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Secondary Spatial Range of Transformation Products: A New Proxy Measure for the Spatial Extent of the Overall Chemical Impact of a Pollutant.

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Summary

The release of a chemical in the environment may cause adverse effects. These effects result from the exposure to the chemical released, but also from the exposure to its transformation products. Accordingly, the *direct* impact is defined here as the sum of the effects caused by the chemical released, whereas the *overall* impact is the sum of the effects caused by the chemical released and its transformation products.

In the first part of this work, the status of transformation products in the current practice of chemical assessment is briefly reviewed, with the legislation of the European Union (Directives 67/548/EEC, 93/67/EEC, 91/414/EEC and Regulation 1488/98) taken as representative example. As it turns out, relevant transformation products of pesticides must be assessed at the same level as their precursors, but transformation products of non-pesticides are usually not assessed at all.

In the second part, it is shown that transformation products can be perfectly integrated in an assessment based on *spatial range*. The spatial range of a chemical is a proxy measure of the spatial extent of its impact. This concept was proposed by Scheringer, Berg and Müller-Herold (38). So far, only the spatial extent of the *direct* impact has been estimated (41; 40; 30), and the corresponding spatial range was called *characteristic spatial range*. The goal of this thesis is to estimate the spatial extent of the *overall* impact. The approach

chosen is based on the analytic method developed by Müller-Herold and Nickel for the calculation of characteristic spatial range (30). The model framework covers global long-range transport and first-order reactions. The result obtained is a closed formula for the *secondary spatial range* ϱ_{AB}, expressed as a function of the respective characteristic ranges ϱ_{A} and ϱ_{B} of a precursor A and its first-generation transformation product B. The exact form of secondary spatial range —given in Equation 6.30— is too complicated to provide an intuitive picture of the role of the different parameters involved. To this end, a simple, yet precise approximation is given:

$$\boxed{\varrho_{\mathrm{AB}} \cong \frac{\varrho_{\mathrm{A}} + \varrho_{\mathrm{B}}}{2} + \frac{\varrho_{\mathrm{B}}}{2^{1+\varrho_{\mathrm{A}}/\varrho_{\mathrm{B}}}} + \frac{\varrho_{\mathrm{A}}}{2^{1+\varrho_{\mathrm{B}}/\varrho_{\mathrm{A}}}}}$$

Secondary spatial range ϱ_{AB} is interpreted as a proxy measure of the spatial extent of the overall impact, whereas the characteristic spatial range ϱ_{A} is a proxy measure of the direct impact of chemical A.

Quite surprisingly, the first-order rate constant k_{AB} of the reaction transforming A into B does not appear in the expression of secondary range. Moreover, it turns out that in a precursor/transformation product pair, the chemical with the larger characteristic range dominates the secondary range, regardless of being the precursor or the transformation product.

$$\boxed{\max\{\varrho_{\mathrm{A}}, \varrho_{\mathrm{B}}\} \leq \varrho_{\mathrm{AB}} \leq 1.4843 \cdot \max\{\varrho_{\mathrm{A}}, \varrho_{\mathrm{B}}\}}$$

In particular, it was shown that the overall impact is significantly larger than the direct impact if the characteristic spatial range of the transformation product B is larger than the characteristic spatial range of its precursor A:

$$\boxed{\varrho_{\mathrm{B}} > \varrho_{\mathrm{A}} \qquad \Longrightarrow \qquad \varrho_{\mathrm{AB}} > 1.5 \cdot \varrho_{\mathrm{A}}}$$

Résumé

L'émission d'un polluant dans l'environnement peut causer des effets néfastes. Ces effets peuvent être causés par le polluant, mais aussi par ses produits de dégradation. Ainsi, l'impact *direct* est défini ici comme la somme des effets du polluant lui-même, alors que l'impact *total* est défini comme la somme des effets du polluant et de ses produits de transformation.

Dans la première partie de ce travail, le statut des produits de transformation dans l'évaluation des risques liés aux produits chimiques est brièvement discuté, la législation de l'Union Européenne sur les produits chimiques (Directives 67/548/EEC, 93/67/EEC, 91/414/EEC et Régulation 1488/98) étant prise comme exemple représentatif de la pratique courante. Il apparaît que les produits de transformation des pesticides sont soumis au même processus d'évaluation que leurs précurseurs. Par contre, pour les substances qui ne sont pas des pesticides, l'évaluation des produits de transformation n'est en général pas requise.

Dans la seconde partie, on démontre que les produits de transformation peuvent parfaitement être intégrés dans une évaluation basée sur la *portée*. La portée d'un polluant est une mesure de l'étendue spatiale de son impact. Ce concept a été proposé par Scheringer, Berg et Müller-Herold (38). Jusqu'ici, seule l'étendue spatiale de l'impact direct a pu être estimée, la portée correspondante ayant été nommée *portée caractéristique*. Le but de cette thèse est d'estimer

l'étendue de l'impact total. L'approche choisie est basée sur la méthode développée par Müller-Herold et Nickel pour le calcul de la portée caractéristique. Le modèle utilisé intègre la diffusion turbulente à grand échelle et les réactions chimiques de premier ordre. Le résultat obtenu est une expression analytique de la portée secondaire ϱ_{AB}, exprimée comme fonction des portées caractéristiques respectives ϱ_{A} et ϱ_{B} d'un précurseur A et de B, l'un de ses produits de transformation de première génération. L'expression exacte de la portée secondaire (voir équation 6.30) étant trop compliquée pour permettre une interprétation directe du rôle des différents paramètres impliqués, une approximation plus simple mais néanmoins précise a été développée:

$$\boxed{\varrho_{\mathrm{AB}} \cong \frac{\varrho_{\mathrm{A}} + \varrho_{\mathrm{B}}}{2} + \frac{\varrho_{\mathrm{B}}}{2^{1+\varrho_{\mathrm{A}}/\varrho_{\mathrm{B}}}} + \frac{\varrho_{\mathrm{A}}}{2^{1+\varrho_{\mathrm{B}}/\varrho_{\mathrm{A}}}}}$$

La portée secondaire ϱ_{AB} est interprétée comme une mesure de l'étendue spatiale de l'impact total, à la différence de la portée caractéristique ϱ_{A}, qui est une mesure de l'étendue de l'impact direct.

Etonnament, la constante de vitesse de la réaction de transformation du precureur A en produit de transformation B, k_{AB}, n'intervient pas dans l'expression de la portée secondaire. De plus, il apparaît que, dans une paire précurseur/produit de transformation, c'est la substance ayant la plus grande portée caractéristique qui domine la portée secondaire, que ce soit le précurseur ou le produit de transformation.

$$\boxed{\max\{\varrho_{\mathrm{A}}, \varrho_{\mathrm{B}}\} \leq \varrho_{\mathrm{AB}} \leq 1.4843 \cdot \max\{\varrho_{\mathrm{A}}, \varrho_{\mathrm{B}}\}}$$

En particulier, il est montré ici que l'impact total est significativement plus étendu que l'impact direct si la portée caractéristique du produit de transformation est plus grande que celle du précurseur:

$$\boxed{\varrho_{\mathrm{B}} > \varrho_{\mathrm{A}} \qquad \Longrightarrow \qquad \varrho_{\mathrm{AB}} > 1.5 \cdot \varrho_{\mathrm{A}}}$$

Chapter 1

Introduction

1.1 Environmental relevance of transformation products

The release of a chemical in the environment may cause adverse effects. These effects result from the exposure to the chemical itself, but also from the exposure to its transformation products.

Most evidently, this applies to pesticides, as their transformation products frequently inherit the pesticidal activity of their precursors. As a matter of fact, many transformation products of pesticides are themselves commercialized as pesticides (45). Consequently, all adverse effects associated with pesticides may also be caused by their transformation products. In addition to their potential pesticidal activity, transformation products of pesticides may cause further specific adverse effects. A well-known example is DDE, a degradation product of DDT: DDE, like its precursor DDT, is an insecticide. Besides, it causes thinning of the eggshell of raptorial birds (19), and has endocrine-disrupting properties (25). More recently, transformation products of the insecticide S-methropene have been suspected to induce malformations in amphibians (27).

