospheric dispersion modelling can be used to quantify the link between load (emission to air) and the resulting concentrations in air and flux in wet and dry deposition. The “worst case” approach follows the precautionary principle and sets the most severe toxicological effect (lowest concentration at which an undesirable effect occurs) in relation to the expected maximum emission (Karl et al., 2008). In the “worst case” scenario, the compound is emitted at a point source with scalable source strength. All compounds are transported as passive scalars (i.e. are assumed to be chemically inert) and maximum tolerable emissions are determined by comparison of computed air concentrations with the respective toxicological endpoints. If maximum tolerable emission of a compound is lower than its expected emission (from the CO_2 capture plant) it should be classified as harmful compound with high risk for environment and health.

Procedure for the test protocol

Part E: Selection of parent amines for atmospheric fate studies

This section refers to Part E shown in the overview diagram in **Figure 2**. Due to various reasons it may not be adequate to study the degradation of the parent amine in photochemical chamber experiments. **Figure 6** shows the procedure for the decision process. A first check is the volatility of the amine. The volatility has to be high enough to allow experiments in the gas phase. Amines which have a low volatility are difficult to inject into the air volume of the experiment reactor and tend to stick to all kinds of surfaces and are rapidly lost to the reactor walls. This implies that the wall loss of these amines is assumed to be faster than the gas phase chemistry or to be more precise: its lifetime towards wall losses is shorter than its lifetime towards chemistry. A critical vapour pressure value of 1 Pa is estimated in this protocol; amines with higher vapour pressure are further checked while amines with lower vapour pressure are only tested with respect to their fate in the terrestrial and aquatic environment.

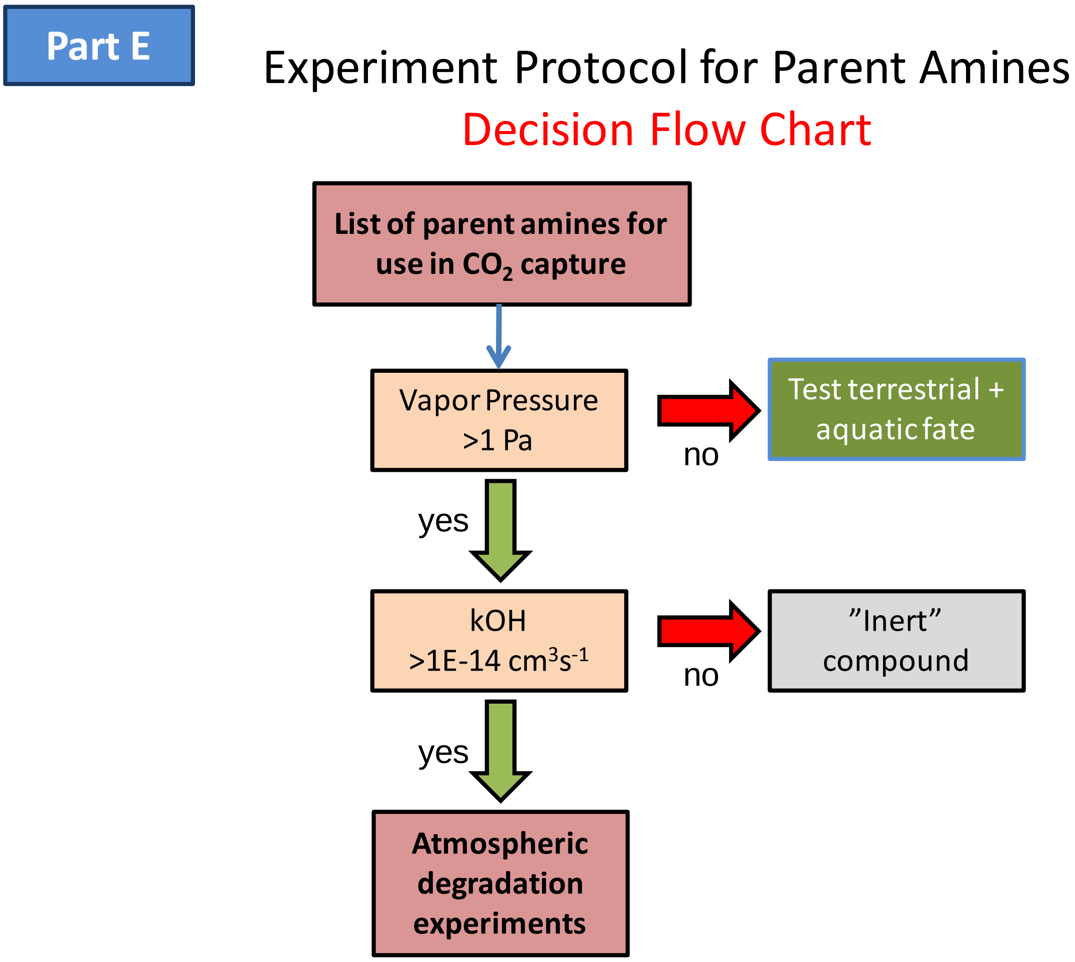


Figure 6: Protocol Part E. Decision chart for parent amine (solvent)

The second check is the reactivity of the amine. If the rate constant of the reaction with OH radicals is greater than $1x10^{-14}$ molecules cm^3 s^{-1}, the experiments to test the atmospheric degradation can be performed. If the water solubility is below 1 g/100ml (water) and *k*(OH) is not greater than $1x10^{-14}$ molecules cm^3 s^{-1}, the amine can be considered to be an inert compound. An inert compound (non-reactive gas) can be transported in the atmosphere over long distances. It would only be removed from the atmosphere by dry deposition. For solvent amines, k(OH) is generally greater than $1x10^{-14}$ molecules cm^3 s^{-1}, and it is very unlikely that it will be classified as inert compound.

For all those amines which are not evaluated in experiments, the atmospheric fate will be predicted with theoretical methods (EPI Suite TM and quantum chemistry calculations, **Figure 2**). The environmental fate of an inert amine does not need to be evaluated further. For inert amines, toxicity testing should be carried out.

Part F: Determination of atmospheric degradation products from parent amines

This section refers to Part F shown in the overview diagram in **Figure 2**.

F1. EUPHORE large photochemical reactor experiments

A set of five experiments in the large photochemical reactor (EUPHORE) is planned per parent amine. Three of the five experiments are under dark conditions and therefore independent of weather conditions. It is not recommended to test parent amines (=generic solvent amines) in a lab-scale facility. There are three reasons for not using a lab-scale reactor for the evaluation of parent amines. Parent (solvent) amines have relatively low vapour pressures (this is a useful property in the post-combustion process) and hence tend to “stick” to surfaces and to partition to condensed phases (particles). Parent amines are also likely subject to reaction with nitric acid to form nitrate salt particles. For MEA this has been demonstrated in the ADA project (Nielsen et al., 2010). This physical and chemical behaviour complicates the investigation of the atmospheric chemistry of parent amines. In a small-scale laboratory reactor losses to the chamber walls will be large (due to the high surface-to-volume ratio of small chambers). Losses of the parent amine to particles are expected to be very large in a small lab reactor. Third, in a lab-scale reactor heterogeneous formation of secondary products on the wall and on particle surfaces will affect the gas-phase chemistry. In a large photochemical reactor such as EUPHORE (volume is 200 m^3) all stated factors can be controlled due to the small surface-to-volume ratio (close to unity).