With respect to non-pesticides, data on transformation products is rather scarce. As an illustration,three environmentally relevant examples are listed below. Trifluoroacetic acid is an atmospheric transformation product of the hydrogenated chlorofluorocarbons introduced to substitute the ozone-killing chlorofluorocarbons. Trifluoroacetic acid is ubiquitous, has no known significant abiotic sinks in the environment, and appears to be rather refractory to microbial degradation (44). No adverse effects of trifluoroacetic acid have been reported yet, but alone the ubiquity of this compound is a source of concern (26). In polluted urban air, polycyclic aromatic hydrocarbons are oxidized to their strongly mutagenic and possibly more persistent nitro-derivatives (5). Nonylphenol ethoxylates are widely used as surface active agents in industrial cleansing, textiles and leather industry, and agriculture. They degrade to nonylphenols in the environment, which are more toxic than their precursors and have estrogenic properties (46).

1.2 Overall impact

From the above, it clearly appears that the impact of a pollutant is not restricted to the effects caused by the pollutant itself. As a matter of fact, one may distinguish between *direct* and *overall* impact:

- The *direct impact* is defined here as the sum of all direct effects. The direct effects are the effects involving the pollutant *itself.*
- The *overall impact* is the sum of the direct and indirect effects. The indirect (chemical) effects are the effects involving the *transformation products.*

Thus, the overall impact is larger than the direct impact with respect to biological effects but also with respect to the physical dimensions of space and time. In fact, transformation products are formed as long as precursor molecules exist, and they appear everywhere in the environment given the existence of precursor. Consequently, transformation products spread over a larger area, and remain longer in the environment than their precursors (Fig. 1.1). In this thesis, a quantitative estimation of the spatial extent of the overall impact is presented. The extent of the overall impact in *time* has been addressed lately by Fenner *et al.* (17).

Note that only the *chemical impact*, i.e the impact directly resulting from chemical reactions involving precursors or transformation products, are considered here. Other types of impacts (economical or social, for example) are beyond the scope of this work.

1.3 Scope of this work

From the environmental point of view, transformation products are pollutants just like their precursors. However, transformation products, forming in the environment, are neither directly produced nor sold by humans, and testing them costs time and money. Thus, one may wonder if the threat posed by transformation products is perceived as serious enough to justify costly and time consuming testing. This question is addressed in the first part of this work by means of a review of the status of transformation products in the legislation on chemicals of the European Union, chosen here as a representative example of current assessment practice.

This is followed by an introduction to the concept of *spatial range*, a new assessment tool originally proposed by Scheringer, Berg and Müller-Herold (38). Spatial range is a measure of the spatial extent of the impact of a pollutant. So far, only the spatial extent of the *direct* impact has been estimated (41; 40; 30), and the corresponding spatial range was called *characteristic spatial range*[1]. The goal of this thesis is to estimate the spatial extent of the *overall* impact. The approach chosen is based on the analytic method developed by

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[1] The adjective "characteristic" was later introduced by Müller-Herold and Nickel (30) in order to emphasize the generic nature of the concept of spatial range which essentially corresponds to an average value, the average being taken over all positions of release.

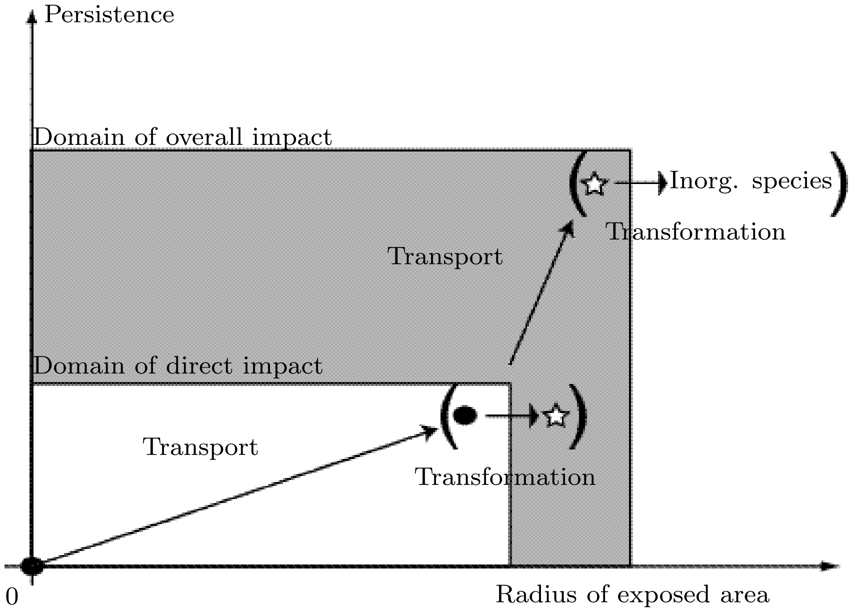

Figure 1.1: Schematic representation of the environmental fate of a precursor (black dot) and that of one its transformation product (white star). The persistence of each species is reported on the vertical axis. During their respective lifetimes, precursor and transformation product are transported over a given distance. This distance determines the radius of the area exposed to precursor and transformation product. The persistence and the radius of the area exposed define the respective domain of impacts: The domain of *direct* impact is the domain of impact of the precursor. The domain of *overall* impact is the domain of impact of the precursor *and* its transformation products.

Müller-Herold and Nickel for the calculation of characteristic spatial range(30)

The second part of this work contains the technical details of the calculations leading to the main result of this thesis: a closed formula for *secondary spatial range*. Secondary spatial range represents the radius of the area exposed to transformation products of the first generation. It is interpreted as a proxy measure of the spatial extent of the overall impact. Of course, later generations of transformation products also contribute to the overall impact, and they can be included in the method presented here with only minor changes. The essential point, however, is that with the shift to first-generation transformation products, one makes a first incursion beyond the direct impact, in the dimension of indirect impacts.

Part I

Assessment of transformation products

Chapter 2

Transformation products the assessment of chemicals

The status of transformation products in the assessment of chemicals legally required in the European Union is reviewed in the present chapter. More specifically, the difference between pesticides and non-pesticide regarding the assessment of transformation products is exposed in some details, following a brief introduction to the general principle of chemical risk assessment.

The legislation of the European Union was chosen because it provides the guidelines for the legislation of the member states, and can therefore be seen as a kind of common denominator of the chemical legislation of European states (Switzerland, though not a member of the European Union, is in the process of making its chemical legislation euro-compatible). Moreover, most of the chemical legislation around the world are based on OECD guidelines, and as a result, tend to become more and more similar.

2.1 Risk assessment of chemicals in the European Union

First, the notifier of a new substance has to provide the competent authorities with the technical dossier of the substance. The technical dossier must contain toxicity data, the physicochemical properties of the substance, information on its environmental fate, on the expected marketed quantity and its pattern of use. The exact requirements of the technical dossier can be found in Directive 67/548/EEC, the so-called "Dangerous Substance Directive", and the corresponding Technical Guidance Document (15). The amount of data to be included in the notification dossier increases with the quantity of substance marketed. However, a minimal set of data (the baseset) must be provided for all new substances marketed in more than 1000kg yearly, and for all existing substances [1] produced in quantities of more than 1000 tons yearly (the so-called High Production Volume chemicals, HPV). Once in possession of the legally required data, the competent authority must carry out an assessment of the risk of the substance to man and the environment. The subsequent decision on restriction or ban of the substance depends on the results of this risk assessment.

The principles of risk assessment of chemicals are laid down in Directive 93/67 for new chemicals and in Regulation 1488/98 for existing chemicals. The technical implementation of both legislation is laid down in a single Technical Guidance Document on risk assessment (14). Human health risks and environmental risks are addressed in this Technical Guidance Document, but only the environmental risks are discussed in this chapter. In essence, the environmental risk assessment of a substance is the comparison of the estimated concentration of the substance in the environment with a toxicity threshold for this substance.

The process of estimating the environmental concentration is called *exposure assessment*. Exposure assessment is based on model calculations. The model input consist of the quantity of substance emitted, its release pattern, its physicochemical properties, and its environmental degradation rates. The output, called *Predicted Environmental Concentration* (PEC), is an estimation of the environmental concentration of the substance.

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[1] The existing substances are the substances that were already on the market before the entry into force of the Dangerous Substance Directive on 18 September 1981.

The *effect assessment* is the process of evaluating the toxicity threshold of the substance. In the Technical Guidance Document, the toxicity threshold is defined as "a concentration below which an unacceptable effect will most likely not occur". It is further mentioned that "It is not intended to be a level below which the chemical is considered to be safe". The official denomination of the toxicity threshold is *Predicted No-Effect Concentration* (PNEC). The PNEC is obtained by dividing the concentration data gathered from laboratory toxicity tests by an assessment factor. In the base-set of information, only short-term toxicity data for three species (algae, Daphnia and fish) are available. In this case, the assessment factor is set equal to 1000, and the PNEC is obtained by dividing the smallest of the three acute effect concentrations by 1000 (14).

$$PNEC = \frac{\text{Acute effect concentration}}{1000} \tag{2.1}$$

The magnitude of the assessment factor depends on the toxicity data available: It is equal to 1000 when only the three short-term toxicity levels required for the base-set are available, but it can decrease to 50 if results from multi-species, long-term studies are at hand.

The actual risk assessment begins with a first, conservative, estimation of the ratio $PEC/PNEC$ between predicted environmental concentration and predicted no-effect concentration. If the predicted environmental concentration turns out to be lower than the predicted no-effect concentration, $PEC/PNEC < 1$, it is concluded that the risk for the substance to cause an unacceptable effect is low, the risk assessment is stopped, and the substance authorized. If, in contrast, the predicted environmental concentration is similar to or higher than the toxic threshold, i.e the ratio $PEC/PNEC$ is larger than 1, then the substance has to be investigated more closely, as illustrated in Fig. 2.1. New data on the emission pattern and the environmental fate is generated, and the calculation of the predicted environmental concentration is repeated using the new data as input, together with more realistic and less conservative assumptions. Similarly, additional toxicity tests are carried out. With more toxicity data, the confidence of the assessor in extrapolating the laboratory data to the environment is higher. Accordingly, the assessment factor used in the calculation of the PEC can be lowered. If, despite additional data, the predicted environmental concentration is still similar to or higher than the predicted no-effect concentration, risk reduction measures (restriction of uses or total ban of the chemical) are taken.

2.2 Transformation products of non-pesticides

Transformation products are not formally defined in the Dangerous Substance Directive, and the only mandatory information on transformation products concerns the monitoring of transformation products in the environment:

> "Apart from methods of detection and determination, information shall be given on analytical methods which are known to the notifier and allow detection of a substance and its transformation products after discharge in the environment". (art. 1.4, Annex VII.A, Directive 67/548/EC)

However, the competent authority has the power to require more information, as stated in Article 16 of the Dangerous Substance Directive:

> "If it can be shown to be necessary for the evaluation of risks which may be caused by the substance, the competent authorities may ask for further information, verification and/or confirmatory tests concerning the substances or their transformation products". (art. 16, Directive 67/548/EC)

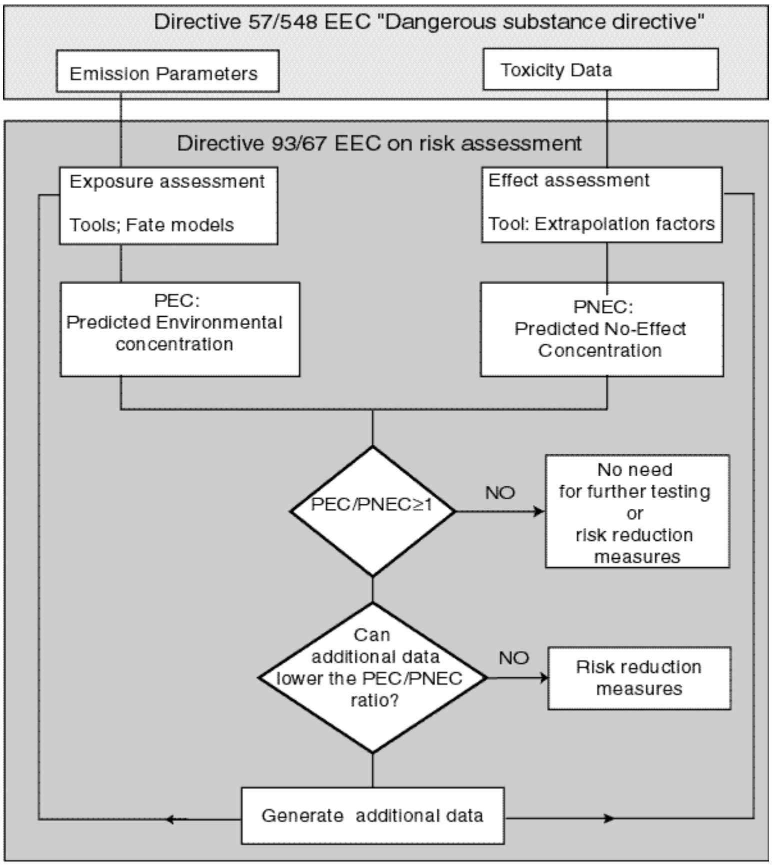

Figure 2.1: Environmental risk assessment of chemicals is based on the comparison of the Predicted Environmental Concentration (PEC) with a concentration below which adverse effects are unlikely to occur, the Predicted no-effect Concentration (PNEC). First, conservative values of PEC and PNEC are calculated using the data of the base-set and a "reasonable worst case scenario". If the predicted environmental concentration is smaller than the predicted no-effect concentration even in the initial worst case scenario, the substance is authorized. If is similar or larger ($PEC/PNEC \geq 1$), a new estimation of both concentrations is done on the basis of new data and more realistic assumptions. If the PEC/PNEC ratio is still larger than 1, risk reduction measures must be taken.

First, Article 16 clearly implies that transformation products can contribute to the overall risk caused by a substance [2]. Concretely, Article 16 empowers the authority to request further information concerning transformation products. However, the authority must show that these additional information are necessary for the proper evaluation of the risks. But how can this be shown? What are the criteria that transformation products must meet in order to be integrated in the risk assessment procedure? An answer to these questions can be found in the Technical Guidance Document on risk assessment:

> "Consideration should be given to whether the substance being assessed can be degraded biotically or abiotically, to give stable and/or toxic degradation products. Where such degradation can occur, the assessment should give due consideration to the effects which might arise. For new substances, it is unlikely that information will be available on such degradation products and thus only a qualitative assessment can be made. For HPV substances (nb: High Production Volume existing substances), however, known significant degradation products should also be subject to risk assessment. Where no information is available, a qualitative description of the degradation pathways can be made."(Technical Guidance Document on risk assessment, p.253)

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[2] The German "Bundeschemikaliengesetz" is more explicit on transformation products: They are included in the definition of "dangerous for the environment":

> " Umweltgefährlich sind Stoffe oder Zubereitungen, die selbst oder deren Umwandlungsprodukte geeignet sind, die Beschaffenheit des Naturhaushaltes , von Wasser, Boden oder Luft, Klima, Tieren, Pflanzen oder Mikroorganismen derart zu verändern, dass dadurch sofort oder später Gefahren für die Umwelt herbeigeführt werden können." (ChemG, §3.a.15)

Thus, the authority can request more information on transformation products if it can show that the said transformation products are stable and/or toxic. However, it is explicitly admitted in the text quoted above that, in most cases, information on toxic and/or stable transformation products will not be available. Consequently, the authority will not have the necessary information to justify its request for additional information on transformation products. As a matter of fact, it is not in the interest of the notifier to provide information on transformation products, since this information could be used to justify costly additional testing, or even restrictions of the use of the notified substance. Worse, the notifier has an interest in *not* investigating the transformation products at all, so that he cannot be charged for concealing relevant information! This may partly explain the lack of data on transformation products.

Aside from stable or toxic transformation products, transformation products of readily hydrolyzable precursors are also mentioned in the Technical Guidance Document (p.277). As a matter of fact, if hydrolysis of the precursor is very fast, the relevant compound in case of a discharge in water is the transformation product rather than the precursor.