Different atmospheric conditions and chemical pathways are taken into account. The series consists of the following experiments (**Figure 7**):

1. Photo-oxidation under low NO_x (in sunlight);
2. Photo-oxidation under high NO_x (in sunlight);
3. Night chemistry with NO_3 (in dark);
4. Heterogeneous chemistry with NO_x (in dark, dry conditions).
5. Heterogeneous chemistry with NO_x (in dark, wet conditions)

The following information on chemical lifetime and production yield will be derived as output from the interpretation of the respective experiments:

1. Rate constant in the reaction parent amine + OH. Production yield of nitrosamines and nitramines. Production yield of other reaction products with apparent yield >10%.
2. Rate constant in the reaction parent amine + OH. Production yield of nitrosamines and nitramines. Production yield of other reaction products with apparent yield >10%.
3. Rate constant in the reaction parent amine +NO_3. Production yield of nitrosamines and nitramines. Production yield of other reaction products with apparent yield >10%.
4. Upper estimate of homogeneous gas-phase production of nitrosamines in dark.
5. Upper estimate of heterogeneous production of nitrosamines in dark.

Atmospheric box models (e.g. MCM, MAFOR) should be applied to derive this chemical output information. Apparent yields are determined by the ratio of the concentration increase of product to the consumed concentration of parent amine (using only measured concentration time series of parent amines and products).

In the photo-oxidation experiment under low NO_x conditions (less than 10 ppb NO_x), the OH-induced oxidation of the amine in a remote atmospheric environment is evaluated. In the photo-oxidation experiment under high NO_x conditions (100-500 ppb NOx), the OH-induced oxidation of the amine in an urban atmospheric environment, or in the air close to the emission source is evaluated. In the night chemistry experiment, the oxidation of the amine through NO_3 radicals is evaluated. The NO_3 radical is not stable in sunlight; it undergoes rapid photolysis, and is only relevant during night in the atmosphere. Finally, the heterogeneous chemistry (surface-catalyzed reactions) of the amine involving NO_x is evaluated in a dark experiment under dry and wet conditions. This experiment is important to evaluate the potential of the amine to produce nitrosamines. In sunlight, nitrosamines undergo rapid photolysis, but they are stable in the dark.

The photo-oxidation experiments are done in dry conditions, with relative humidity (RH) below 3%. It is important that humidity is relatively low in the experiments to study the gas-phase chemistry. At increased relative humidity more of the amine is lost to the wall surface of the reactor. Propane can be added to the gas mixture as a reference hydrocarbon. The rate constant of the reaction of OH with propane is well defined. From the time series of the amine and propane, the rate constant of the reaction between OH and amine can be determined. Ozone could be added (50-100 ppb) to accelerate the turnover rates of photochemistry. The gas mixture is exposed to sunlight for several hours and the amine decay and the formation of products is monitored.

The night chemistry experiment with NO_3 radicals is done in dry conditions, with relative humidity (RH) below 3%. It is important that humidity is relatively low in the experiments to study the gas-phase chemistry. At increased relative humidity more of the amine is lost to the wall surface of the reactor. NO_3 radicals are produced in a separate container in a mixture of 0.5 ppm dinitrogen pentoxide (N_2O_5) and NO_2. The mixture is injected into the reactor before experiment start. The gas mixture is reacted for several hours and the amine decay and the formation of products is monitored.

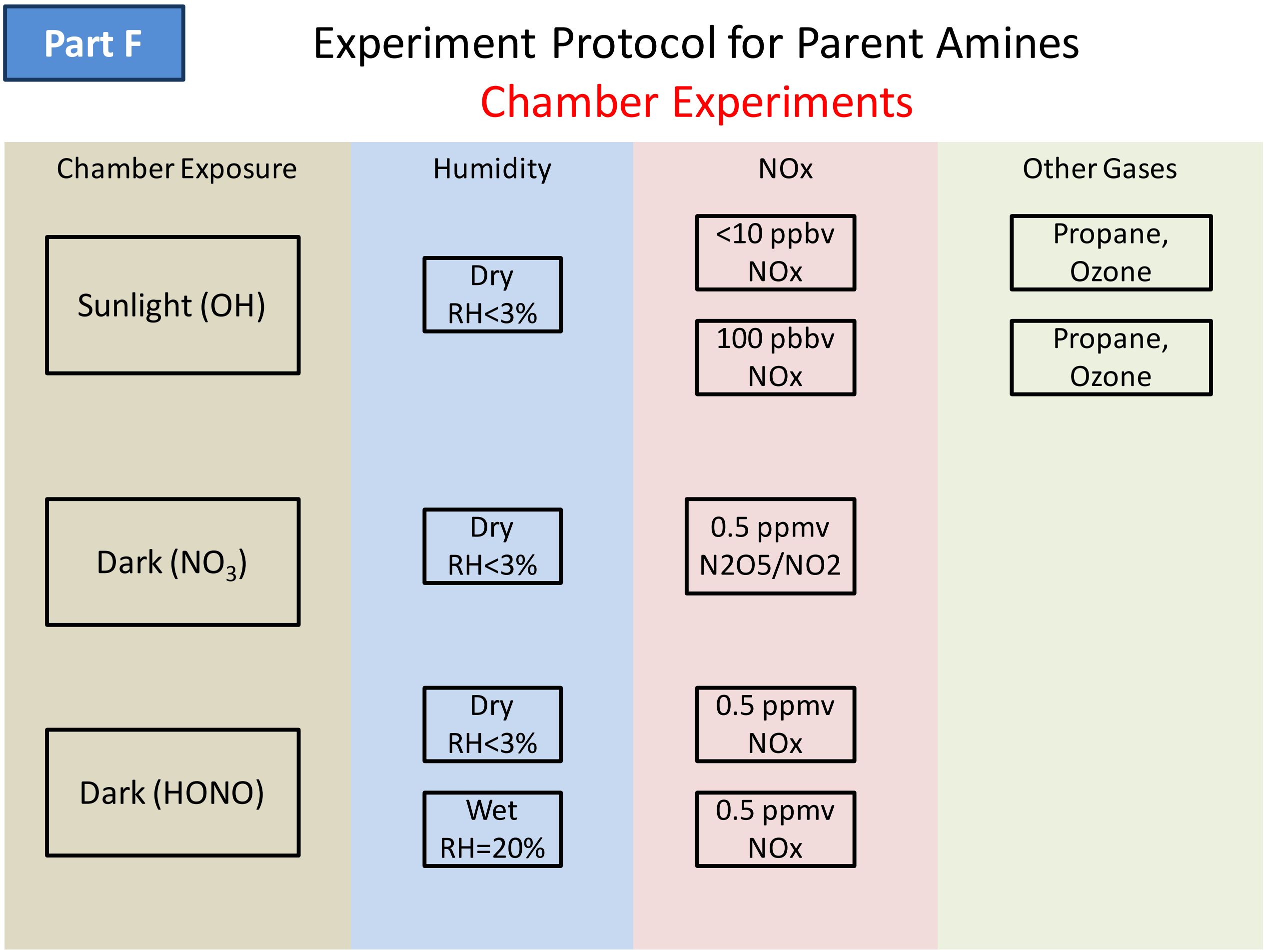


Figure 7: Protocol Part F. Experiment series for parent amines in the photochemical reactor