2.3 Transformation products of pesticides

Pesticides[3] have three specific features that strongly differentiate them from non-pesticide chemicals

1. Pesticides are meant to be released. Their occurrence in the environment is not a side effect, as for non-pesticide chemicals.

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[3] In this section, the meaning of the term ”pesticide” is restricted to agricultural plant protection products.

2. Pesticides are bioactive compounds released in the environment at concentrations high enough to cause acute effects on target pests. Non-pesticide chemicals are released at concentrations much below their threshold for acute effects (this is the paradigm of the risk assessment presented in the preceding section).

3. Pesticides are used on plants that are meant to be consumed, and the consumer may be exposed through diet to residues of pesticides. This particular consumer health aspect is not relevant for most non-pesticide chemicals.

Accordingly, pesticides are regulated by specific legislation. The central regulatory text on agricultural pesticides in the European Union is Directive 91/414 on the placing of plant protection products on the market. Directive 91/414 regulates both the data collection (Annex II) and the risk assessment (Annex VI) of pesticides. The place of transformation products of pesticides in this directive will be discussed, and it will appear that the transformation products of pesticides are given much more importance than the transformation products of non-pesticide chemicals.

In Directive 91/414, much emphasis is put on pesticides's *residues*. The term "residue" is defined as

> "one or more substances present in or on plants or products of plant origin, edible animal products or elsewhere in the environment and resulting from the use of a plant protection product, including their metabolites and products resulting from their degradation or reaction". (art. 2.2, Directive 91/414).

This definition is rather general, including all the substances that result from the use of the pesticides: The parent compound, the products of metabolic reactions of the pesticide in plants or animals, as well as the environmental transformation products as we understand them in the context of this work. The decisive importance of residues in the registration of pesticides clearly appears in Article 5b: Authorization of new pesticides shall be granted only if

> "their residues, consequent on application consistent with good plant protection practice, do not have any harmful effects on humans or animal health or on groundwater or any unacceptable influence on the environment, and the said residues, in so far as they are of toxicological or environmental significance, can be measured by methods in general use". (art.5b, Directive 91/414)

This is a strong statement, which clearly implies that the *overall* impact of pesticides has to be considered. However, how does one decide which transformation products are "of toxicological or environmental significance", and which ones are not? This point apparently needed clarification, and the European Union commissioned the College voor de toelating van bestrijidingsmiddelen (CTB) to write a guidance document on relevant transformation products. This document is still at the consultation stage. In the draft version published in February 1999 (8) a transformation products is considered *potentially* relevant if:

1. It is formed in amounts of more than 10% of the applied amount of active substance.
2. It is an organic compound (excluding CO_2)
3. It has a chain length of more than 4 carbon atoms (with an aliphatic structure) or contains other elements than C, H, N, or O.

All potentially relevant transformation products are further tested for their pesticidal activity, human toxicity and ecotoxicological effects, including groundwater contamination. If a transformation product has a pesticidal activity, or if any of the other test delivers a positive result, the transformation product is considered *relevant* and it must be evaluated at the same level as the parent compound, with the same data requirements. The registration costs of the pesticide increase by about 10% for each transformation product found to be relevant (9).

2.4 Concluding Remarks

In the pesticide legislation, it is recognized that transformation products can significantly contribute to the impact of a pesticide and the relevant transformation products must be assessed at the same level as their parent compounds. In the legislation on non-pesticide chemicals, however, almost no information is required on transformation products. Thus, one can conclude that relevant transformation products of pesticides are perceived as a serious threat, whereas transformation products of non-pesticides are not.

This discrepancy between pesticides and non-pesticides is an expression of the facts that current assessment practice is mainly focused on human health protection, and relies exclusively on toxicity testing. In this context, transformation products of pesticides are relevant, because they pose a direct threat to the consumer: They may inherit the bioactivity of their precursors, occur in relatively high concentrations, and come in contact with foodstuff. Concerning transformation products of non-pesticides, note that the original goal of the Dangerous Substance Directive, issued in 1967, is "to protect the public, and in particular the workers using such substances" [4]. For this purpose, the precursor is unquestionably more relevant than its environmental transformation products. Indeed, there is *a priori* no reason to suspect these

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[4] The protection of the environment as an official goal was introduced twelve years later, in the sixth amendment of the Dangerous Substance Directive

transformation products of some kind of bioactivity. Moreover, they are typically more diluted than their precursors. Adverse effects of the kind routinely tested in current assessment practice are thus unlikely. Hence, transformation products of non-pesticides are perceived as relatively harmless and neglected in the assessment procedure.

Chapter 3

Spatial range

3.1 Dealing with local pollution

The usual way of dealing with local pollution can be outlined as follows: First, a chemical is used and released without restriction. Then, effects on human health or the environment are observed and associated with exposure to the chemical. The adverse effects are weighed against the benefits gained from the use of the chemical. If the adverse effects outweigh the benefits, the emissions are cut down until a balance is re-established. This process can be applied preventively: On the basis of previous experiences, one can define which effects are unacceptable and must be avoided. All chemicals must then be tested for their potential to cause the effects deemed unacceptable, and their use restricted accordingly. The process outlined above works satisfactorily only if the following conditions can be fulfilled:

1. The effects can be identified.
2. The causality relationship between exposure and effects can be demonstrated.
3. A consensus on the respective valuation of effects (”costs”) and benefits can be reached.
4. The emission of the pollutant can be regulated within the scope of national legislation.

At a local scale, these conditions are likely to be fulfilled: The effects, caused by a high local concentration, appear with some clarity, and the causality relationship between exposure to the chemical and adverse effects can be established convincingly. Moreover, the socio-economic values at the local scale are homogeneous enough for a consensus on the cost-benefits analysis to be reached. Finally, the source of the pollutant and the observed adverse effects are likely to lie within the same jurisdiction, which makes it easier to issue and enforce emission restrictions.

3.2 Beyond locality

It is very difficult to apply the process outlined above to pollutants like the POPs (Persistent Organic Pollutants) or the chlorofluorocarbons, which have environmental impacts extending far beyond the local scale. Indeed, the effects caused by widespread, low-level, long term exposure to such chemicals may take a long time to manifest, and their detection requires intensive measurement campaigns. The effects are often multi-factorial, and exposure to the pollutant is only one factor among many. The relation between effects and exposure usually takes the form of a statistical correlation. Thus, the causality relationship can never be proven with absolute certainty, which opens the door to endless controversy.

Detecting effects and associating them with a pollutant is difficult enough, but reaching a consensus on the cost-benefits analysis might be even more challenging, as the geographic distribution of costs and benefits is likely to be uneven. Moreover, national jurisdictions are powerless in regulating pollutants emitted in another state, and long-range pollutants must be dealt with in international conventions, like the Convention on Long-Range Transboundary Air Pollution (7). The ratification of such conventions is a very slow process: For example, DDT is ”scheduled for elimination at a later stage” in the Convention on Long-Range Transboundary Air Pollution. This convention was ratified in 1998, about thirty years after the demonstration of the adverse effects of DDT on birds populations!

Thus, it appears that the spatial extent of the exposure resulting from the release of a chemical has a dramatic influence on the ways and possibilities to deal with it. This is well illustrated by this quote form K. Ballschmiter (2)

> "local pollution can easily be controlled, but already a regional pollution is difficult to be cleared off and in any case global contamination is out of control of men".

Clearly, large-scale contamination must be avoided. It can be prevented if pollutants with a strong potential for widespread contamination are recognized early. The concept of spatial range was introduced to this end.

3.3 Spatial range

What follows is the author's interpretation of the concept of spatial range, originally introduced by Scheringer, Berg and Müller-Herold (38), and extensively discussed by M. Scheringer in his book *Persistenz und Reichweite von Umweltchemikalien* (43).

Spatial range is a measure of the spatial extent of exposure. Exposure, to a pollutant or its transformation products, is the necessary prerequisite to any adverse effect (38). Therefore, the impact being defined as the sum of all effects, exposure can be interpreted as *impact potential*[1]. But exposure, the mere presence of a chemical in the environment, is an immediate consequence of the release of the chemical itself, or of its precursor. Accordingly, one can argue that exposure *is* an effect of the release, and thus a part of the impact. Moreover, from the point of view of the spatial extent, it is the largest

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[1] The term "impact potential" is used here as a synonym for the terms *environmental threat* introduced by Scheringer (39), and *endangerment* used by Müller-Herold (29).

effect. Thus, spatial range, as a measure of the spatial extent of exposure, is a measure of the spatial extent of the impact.

In the real world, the spatial extent of exposure is determined by the release pattern of the precursor, the environmental conditions, and finally the specific properties of the precursor and its transformation products. The indicator spatial range, however, is substance-specific: The same standardized release event is assumed for all precursors, and the release, transport and transformations are assumed to take place in a generic environment with average geochemical properties. As a matter of fact, spatial range was presented by Scheringer, Berg and Müller-Herold (38) as a spatial analogue to persistence: while persistence is a measure of the *duration* of exposure, spatial range is a measure of its *spatial extent.* Just like persistence, spatial range depends on substance-specific properties and generic environmental values. Since both indicators are independent of the emission pattern and of the quantity released, neither persistence nor spatial range provide any indications on the actual *magnitude* of exposure. Consequently, persistence and spatial range are only *proxy* measures. Thus, spatial range should not be misinterpreted as an actual prevision of the spatial extent of the exposure pattern resulting from a particular release event in the real world. It should rather be understood as an average value, the average being taken over all positions of release.

3.4 Spatial range as an assessment tool

The main purpose of spatial range is the identification and quantification of the potential for widespread contamination of organic chemicals. Interpreting spatial range as a distance on the earth surface, chemicals can be assigned to different categories according to their spatial range. For example, Müller-Herold and Nickel (30) proposed the following range categories:

1. Local: Spatial range up to 2000 km
2. Hemispherical: Spatial range between 2000 km and 10’000 km
3. Global: Spatial range above 10’000 km

Such categories have a clear meaning as assessment endpoints. Thus, it has been argued by Scheringer and Winter (42) that, on the basis of the precautionary principle, chemicals with a global spatial range should be banned, or at least restricted to uses in closed-systems only, even if they have no demonstrated adverse effects.

Spatial range could also be integrated integrated in the existing assessment practice. In fact, current legislation already seems to hint at the concept of spatial range, as shown in this example out of the pesticide legislation:

> ”Member States shall evaluate the possibility of the plant protection product reaching surface water under the proposed conditions of use; if this possibility exists, they shall estimate, using a suitable calculation model validated at Community level, the short-term and long-term predicted concentration of the active substance and of metabolites, degradation and reaction products that could be expected in the surface water [...].” (art. 2.5.1.3, annex VI, Directive 91/414).

To evaluate the possibility of the pesticide or its transformation products (metabolites) reaching surface water, one could simply compare spatial range with the average distance between the point of release of the pesticide and neighboring water bodies. Moreover, one could use the value of the spatial range for determining the spatial scale of the ”suitable calculation model” mentioned.

3.5 Characteristic and secondary spatial ranges

Until now, calculations of spatial range were limited to directly-released chemicals (precursors) only. The spatial range of directly-released chemicals was called *characteristic spatial range* by Müller-Herold (30). Characteristic spatial range is a length measuring the spatial extent of the exposure to a pollutant, pulse-released in a generic model environment. In the terminology used here, characteristic spatial range is thus a proxy measure for the spatial extent of the *direct* impact of a pollutant. Conceptually comparable but technically different definitions were proposed by van Pul *et al.* (34), and Bennett *et al.* (3).

The major contribution of this work is to include transformation products in the calculation of spatial range. The result obtained is called *secondary spatial range.* Strictly speaking, secondary spatial range is a measure of the spatial extent of the exposure to transformation products. It follows quite naturally that secondary spatial range is always larger than the characteristic spatial range of the precursor (see fig.1.1). Since it includes transformation products, secondary spatial range is presented here as measure for the spatial extent of the *overall* impact of a pollutant. For the same reasons as characteristic spatial range, secondary spatial range is only a proxy measure. Moreover, secondary spatial range only includes the first-generation transformation products[2], but the model presented here could be extended to higher-generation transformation products with only minor changes.

Note that, for assessment purpose, using secondary range instead of characteristic range will result to a shift to higher range categories: For example, using the categories proposed by Müller-Herold and Nickel (30), the pesticide heptachlor

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[2] A transformation product B is considered a first-generation transformation product of a precursor A if the environmental reaction transforming A into B follows a first-oder kinetics.

would be considered a local chemical on the basis of its characteristic spatial range (860 km), but a hemispherical chemical on the basis of its secondary range (2140 km), which takes its transformation product heptachlor epoxide into account. (See chapter 7 for the detailed calculation of this example).

Part II

Technical part

Chapter 4

The instant-equilibrium assumption

The instant-equilibrium assumption is an elegant way to make spatial range independent of the environmental compartment where the release takes place. It simply assumes thermodynamic equilibrium between the various compartment of a multi-compartment environment. It follows that the concentration of a pollutant in any given environmental compartment is proportional to the concentration in an arbitrary chosen reference compartment. Thus, using the instant-equilibrium assumption, a multi-compartment, spatially structured model environment can be aggregated to a single-compartment, spatially structured model environment.

The instant-equilibrium assumption is widely used in gas chromatography, where the chemical potential of a compound in the mobile phase is assumed to be equal to the chemical potential of this same compound in the stationary phase. The environment, in analogy to a gas chromatographic system, is also composed of mobile phases (the atmosphere and the oceans) and stationary phases (soil and vegetation), and the exchange between phases is governed by the difference in fugacity (or chemical potential) between the phases. The use of the instant-equilibrium assumption in the context of environmental modelling was advocated by Risenbrough in a paper intituled ”Beyond long-range transport: A model of a global gas chromatographic system” (37). It was used by Müller-Herold and Nickel for their calculation of characteristic spatial range. They also demonstrated the reliability of this assumption by comparing their results with the results obtained by Scheringer using the full dynamics of phase transfer (41).

4.1 Partition coefficients

Assuming instant equilibrium, the concentrations of a given pollutant in soil and water are proportional to the concentration of the same pollutant in air. The respective proportionality factors, called *partition coefficients*, will be derived below.

Let us start with the partition coefficient between water and air, K_{wa}. Assuming thermodynamic equilibrium, the concentration in water is related to the concentration in air through Henry's law:

$$c_w = \frac{\mathrm{R}T}{K_H} c_a \tag{4.1}$$

with K_H the Henry's constant of the substance, R the gas constant, and T the temperature. Introducing the *partition coefficient* K_{wa}

$$K_{wa} := \frac{c_w}{c_a} = \frac{\mathrm{R}T}{K_H} \tag{4.2}$$

equation 4.1 rewrites to

$$c_w = K_{wa} \cdot c_a \tag{4.3}$$

and it clearly appears that, at equilibrium, the concentration in water is proportional to the concentration in air.

The derivation of the partition coefficient K_{sa} between air and soil is more complicated. It is usually calculated from the soil/water partition coefficient K_{sw} and air/water partition coefficient K_{wa}:

$$K_{sa} = \frac{c_s}{c_a} = \frac{c_s}{C_w}\frac{c_w}{c_a} = K_{sw}\frac{\mathrm{R}T}{K_H} \tag{4.4}$$

A commonly used expression for K_{sw} is the semi-empirical relation derived by Karickhoff (24)

$$K_{sw} = f_{oc}K_{oc} = 0.41 f_{oc}\rho K_{ow} \tag{4.5}$$

where f_{oc} is the organic carbon fraction of the soil, K_{oc} is the organic carbon/water partition coefficient, ρ is the relative soil density, and K_{ow} is the octanol/water partition coefficient. Substituting this in equation 4.4 yields

$$K_{sa} = \frac{f_{oc} \cdot \rho_s \cdot 0.41 K_{ow} \cdot \mathrm{R}T}{K_H} \tag{4.6}$$

In the present work, the relative soil density ρ_s is set to 1, and the organic carbon fraction of the soil to $f_{oc} = 0.02$, as in ref. (28). According to eq. 4.4 and 4.6, the concentration in the soil compartment is proportional to the concentration in the air compartment:

$$c_s = K_{sa} \cdot c_a = \frac{f_{oc} \cdot \rho_s \cdot 0.41 K_{ow} \cdot \mathrm{R}T}{K_H} \cdot c_a \tag{4.7}$$

4.2 From n compartments to one

It will now be shown that, using the instant-equilibrium assumption, the rate equation for a pollutant in a multi-compartment, spatially structured environment can be simplified to a rate equation in a single-compartment, spatially structuredenvironment.