The heterogeneous chemistry experiment with NO_x is performed in the dark reactor. The experiment starts with first adding NO_x and then adding the amine. The gas mixture is reacted for six hours and the amine decay and the formation of products is monitored. The relative humidity is increased from initially dry conditions (<3%) to wet conditions (=20%). This can be done by stepwise addition of water vapour or by a single addition of water vapour after ca. 3 hours. The actual formation of mechanism of nitrosamines with gas-phase NOx and nitrous acid (HONO) is highly uncertain. It the time of writing the protocol several different reactions in the gas-phase (homogeneous chemistry) and surface-catalyzed reactions have been proposed in the literature. In the proposed dark experiment it is not possible to separate between homogeneous gas phase reactions and heterogeneous reactions involving the dry/wet reactor surfaces. The experiments results can be interpreted either as 1) an upper estimate for the homogeneous gas-phase production (assuming no surface reactions occur) or as 2) an upper estimate for the heterogeneous production. The experiment will allow some conclusions on the importance of the heterogeneous chemistry, because with increasing humidity the relative amounts of produced nitrosamines should increase if the production is dominated by reactions on the surface water film.

Amines and their reaction products may be lost in transfer lines and in inlet lines of sampling devices. This can represent a large uncertainty in the determination of reactant concentrations. It is thus recommended to use only short connection lines, and if possible, to heat the lines. All transfer lines between chamber and on-line and off-line instruments and sampling devices have to be documented.

Amines are “sticky” compounds which tend to absorb strongly to many types of surfaces. It has been found in photochemical experiments, that a substantial amount of amines can be lost to the wall surfaces of the reactor. The rate of this loss process should be determined before the beginning of each experiment. To this end, the amine is injected into the clean dark chamber, and its decay is monitored for roughly one hour. The procedure is repeated after the experiment run. From the measured amine concentration decrease, a first order loss rate can be derived. It is assumed that absorption equilibrium will be established after an extended period. For the quality assurance within the protocol it is however sufficient to determine a first order loss rate, since experience showed that adsorption is much stronger than desorption.

A consequence of the (irreversible) adsorption is a “memory” effect of the reactor walls. This means that amines that absorbed to the wall surfaces in previous experiments in the reactor can be released from the wall in later experiments and cause irreproducible concentrations. To reduce the influence of the memory effect, the above described procedure may help. The amine of interest is injected into the clean dark chamber and remains there for one hour or longer. After these “conditioning” phases, the reaction chamber should be “flushed”, i.e. air streams with a high flux rate through the chamber, in order to dilute the concentration of the amines and all possible trace gases inside the chamber volume. The described procedure can be applied to determine the first order loss rate to wall surfaces and to reduce the effect of previously absorbed amines.

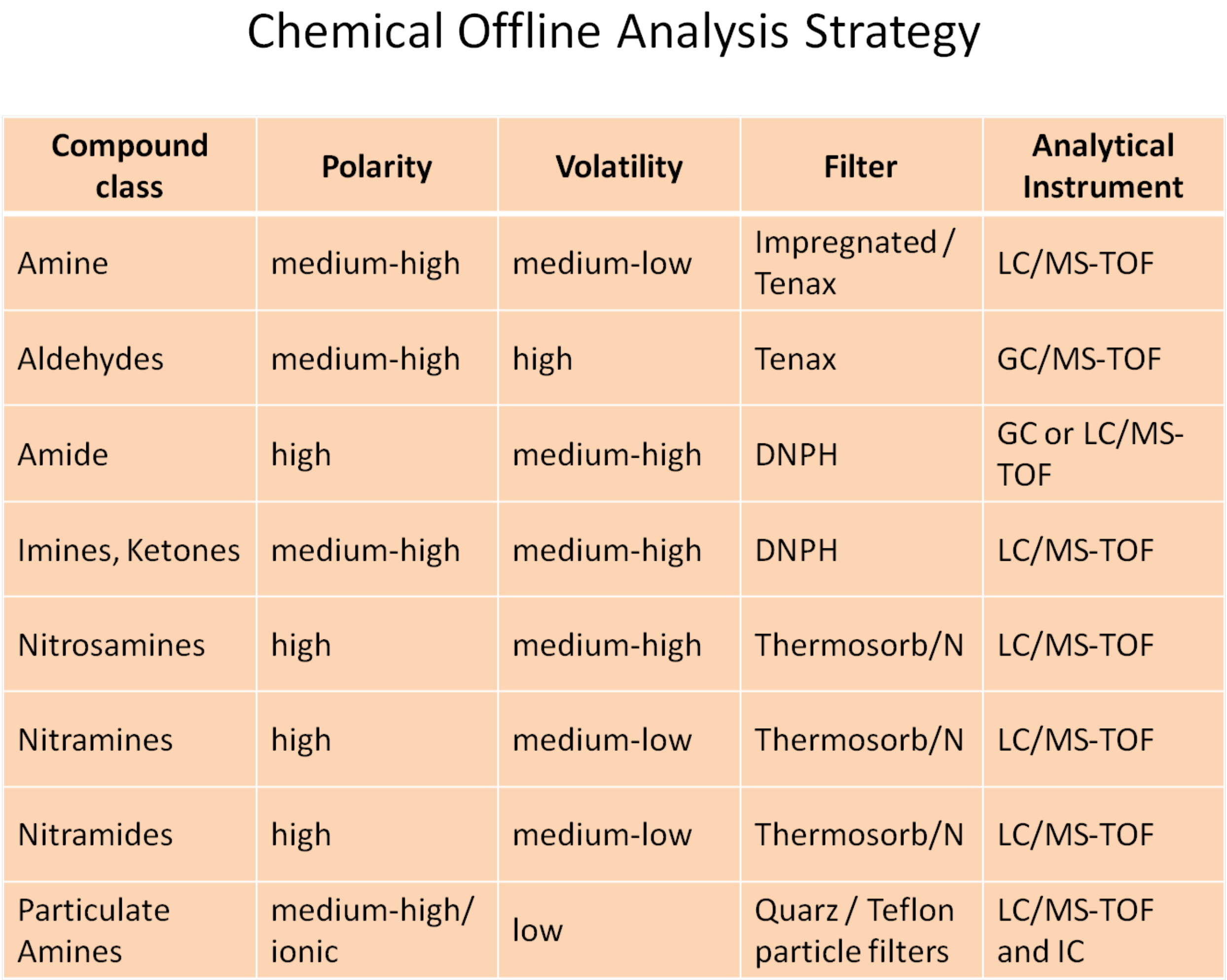
The reaction of amines with gaseous nitric acid (HNO_3) in the sunlit reaction chamber has been found to generate substantial amounts nitrate particles (Murphy et al., 2007; Carter et al., 2008; Nielsen et al., 2010). This reaction has to be considered as a further loss process of the parent amine. Online measurement of the particle size distribution and size-resolved mass concentration of the chamber aerosol is necessary throughout the photo-oxidation experiments (in sunlight). Using the measured total aerosol mass concentration and an aerosol box model, the loss rate to the particles can be estimated. Alternatively a first order loss rate of amines to particles may be determined as a function of the total particle surface during the experiment. This could be achieved in a dark experiment using a known seed aerosol, onto which gas-phase amine condenses.