In a n-compartment environment, the total concentration at position x and time t can be defined as

$$c(x,t) := \frac{\sum\limits_{i=1}^{n} c_i(x,t) V_i}{\sum\limits_{i=1}^{n} V_i} \tag{4.8}$$

with $c_i(x,t)$ $[mol\ m^{-3}]$ the concentration in compartment i at position x and time t, and V_i the relative volume of compartment i. Derivation with respect to time yields

$$\dot{c}(x,t) = \frac{\sum\limits_{i=1}^{n} \dot{c}_i(x,t) V_i}{\sum\limits_{i=1}^{n} V_i} \tag{4.9}$$

One can assume the following rate equation in each compartment i:

$$\dot{c_i}(x,t) = D_i \frac{\partial^2 c_i(x,t)}{\partial x^2} - k_i c_i(x,t) + \mathit{input} - \mathit{output} \tag{4.10}$$

with D_i the eddy diffusion coefficient in compartment i, k_i the (pseudo) first-order rate constant of the degradation reaction of the pollutant in compartment i, and *input* and *output* symbolizing the exchange terms between compartments. Substitution in Equ.4.9 yields (The exchange terms cancel out because of mass conservation.)

$$\dot{c}(x,t) = \frac{\sum\limits_{i=1}^{n} V_i D_i \frac{\partial^2 c_i(x,t)}{\partial x^2}}{\sum\limits_{i=1}^{n} V_i} - \frac{\sum\limits_{i=1}^{n} V_i k_i c_i(x,t)}{\sum\limits_{i=1}^{n} V_i} \tag{4.11}$$

Let us now make use of the local instant-equilibrium assumption in order to express all concentrations as functions of the concentration in a reference compartment $i = 1$.

$$c_i(x,t) = K_{i1} c_1(x,t) \tag{4.12}$$

$$K_{11} = 1 \tag{4.13}$$

Thus, the first term of the right-hand side of expression 4.11 rewrites as

$$\frac{\sum\limits_{i=1}^{n} V_i D_i \frac{\partial^2 c_i(x,t)}{\partial x^2}}{\sum\limits_{i=1}^{n} V_i} = \frac{\partial^2 c_1(x,t)}{\partial x^2} \frac{\sum\limits_{i=1}^{n} V_i D_i K_{i1}}{\sum\limits_{i=1}^{n} V_i} \tag{4.14}$$

and the second term as

$$\frac{\sum\limits_{i=1}^{n} V_i k_i c_i(x,t)}{\sum\limits_{i=1}^{n} V_i} = c_1(x,t) \frac{\sum\limits_{i=1}^{n} V_i k_i K_{i1}}{\sum\limits_{i=1}^{n} V_i} \tag{4.15}$$

Moreover, starting from equation 4.8, one can also express the total concentration as a function of the concentration in the reference compartment.

$$c(x,t) = c_1(x,t)\frac{\sum_{i=1}^{n} K_{i1}V_i}{\sum_{i=1}^{n} V_i} \tag{4.16}$$

This proportionality relationship can of course be inverted

$$c(x,t)\frac{\sum_{i=1}^{n} V_i}{\sum_{i=1}^{n} K_{i1}V_i} = c_1(x,t) \tag{4.17}$$

After substitution of $c_1(x,t)$ in equation 4.14 and 4.15, one can rewrite rate equation 4.11 as

$$\dot{c}(x,t) = \frac{\partial^2 c(x,t)}{\partial x^2}\frac{\sum_{i=1}^{n} V_iD_iK_{i1}}{\sum_{i=1}^{n} V_iK_{i1}} - c(x,t)\frac{\sum_{i=1}^{n} V_ik_iK_{i1}}{\sum_{i=1}^{n} V_iK_{i1}} \tag{4.18}$$

Thus, one can write the rate equation in a single, homogeneous compartment:

$$\dot{c}(x,t) = D\frac{\partial^2 c(x,t)}{\partial x^2} - kc(x,t) \tag{4.19}$$

with

$$D = \frac{\sum_{i=1}^{n} V_iD_iK_{i1}}{\sum_{i=1}^{n} V_iK_{i1}} \tag{4.20}$$

and

$$k = \frac{\sum_{i=1}^{n} V_ik_iK_{i1}}{\sum_{i=1}^{n} V_iK_{i1}} \tag{4.21}$$

4.3 Application to a three-compartment model

Let us consider a model environment consisting of the three compartment air, water and soil, with air taken as reference compartment. The partition coefficient K_{wa} and K_{sa} are given by 4.2 and 4.6 respectively. The effective (eddy) diffusion coefficient is

$$D = \frac{V_a D_a + V_w D_w K_{wa} + V_s D_s K_{sa}}{V_a + V_w K_{wa} + V_s K_{sa}} \tag{4.22}$$

with D_a, D_w and D_s the (eddy) diffusion coefficient in air, water and soil respectively, and V_a, V_w and V_s the relative volume of each compartment. Similarly, the effective first-order degradation rate is given by

$$k = \frac{V_a k_a + V_w k_w K_{wa} + V_s k_s K_{sa}}{V_a + V_w K_{wa} + V_s K_{sa}} \tag{4.23}$$

with k_a, k_w and k_s the (pseudo) first-order degradation rates in air, water and soil respectively.

4.3.1 Numerical example

The temperature T of the system is set to 298K. The coefficient of macroscopic diffusions and the relative volumina of the respective compartments are taken in accordance with Scheringer (ref. (43) p.114 and 117).

Compartment	D_i (km^2 s^{-1})	$V_i[-]$
water	0.01	233
air	2	200 000
soil	0	1

The air compartment is much larger and more mobile than the other compartments, and one could thus expect the air compartment to dominate the effective diffusion coefficient, $D \approx D_a$. However, this is not necessarily the case. For example, *tert*-butyl alcohol (TBA), a transformation product of the gasoline additive Methyl-*tert*-butyl-ether (MTBE), has an effectiv eddy diffusion coefficient $D = 0.644\mathrm{km}^2\,\mathrm{s}^{-1}$, which is much smaller than $D_a = 2\mathrm{km}^2\,\mathrm{s}^{-1}$.

	MTBE	TBA	Units
$\mathrm{Log}K_{ow}$	0.94	0.35	[–]
K_H	$5.87 \cdot 10^{-4}$	$1.44 \cdot 10^{-5}$	$[\mathrm{atm} \cdot \mathrm{m}^3 \cdot \mathrm{mol}^{-1}]$
k_{s}	$4.46 \cdot 10^{-8}$	$4.01 \cdot 10^{-8}$	$[\mathrm{s}^{-1}]$
k_{a}	$7.27 \cdot 10^{-7}$	$3.26 \cdot 10^{-7}$	$[\mathrm{s}^{-1}]$
k_{w}	$1.49 \cdot 10^{-6}$	$1.45 \cdot 10^{-8}$	$[\mathrm{s}^{-1}]$
D	1.9	0.644	$[\mathrm{km}^2\,\mathrm{s}^{-1}]$
k	$6.93 \cdot 10^{-7}$	$1.34 \cdot 10^{-7}$	$[\mathrm{s}^{-1}]$

(Data from Howard (20; 21). Degradation rates calculated using the upper limit of the lifetimes given in (20))

4.4 First-generation transformation products

Assuming first-order reaction rates for the transformation reactions in the various compartments, the rate equation for a transformation product B formed by the degradation of a precursor A in a compartment i is given by:

$$\begin{aligned} \dot{c}_{\mathrm{B},i}(x,t) = \quad & D_{\mathrm{B},i} \quad \frac{\partial^2 c_{\mathrm{B},i}(x,t)}{\partial x^2} - k_{\mathrm{B},i} c_{\mathrm{B},i}(x,t) + k_{\mathrm{AB},i} c_{\mathrm{A},i}(x,t) \\ & + \quad \mathit{input} - \mathit{output} \end{aligned} \tag{4.24}$$

with $D_{\mathrm{B},i}$ the coefficient of turbulent (eddy) diffusion of transformation product B in the compartment i, $k_{\mathrm{B},i} > 0$ the first-oder degradation rate of B and $k_{\mathrm{AB},i}$ the (pseudo) first-order reaction rate of the transformation reaction A $\longrightarrow$ B, degradation and transformation reactions taking place in compartment i.

Transformation products which obey a rate equation such as 4.24 are defined here as *first-generation transformation products*.

Following the same procedure as for the precursor (eq. 4.8 to 4.21), one can aggregate the i rate equations into one single rate equation using the instant-equilibrium assumption.

$$\dot{c}_{\mathrm{B}}(x,t) = D_{\mathrm{B}} \frac{\partial^2 c_{\mathrm{B}}(x,t)}{\partial x^2} - k_{\mathrm{B}} c_{\mathrm{B}}(x,t) + k_{\mathrm{AB}} c_{\mathrm{A}}(x,t) \tag{4.25}$$

The effective eddy diffusion coefficient and first-order degradation rate of transformation product B can be calculated using expressions 4.20 and 4.21, and the effective transformation rate k_{AB} of A into B is given by:

$$k_{\mathrm{AB}} = \frac{\sum\limits_{i=1}^{n} V_i k_{\mathrm{AB},i} K_{i1}}{\sum\limits_{i=1}^{n} V_i K_{i1}} \tag{4.26}$$

Chapter 5

Characteristic spatial range

The major contribution of the present work is the extension to transformation products of the analytic method developed by Müller-Herold and Nickel (30) for the calculation of the spatial range of precursors. As a necessary prerequisite for the rest of this work, this method is presented in some details in the present chapter.

5.1 One-dimensional, flat geometry

5.1.1 Dynamics

As shown in the previous chapter, if one assumes thermodynamic equilibrium between the compartments, a multi-compartment model environment can be simplified to a single-compartment, homogeneous model environment. To start with, this compartment will be given a one-dimensional, flat geometry. After a pulse release of quantity M_0 at point $x = 0$, the chemical spreads out. Assuming first-order degradation, one obtains the following reaction-diffusion equation:

$$\begin{aligned} \dot{c}(x,t) &= D\frac{\partial^2 c(x,t)}{\partial x^2} - kc(x,t) && (5.1) \\ c(x,0) &= M_0\delta(x) && (5.2) \end{aligned}$$

with $\delta(x)$ the Dirac delta distribution, $D > 0$ the effective eddy diffusion coefficient and $k > 0$ the effective first-oder degradation rate defined in the preceding chapter (eq.4.20 and

4.21 respectively). Due to first-order degradation, the released quantity M_0 will eventually be completely degraded, which implies

$$\lim_{t\to\infty} c(x,t) = 0 \tag{5.3}$$

5.1.2 Exposure

Exposure is defined here as the integral of the concentration over time

$$e(x) := \int_0^\infty c(x,t)\,dt \tag{5.4}$$

It can be interpreted as the total amount of a chemical available at position x in the time between the release event and the complete degradation of the chemical. To calculate the exposure, one first integrates the dynamics with respect to time:

$$\int_0^\infty \dot{c}(x,t)\,dt = D\int_0^\infty \frac{\partial^2 c(x,t)}{\partial x^2}\,dt - k\int_0^\infty c(x,t)\,dt \tag{5.5}$$

The left-hand side is given by the two limiting conditions 5.2 and 5.3. Moreover, time and position are independent variables, so that one can write

$$-M_0\delta(x) = D\frac{\partial^2}{\partial x^2}\int_0^\infty c(x,t)dt - k\int_0^\infty c(x,t)\,dt \tag{5.6}$$

According to the definition of exposure as the time-integrated concentration, equation 5.6 rewrites as an ordinary differential equation

$$-M_0\delta(x) = D\frac{\partial^2 e(x)}{\partial x^2} - ke(x) \tag{5.7}$$

which can be solved for $e(x)$ by Fourier transformation. The Fourier transform of the exposure is noted $\hat{e}(u)$ and defined as :

$$\hat{e}(u) := \sqrt{\frac{2}{\pi}}\int_{-\infty}^{\infty} \mathrm{e}^{iux} e(x)dx \tag{5.8}$$

One can easily show by partial integration that the Fourier transformation of exposure' s second derivative is equal to

$$\sqrt{\frac{2}{\pi}} \int_{-\infty}^{\infty} \mathrm{e}^{iux} \frac{\partial^2 e(x)}{\partial x^2} dx = -u^2 \hat{e}(u) \tag{5.9}$$

Using the Dirac identity, $\int_{-\infty}^{\infty} g(x) \cdot \delta(0)\, dx = \; f(0)$, the Fourier transform of the delta distribution is simply

$$\sqrt{\frac{2}{\pi}} \int_{-\infty}^{\infty} \mathrm{e}^{iux} M_0 \delta(x) dx = \sqrt{\frac{2}{\pi}} M_0 \tag{5.10}$$

Finally, the Fourier transform of differential equation 5.7 is a linear equation for $\hat{e}(u)$.

$$-\sqrt{\frac{2}{\pi}} M_0 = -Du^2 \hat{e}(u) - k\hat{e}(u) \tag{5.11}$$

which is easily solved for $\hat{e}(u)$:

$$\hat{e}(u) = \sqrt{\frac{2}{\pi}} \frac{M_0}{D} \frac{1}{u^2 + k/D} \tag{5.12}$$

Applying reverse Fourier transform to $\hat{e}(u)$ (Oberhettinger, ref.(31), p.5), one gets the exposure:

$$e(x) = \frac{M_0}{2D} \frac{\exp[-\sqrt{k/D}\ |x|]}{\sqrt{k/D}} \tag{5.13}$$

The exposure as a function of distance x from the emission point is plotted on figure 5.1.

In order to simplify the notation, let us introduce the parameter $z := \sqrt{D/k}$. The exposure then simplifies to

$$e(x) = \frac{M_0}{2D} \cdot z \cdot \mathrm{e}^{-|x|/z} \tag{5.14}$$

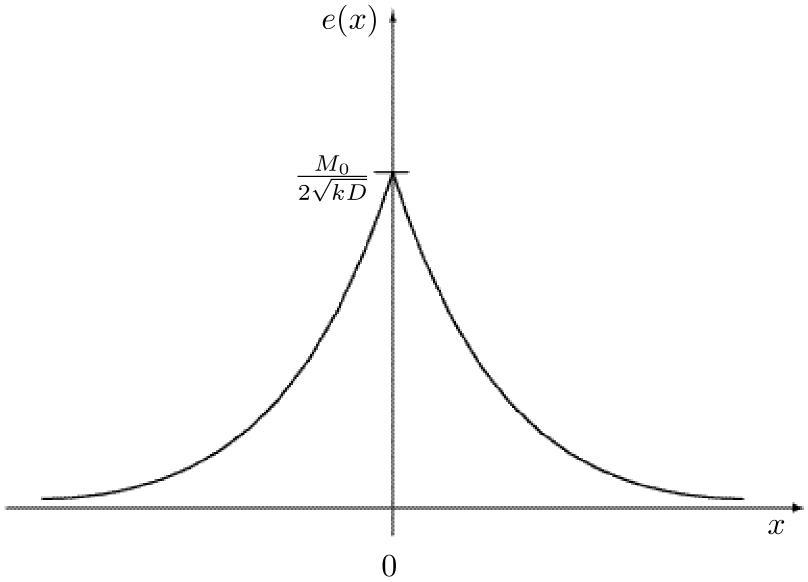


Figure 5.1: Exposure to a pulse-released chemical, plotted as function of the distance x from the emission point $x = 0$ of the chemical.