All observed losses of the injected amine in the experiment reactor, i.e. losses by replenishment air flow, losses to the wall surfaces, and losses to particle surfaces have to be quantified on a day-to-day basis and estimated during the experiment runs, e.g. by use of box modelling.

Due to the low reactivity of some amines, wall loss of amines could occur faster than reaction with OH radicals. In this case, only the heterogeneous chemistry experiment with NO_x in the dark reactor should be conducted. It is advised to use theoretical methods to determine the atmospheric degradation products of the respective amine.

F2. Chemical analysis strategy

In this protocol importance is attached to the use of offline analytical methods in the determinate on gas-phase concentrations of parent amines and their photochemical oxidation products. There are several on-line and in-field techniques available. The instrument with the highest applicability is proton transfer reaction time-of-flight mass spectrometry (PTR-TOF-MS) (de Gouw, 2007). Use of online methods allow for a high time resolution of concentration measurements. Offline methods should be improved in order to increase the collection efficiency of the filters and cartridges are increased and the collection period can be reduced. Offline techniques usually collect both gas phase and particulate matter (aerosols), while online methods sample either gas phase or particulate matter. For this reason the online measurement results are not directly comparable with the offline analysis of the same compound, if the compound partitions to particles. **Figure 8** displays the suggested offline techniques for use in the test protocol. Depending on polarity and volatility of the compound class, different adsorbents (filter / cartridge) and analytical method is proposed.



Chemical Offline Analysis Strategy

Compound class	Polarity	Volatility	Filter	Analytical Instrument
Amine	medium-high	medium-low	Impregnated / Tenax	LC/MS-TOF
Aldehydes	medium-high	high	Tenax	GC/MS-TOF
Amide	high	medium-high	DNPH	GC or LC/MS-TOF
Imines, Ketones	medium-high	medium-high	DNPH	LC/MS-TOF
Nitrosamines	high	medium-high	Thermosorb/N	LC/MS-TOF
Nitramines	high	medium-low	Thermosorb/N	LC/MS-TOF
Nitramides	high	medium-low	Thermosorb/N	LC/MS-TOF
Particulate Amines	medium-high/ ionic	low	Quarz / Teflon particle filters	LC/MS-TOF and IC

Figure 8: Chemical analysis strategy (offline methods) for use in Part F.

This test protocol includes the use of two different offline methods: GC/MS-TOF and LC/MS-TOF. The three major advances of the GC/MS offline method are (1) separation capacity, (2) library identification, and (3) quantification (Dye et al., 2008). Even without isolated standard compounds available, this method allows a semi-quantitative estimation of the concentrations of all identified compounds. With isolated standard compounds this method can become fully quantitative and fully validated. The major drawback of GC-methods is their weakness towards the separation of polar compounds. Since the principle of gas chromatography requires analytes in the gas phase, this method is in no case applicable for thermo-labile compounds. LC/MS, on the other hand, has been shown to be very suitable for polar compounds, even for thermo-labile substances. The limiting prerequisites for LC/MS analysis are that the analytes are soluble, stabile in solution and can be ionized within the ion source of the LC/MS instrument. The most important drawback of LC/MS is that the response factor can vary several orders of magnitude from one compound to another. Furthermore, co-eluting compounds may cause suppression of the analyte signal. This means that the method must be calibrated and validated with isolated standards for quantification (Dye et al., 2008).

The limit of detection (LoD) is dependent on a lot of different factors like sample volume, recovery rate, chromatographic separation, interfering compounds, instrumental sensitivity, and the response factor of a given compound (Dye et al., 2008).

Resulting concentrations from samples collected at the same time during an experiment may vary due to different sample inlets, pump fluxes, leakages, etc. Sampling conditions should be well-documented and be part of the routine log protocol for each performed experiment.

Analytical results for the same sample may produce different results depending on the analytical laboratory chosen for the analysis of the filter sample. An option is to send out multiple samples taken at identical sampling conditions to different analytical groups and ask for reporting the analyzed mass of compound x in the sample to cross-check the validity of analytical results. For Unique identification a reference standard is required for nitrosamine and nitramine compounds.

Online methods, in particular online gas chromatography - mass spectrometry (GC/MS) and/or proton transfer reaction - mass spectrometry (PTR/MS) should be used in addition to offline techniques during photochemical experiments with the parent amines in the large-scale reactor EUPHORE.

Instrumentation and analytical methodologies should be documented in agreement with practice in international journals of atmospheric and analytical chemistry. Development of an analytical protocol for measurement of nitramines is part of the CCM / H&ETQP Amine 5 activity.

Part G: Determination of atmospheric lifetimes, aquatic fate, and terrestrial fate of atmospheric degradation products

This section refers to Part G shown in the overview diagram in **Figure 2**. This part of the protocol describes a decision procedure for atmospheric degradation products of the parent amine (solvent). Based on this procedure it should be possible to decide for which of the atmospheric degradation products evaluation in experiments should be carried out. In general, prioritization of compounds should be done according to toxicity; e.g. nitramines and nitrosamines are considered highly toxic and carcinogenic, aldehydes and amides are known irritants and toxic in higher doses. Aliphatic hydrocarbons and most alcohols are considered less toxic and thus have lowest priority for experimental evaluation.

It is recommended to establish a (web-based) database system for the atmospheric and process degradation products. Identical degradation products may be obtained in the atmospheric degradation of different parent amines or directly emitted in the post-combustion process. The information from this new database is used for the decision on the further procedure for degradation products. All relevant information on molecular properties, toxicological endpoints, abiotic degradation, and biotic degradation should be collected in one database.

G1. Atmospheric degradation products

Due to the high number of individual compounds that could form in the atmospheric degradation of the parent amine, it is not be possible to study the fate of all atmospheric degradation products in photochemical chamber experiments. **Figure 9** shows the procedure for the decision process.

All compounds in the list of atmospheric degradation products, which have been identified in experiments or predicted by theoretical calculations (see **Fig. 2**), will be studied using EPI Suite^{TM}. This first stage of the evaluation includes estimates of k(OH) and $k(NO_3)$ with the AOPWIN module and estimates of the parameters that describe the terrestrial and aquatic fate, i.e. abiotic degradation, biodegradation, bioaccumulation, partitioning to suspended solids, soil retention.

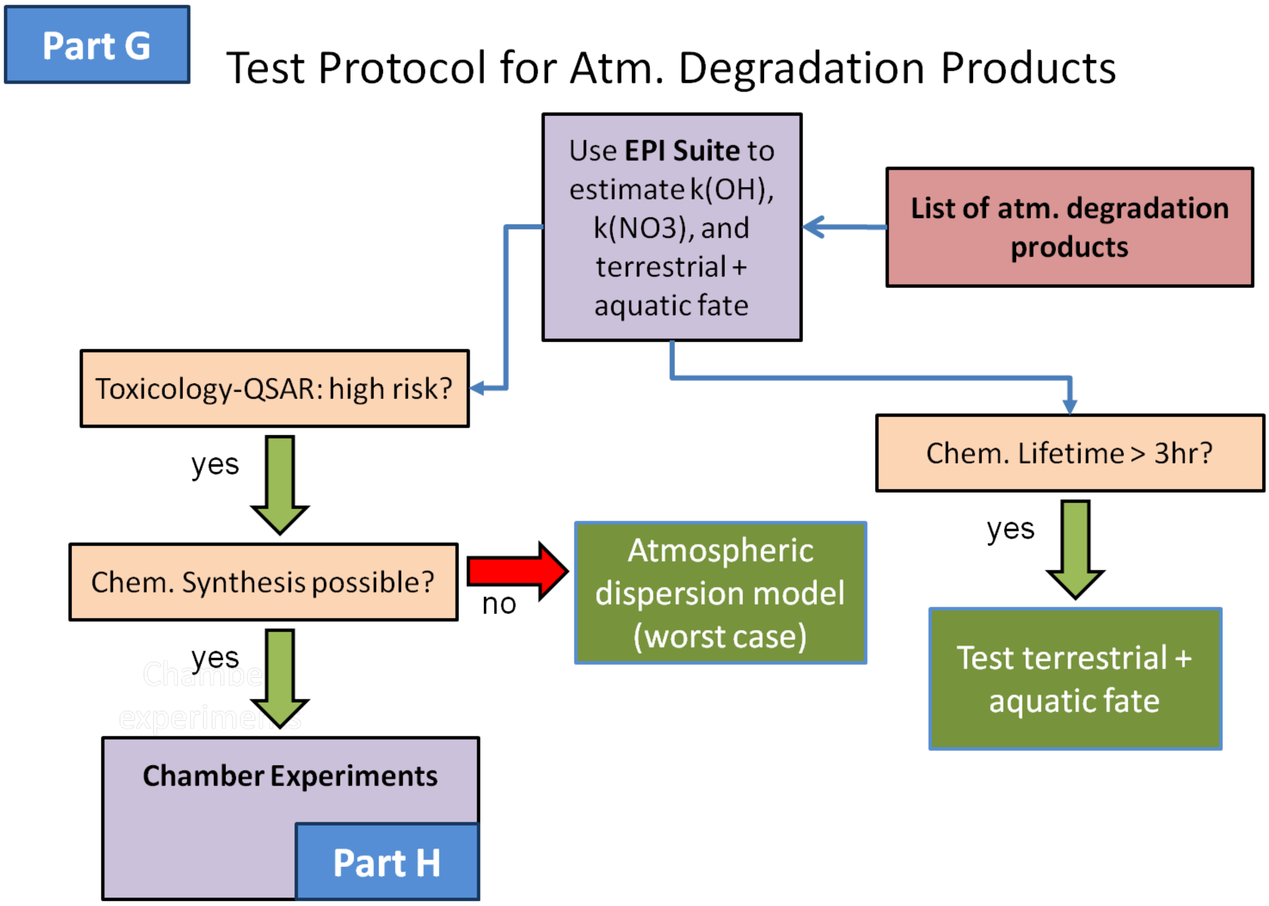


Figure 9: Protocol Part G. Decision chart for atmospheric degradation products

G2. Additional testing of degradation products

Compounds with a long atmospheric lifetime potentially accumulate in the atmosphere and could be transported over long geographic distances. These long-lived compounds also have the potential to accumulate in the terrestrial and aquatic environment. In this test protocol, a critical atmospheric (chemical) lifetime of 3 days is introduced. Compounds with a lifetime >3 hours should be evaluated in terms of their terrestrial and aquatic fate using adequate experiments. This evaluation is done in addition to the evaluation of their atmospheric fate. For shorter-lived compounds, no additional experimental evaluation of their terrestrial and aquatic fate is required.

An additional check is the water solubility of the degradation product. A critical value of 1 g/100ml (water) is assumed for the water solubility in this protocol. If the *water solubility of the compound is below 1 g/100ml*, no tests of terrestrial and aquatic fate will be done. Poorly water-soluble constituents in the atmosphere are mainly removed by dry deposition and not by wet scavenging. It is thus assumed that they do not directly entrain into soils or aquatic ecosystems. They could potentially accumulate on plant and soil surfaces.

Compounds with expected or proven high toxic potential should be studied in experiments independent of their atmospheric lifetime. Short-lived toxic compounds could be relevant to the environment and health in the proximity of the emission point. The toxicology of all compounds in the list of atmospheric degradation products should be evaluated using QSAR methods. This evaluation has to be done outside of the project. The information about toxicology should be entered into the proposed new database of atmospheric degradation products. For compounds which are shown to have a high toxicological risk, experiments should be performed. The criterion for the toxicological risk has to be developed in a different project (CCM / H&ETQP Amine 3) and cannot be defined within this activity. It is proposed in this test protocol that all compounds which belong to the chemical classes of nitrosamines, nitramines, amides, and imines should be treated as potentially highly toxic compounds.

For the practical implementation of experiments, it is often necessary to synthesize the compound. The final decision about experimental evaluation is thus based on the availability of the compound of interest, either from a commercial supplier or from lab-scale chemical synthesis.

If the chemical cannot be acquired, the evaluation in experiments is not possible. For these degradation products, atmospheric dispersion model calculations should be performed. In a simulation with an advanced air quality model the regional concentration distribution of the compound and its deposition to terrestrial and aquatic environments can be obtained. A “worst case” scenario would result the maximum concentration and maximum deposition flux of the compound, by emission of an estimated amount from a point source and taking into account a first-order loss by chemistry (using k(OH) from EPI Suite^{TM} and a fixed concentration of [OH] = $2x10^6$ molecules cm^{-3}). The predicted maximum levels could then be compared to their toxicity risk threshold. As mentioned before, the toxicity threshold has to be defined in a different activity. If the predicted concentrations / deposition rates exceed the toxicity threshold, the compound is of concern for environment and health (Karl et al., 2008).

Implementation of test protocol Section II-B

The test protocol should be executable within a 6 month time frame.

Figure 2 provides an overview of the steps involved in test protocol Section II-B. The initial EPI Suite based evaluation of the parent amines and their associated atmospheric degradation products can be expected to be completed relatively quickly. In a time frame of 6 weeks the first evaluation of parent amines (PART E, decision for experiments) and QSAR prediction of rate constants (kOH, kNO_3) can be achieved. Within this 6 week time frame, the basic structure for the planned database system will be developed. Other partners (toxicology) should contribute in the database building.

From the start, amine degradation will be studied using quantum chemistry calculations. A complete theoretical study of a compound will take about 1 month or longer. However calculations can be submitted in parallel and left to run.

Large scale photochemical reactor experiments with parent amines at the EUPHORE facility (Part F) require a week work for each amine. In case experiments have to be repeated, a second week per amine has to be planned. Additionally 2 months of work to evaluate and process the large amount of data obtained at the chamber must be envisioned. It is recommended to begin with the one-week set of experiments for one or two parent amines in the pre-execution phase of the protocol.

A number of atmospheric degradation products that derive from the parent amines is known from previous theoretical and experiments studies (e.g. for MEA). The list of atmospheric degradation products will be completed during the implementation phase by quantum chemistry calculations and experiments in a large-scale chamber (e.g. EUPHORE) with the selected parent amines. For this reason, EPI Suite predictions for atmospheric degradation products have to be done at a later stage in the implementation phase after the first 3 months and will be achieved in about 6 week time. In this step (Part G) also terrestrial and aquatic fate data will be generated and a decision will be made which of the compounds are to be studied in experiments.

Laboratory scale photochemical chamber product studies (Part H) under different NO_x conditions can be carried out in available chambers and should be feasible in 3 months or less. Gas phase/particle partitioning experiments will only be carried out for compounds with low volatility (Part H.2). This work can be done in a large scale reactor (such as EUPHORE) or in an indoor *batch-flow reactor* (operation as a continuous stirred tank reactor to produce a steady-state gas mixture. Reactants are added to the chamber continuously with the effluent being withdrawn at the same flow rate for filter collection and on-line gas and particle analysis). The number of degradation products studied at EUPHORE (Part H) will be determined by the availability of the chamber which might be limited at any given time due to bookings by other users, but will be a maximum of five.

“Worst Case” simulations (one year) for the location of Mongstad using an advanced air quality model can be done in relatively short time since the meteorological data is already generated. This will be done for a few benchmark compounds (up to five per run). One run and data interpretation will take one month.

Test Protocol Section II-C: Experimental evaluation of process and atmospheric degradation products

Summary of the protocol components

Part H: Experimental evaluation of the process and atmospheric fate of process benchmark and atmospheric degradation products.

Procedure for the test protocol

Part H: Experimental evaluation of the process and atmospheric fate of process benchmark and atmospheric degradation products

This section refers to Part H shown in the overview diagram in **Figure 2**. For atmospheric degradation products that are identified for experimental studies in Part G, experiments are conducted in indoor smog chambers and laboratory scale experimental setups (**Figure 10**). The proposed experiments are designed to investigate the atmospheric fate of three compound groups: nitrosamines, nitramines, and carbonyls (amides, imines, etc.).

H1. Experiments in lab-scale photochemical reactors

Photolysis is the dominant removal process for nitrosamines in the atmosphere and it is important to obtain well-defined photolysis characteristics. It is proposed that for each nitrosamine in question, the wave-length dependent photolysis frequency is determined in lab-scale photolysis experiments. The resulting photolysis rate of the nitrosamine should be provided relative to the photolysis rate of NO_2. Photolysis experiments should be done in a lab-scale reactor with well-characterized light spectrum. For all other products, UV spectra should be measured in the laboratory and/or calculated at the benchmark theoretical level.

For nitramines and carbonyls such as amides and imines, experiments in an indoor photochemical reactor should be performed. Experiments should be interpreted with the use of (zero-dimensional) atmospheric box models, which compute the concentration time series for the compounds of interest. The box model should have an aerosol module. Two different types of experiments are planned.

The first experiment type is a photochemical study under high NO_x conditions, comparable to the one described in Part F for the parent amine. The rate constant for the reaction of the compound with OH will be determined relative to the rate constant of the reaction of propane with OH. Information about products that form in the reaction with OH will not be further used in the protocol. Thus the experiment can be carried out using a minimum of analytical instruments. The minimum instrumentation is one offline method of choice to monitor the degradation of the reacting carbonyl and online-gas chromatography to monitor the concentration of propane.

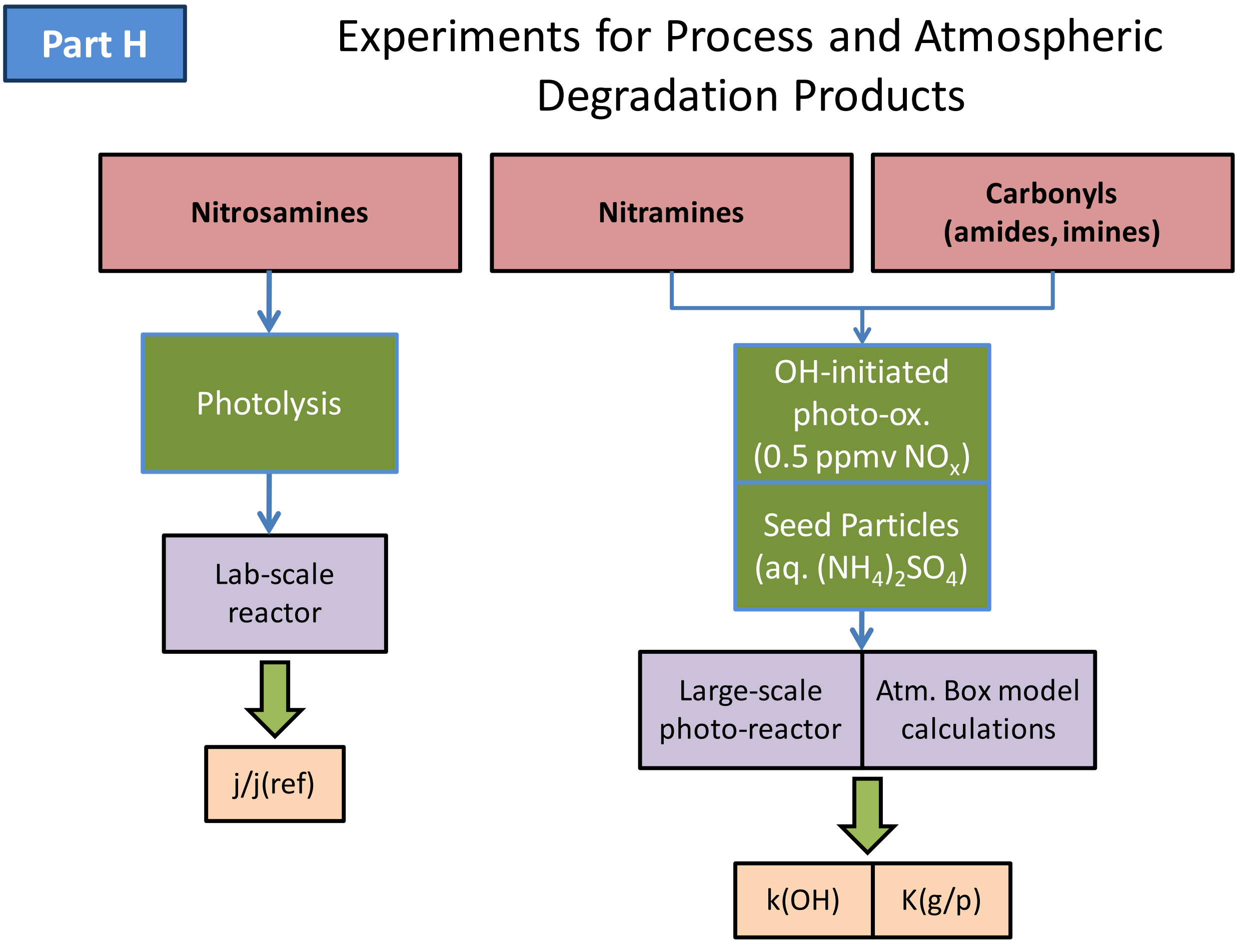


Figure 10: Protocol Part H. Experiments for process and atmospheric degradation products

H2. Experiments in large-scale photochemical reactors

Particle formation potential of selected atmospheric degradation products and selected process degradation benchmark compounds is tested in a second experiment type in the large-scale photochemical reactor. These experiments involve the injection of seed aerosol in the dark reactor to study the gas phase /particle partitioning. Aqueous ammonium sulphate ($(NH_4)_2SO_4$) are injected into the large-scale photochemical reactor before the experiment begins. The chamber should be clean, with no gases or particles present. After addition of the nitramine or carbonyl, the compound will partition between gas phase and the particle phase. Assuming an equilibrium situation between the gas phase and the particle phase, the equilibrium partitioning coefficient *K(g/p)* in units m^3/µg can be determined. Both physical adsorption to particles and absorption into the organic phase of particles may occur. It is assumed that for the compounds of interest, gas phase /particle partitioning is dominated by absorptive partitioning. Gas phase/particle partitioning is determined using monitored time concentration of the compound in the gas phase and the organic aerosol mass concentration, applying a two-product approach as described by Odum et al. (1996). The surface area of particles should also be measured.

Atmospheric box model calculations are required to analyse the experiment and to determine *k*(OH) and *K(g/p)* and the errors of the estimate.

For process degradation benchmark products which are hard to predict and/or difficult to assess in a laboratory facility (low vapour pressure criterion, see Section II-A, Part B) or which have been selected to represent the toxic behaviour of a certain compound class (toxicity criterion, see Section II-A, Part B), more detailed reaction rate and product studies can be carried out at the European Photoreactor Facility (EUPHORE) in Valencia, Spain. In the planned 6-month period this can be done for a maximum of five degradation products (either atmospheric or process degradation products) in total.

H3. Atmospheric modelling to estimate site-specific chemical lifetime

A final step of Part H is atmospheric modelling of the selected process degradation benchmark products and atmospheric degradation products:

1. The chemistry and temporal evolution of these compounds should be evaluated with an atmospheric (FACSIMILE-type gas-phase) box-model including radiation data for the geographical site in question.
2. In a simulation with an advanced air quality model the regional concentration distribution of the compound and its deposition to terrestrial and aquatic environments can be obtained. A “worst case” scenario would result the maximum concentration and maximum deposition flux of the compound, by emission of an estimated amount from a point source and taking into account a first-order loss by chemistry (using experimentally determined k(OH) and a fixed concentration of [OH] = 1.5×10^6 molecules cm^{-3}). The predicted maximum levels should be related to their toxicity risk threshold.

Implementation of test protocol Section II-C

The test protocol should be executable within a 6 month time frame.

The proposed photolysis experiments can be carried out in standard laboratory equipment that is readily available and should not require more than 1-2 weeks of initial testing and preparation. It might prove necessary to construct or order a gas cell that can withstand the corrosive compounds that form when amines and nitrosamines are broken down. This should be done as part of the recommended pre-execution and should not require any additional time during the test protocol. Experimental UV studies can be completed in 1-2 months depending on the commercial availability of the chemicals.

Theoretical calculations of the UV spectra can be carried out in standard computational chemistry facilities. A complete theoretical study of a compound will can 1-4 months as the calculation can take several months at the highest (benchmark) theoretical level. However this should not be a problem as all the calculations can be submitted in parallel and left to run.

Laboratory scale photochemical chamber product studies under different NO_x conditions can be carried out in available chambers and should be feasible in 3 months or less. Large scale photochemical reactor experiments at the EUPHORE facility require a week's work for each key compound. Additionally 1-3 weeks worth of work to evaluate and process the large amount of data obtained at the chamber must be envisioned. The number of compounds studied at EUPHORE will be determined by the availability of the chamber which might be limited at any given time due to bookings by other users.

The one-dimensional box model can be constructed from the get-go and should already mostly be in place from the validation protocol (pre-execution and Call-off two). Construction of the box model is expected to take 1-2 months. The box model should be programmed in KINTECUS which is a commercially available modelling program that runs in Microsoft Excel, and thus easily accessible for most users. The input for the box model is produced during the 6 moth period so the box modelling work should be carried out at the end. The modelling runs are expected to take 1-2 weeks given that the input data is in place. Advanced air quality model runs will be carried out in collaboration with meteorology groups that have such models available and should take about a month given that the input data is in place.

Validation and preparation for the test protocol

It is recommended that the test protocol is tested and implemented in two steps:

1. An initial pre-execution period (pre-CallOff 2)
2. The main implementation period (CallOff 2)

The pre-execution will have a duration of 6 months and its purpose is the testing and building of all apparatus and running through everything for just one or two selected parent amines as a preparation for CallOff 2. The pre-execution will only involve EUPHORE experiments if time permits. CallOff 2 will last 6 months and, with the aid of experience gained during the pre-execution, it will fully test 4-5 parent amines in EUPHORE and in the laboratory. During CallOff 2 the recommended database of degradation compounds and their properties will be compiled. The assumption made within this document is that CallOff 2 will be the implementation of the protocol.

Validation of the protocol in CallOff 2

The protocol will be implemented for the first time as part of CallOff 2, which has a limited time span of 6 months. In this time, the protocol aims to address the most important issues relevant to the project description. These are as follows:

- What are the most important formation mechanisms? (Section I of protocol)
- What are the most important destruction mechanisms? (Section II of protocol)
- What is the atmospheric and environmental fate of the emissions for the plant? (Section II) of protocol)
- What are the most important gas-liquid partitioning emissions?

A 6 month period of time should be sufficient to implement Section I and Sections II-A, II-B and II-C of the test protocol. However, several of the Sections and sub-sections of the test protocol must be performed in parallel in order for it to be completed within the given time frame. Furthermore, the uncertainty regarding elements of Section II-A, Section II-B and Section II-C mean that the user of the protocol must make informed decisions about which experiments can or must be completed and when modeling approaches (e.g. QSAR) can be sufficiently relied upon to provide suitable data and values. As stated previously, the user of the protocol must therefore be sufficiently experienced and knowledgeable to make the appropriate decisions the protocol demands. Furthermore, the protocol makes no assessment of the cost of its implementation, which must also be calculated by the user. Validation of the protocol will be achieved and evaluated through its implementation for the first time.

Toxicity of degradation products

Although this protocol does not deal specifically with the toxicological and ecotoxicological assessment of emissions, it is essential to consider how the data generated in this protocol can be used for such a purpose. The environmental fate assessment outlined in this protocol will provide an essential tool in identifying which process and atmospheric degradation products are most likely to be potential toxicants (both human and environmental). It is important to note that although a particular chemical may be highly toxic, if it degrades rapidly in the atmosphere or ultimately resides in an environmental sink where it is not exposed to humans or other organisms its risk is considered to be low. This protocol will provide this information, and therefore permit targeted and relevant toxicity and ecotoxicity test (which are time consuming and expensive) to be conducted.

A full evaluation of the toxicology of a degradation product including toxicological experiments should only be completed if:

a) high toxicological risk is predicted by EPISuite^{TM}
b) compound emission from post-combustion capture exceed a certain threshold value
c) it is shown that the product forms in substantial amounts in the atmospheric degradation of the parent amine
d) atmospheric modelling of a worst case scenario confirms high risk
e) environmental fate assessment indicates that the compound is likely to enter environmental compartments where there is a high risk of accumulation and exposure to humans or other organisms)

It is recommended that a database system for the atmospheric and process degradation products is established. The information from this new database can then be used to make decisions on the necessity for further evaluation of an individual degradation product. A confidentiality agreement for the joint use and the maintenance of this database should be negotiated.

Main uncertainties and limitations

A maximum of four parent amines can be studied in the large photochemical reactor EUPHORE in CallOff 2. A maximum of ten process degradation products and a maximum of five atmospheric degradation products per parent amine can be studied in lab-scale/indoor chamber experiments. From these a total of five can be further studied in large-scale photochemical experiments in EUPHORE.

However, there are potentially some serious limitations in the use of large photochemical reactor facilities. The EUPHORE Photoreactor in Valencia, Spain, is the only large photochemical reactor (outdoor chamber) in Europe where experiment periods can be reserved and where all routine operations during experiments are performed by the chamber staff. Due to reservations of this facility by other industry and scientific groups, the access throughout the year is limited. In addition, the general weather situation limits the time periods during which experiments can be conducted. It is noted here that three of the five recommended experiments per parent amine are performed under dark conditions and can be conducted independent of the weather situation. Careful planning and coordination will be necessary to conduct and complete the study program of the test protocol. To provide quick access to data and to act as a back-up to the recommended large photochemical reactor experiments, spectroscopic and kinetics experiments will also be performed using laboratory spectrometers and photochemical reactors including a 27 cubic meter aerosol chamber, 100 liter static reactor, flow tube reactor and spectroscopic cells.

Pre-execution protocol

In order for the protocol to function optimally during CallOff 2, it is recommended that a series of pre-protocol execution experiments and studies are completed. The pre-execution should last 6 months and is for testing and building all apparatus and running through everything for one or two selected parent amines as a preparation for Call-off 2. These are essentially preparatory runs aimed at validating elements of the protocol before its full implementation. A document containing the recommended approaches is included as an appendix to this protocol (Appendix 1). A brief overview of the document is provided below.

The goal of the pre-execution is run through the following experiments for one or two parent amines and the most important degradation products:

1. Test the extent of wall effects and memory effects of the amine in a standard 100L laboratory reactor and in UV spectroscopy cells. Prepare such instrumentation for use with amines.
2. Construction of a flow tube reactor and measurements of the reaction rates of the parent amine with OH, Cl and NO_3 radicals.
3. Product study of the degradation of the parent amine in 100L and ~30 m^3 chambers in the laboratory. Complete atmospheric degradation study in the EUPHORE chamber to establish a procedure for EUPHORE chamber experiments.
4. Complete theoretical study of the photolysis of key degradation products of the parent amine and comparison with experimental spectra.
5. Test of the partitioning of the parent amine between the gas phase and the ammonium sulphate aerosol phase in an aerosol test chamber.

These studies will serve to set up and prepare the laboratory instrumentation for use in the test protocol and to discover any unforeseen difficulties. The pre-execution will provide a better handle on the time required for each type of experiment. The experiments will form the initial basis for the recommended database of amine degradation products and their physical properties which will be expanded during Call-off 2. During the pre-execution procedures for each type of experiment will be written which will improve the efficiency of work in the limited time of the Call-off 2 period. Also, such procedures will facilitate the sharing of the work between different external contractors.

Activities deemed beyond the scope of the protocol and CallOff 2 timeframe

A number of activities have been identified during the generation of the report and development of the protocol for H&TQP Amine 4 which relevant for inclusion or are closely connected to the current work. Although many of these activities have been incorporated into the final documents, a number are either beyond the scope of the work outlined in the protocol or are unachievable within the 6 month timeframe allocated to CallOff 2. A brief description of the main points is provided below:

- An effort should be made to measure actual concentrations of emitted compounds at the full-scale site in addition to data from laboratory test plants.
- Several less known but probably important processes were not included in the submitted test protocol because their relative importance for the evaluation of the environmental fate of amines is unknown. Experimental studies of these processes are beyond the scope of the time frame of the present test protocol, but they may be considered in future work.

  At present, the least understood processes are the following:

    1. Heterogeneous reactions on particle surfaces;
    2. Uptake of amines into the liquid phase of aerosols and clouds;
    3. Reactions with free radicals in the aqueous phase.

- A large scale (European or hemispheric) model should be used to test the transport and further fate of the most critical compounds (i.e. high toxicity, high emitted or produced amounts, stable in the atmospheric compartment) including a treatment of aerosol chemistry and deposition. Unfortunately, the implementation of this method and the resources required are considered unachievable within the time constraints of CallOff 2.