5.1.3 Characteristic spatial range as entropy rank of the exposure distribution

Conceptually, spatial range is a measure of the spatial extent of exposure. However, due to diffusion process, exposure is larger than zero for every value of x, and has no well-defined "ends". Accordingly, one has to define a domain of relevant exposure. The spatial extent of this domain will then be taken as the spatial range. The problem of defining a domain of relevant exposure has many solutions: Scheringer (40) chose the 95% quantile of exposure. Bennett et al. (3) and Van Pul et al. (34), both using slightly different approaches, took the point where the exposure drops to 1/e of its value at the emission point. The measure chosen by Müller-Herold and Nickel (30) is the *entropy rank* of the exposure distribution. It is important to note that all these measures describe the *shape* of the exposure, and give no information on its *magnitude*.

The entropy rank is somewhat unusual, but it has the advantage of a clear theoretical meaning: The domain of relevant

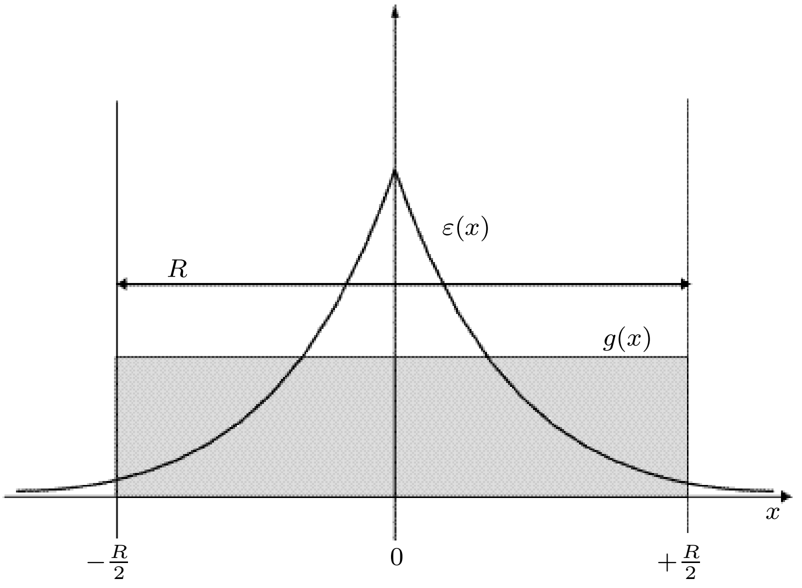


Figure 5.2: Exposure distribution $\varepsilon(x)$ plotted together with an equipartition $g(x)$ with the same entropy rank. The exposure distribution is obtained by dividing the exposure with a normalization factor. Between $x = -R/2$ and $x = +R/2$, the exposure is considered significant and assigned the constant value $1/R$. Beyond these limits, exposure is not considered significant and set to zero. The length R of the equipartition is the entropy rank of the exposure distribution $\varepsilon(x)$, and the distance ϱ is the characteristic spatial range

exposure can be seen as the length of an equipartition distribution (see Fig. 5.2): inside the domain of relevant exposure, the exposure is set to a constant, positive value. Outside the domain of relevant exposure, the exposure is set to zero. The entropy rank is then used to define an adequate equipartition, namely, the equipartition with the same entropy rank as the exposure distribution (A more detailed discussion of entropy and entropy rank can be found in Appendix A).

As a simple introduction, let us calculate the entropy rank of an equipartition

$$g(x) := \begin{cases} \frac{1}{R} \quad \text{for} \quad x \in [-\frac{R}{2}, +\frac{R}{2}] \\ \\ 0 \qquad\quad \text{otherwise} \end{cases} \tag{5.15}$$

The Shannon-Boltzmann entropy of a distribution is defined as the average of the logarithm of the distribution. For an equipartition $g(x)$, it is given by:

$$S_g := - \int\limits_{-\infty}^{\infty} g(x) \ln[g(x)] \; dx = ln[R] \tag{5.16}$$

The entropy rank is in turn defined as the exponential of the Shannon-Boltzmann entropy. Thus, the entropy rank of an equipartition $g(x)$ is equal to

$$\mathrm{e}^{S_g} = R \tag{5.17}$$

Let us now calculate the entropy rank of the exposure distribution $\varepsilon(x)$. The exposure distribution $\varepsilon(x)$ is simply obtained from the exposure $e(x)$:

$$\varepsilon(x) := \frac{e(x)}{\bar{e}} = \frac{1}{2z} \exp[-\frac{|x|}{z}] \tag{5.18}$$

with

$$\bar{e} := \int\limits_{-\infty}^{+\infty} e(x) \; dx = \frac{M_0}{k} \tag{5.19}$$

The exposure distribution is thus equal to:

$$\varepsilon(x) = \frac{1}{2z} \exp[-\frac{|x|}{z}] \tag{5.20}$$

The Shannon-Boltzmann entropy of the exposure distribution is:

$$S_\varepsilon := - \int\limits_{-\infty}^{\infty} \varepsilon(x) \ln[\varepsilon(x)] \; dx = \ln[2z] + 1 \tag{5.21}$$

and its entropy rank is given by

$$\mathrm{e}^{S_\varepsilon} = 2\mathrm{e} \cdot z \tag{5.22}$$

At that point, defining an equipartition with the same entropy rank as the exposure distribution is quite easy: According to 5.17 and 5.22, one only has to set

$$R = 2\mathrm{e} \cdot z \tag{5.23}$$

The characteristic spatial range is then defined as the half of the length of the equivalent equipartition:

$$\varrho^{1f} := \frac{R}{2} = \mathrm{e} \cdot z \tag{5.24}$$

The superscript $1f$ indicates the one-dimensional, flat geometry of the model.

If one compares the exposure at position $x = \varrho^{1f}$ with the exposure at the emission point $x = 0$, one gets

$$\frac{e(x = \varrho^{1f})}{e(x = 0)} = \frac{\varepsilon(x = \varrho^{1f})}{\varepsilon(x = 0)} = \mathrm{e}^{-\mathrm{e}} \approx 6.6\% \tag{5.25}$$

Thus, taking the entropy rank as a measure of the spatial extent of the domain of relevant exposure, one implicitly considers exposure relevant if it is larger than 6.6% of the exposure at the emission point.

5.1.4 Explicit form of characteristic spatial range

Substituting $z = \sqrt{D/k}$ yields

$$\varrho^{1f} = \mathrm{e} \cdot \sqrt{D/k} \tag{5.26}$$

Starting from a three-compartment model environment with air, water and soil, characteristic spatial range can be expressed as an explicit function of the three degradation rates k_a, k_w, k_s, the Henry's constant K_H and the octanol-water partition coefficient K_{ow}: Using the instant-equilibrium assumption, one can calculate the effective macroscopic diffusion coefficient (Eq. 4.22), and the effective first-order degradation rate k (Eq.4.23). Then, one gets for the characteristic spatial range

$$\varrho^{1f} = \mathrm{e} \cdot \sqrt{\frac{D_a V_a + D_w V_w K_{wa} + D_s V_s K_{sa}}{k_a V_a + k_w V_w K_{wa} + k_s V_s K_{sa}}} \tag{5.27}$$

with $K_{wa} = \mathrm{R}T/K_H$ and $K_{sa} = f_{oc} 0.41 K_{ow} \cdot K_{wa}$ (see section 4.1). Illustrative examples of the calculation of the characteristic range in a three-compartment unit-world consisting of the troposphere, the surface layer of the oceans, and the upper layer of continental soil, are presented in chapter 7.

5.1.5 Quantile equivalent of the entropy rank

The entropy rank-based definition of characteristic spatial range yields results that are very close to the ones obtained by Scheringer (40) using the 95% interquantile distance of the exposure distribution. The 95% interquantile distance is defined as the distance $x = q$ so that

$$\int_{-q}^{+q} \varepsilon(x)\, dx = 0.95 \tag{5.28}$$

Integrating the exposure distribution ε between $-\varrho^{1f}$ and ϱ^{1f} yields

$$\int_{-\varrho^{1f}}^{\varrho^{1f}} \varepsilon(x)\, dx = 1 - \mathrm{e}^{-\mathrm{e}} \approx 0.934 \tag{5.29}$$

Indeed, the values of characteristic range obtained by Müller-Herold and Nickel using entropy-rank were found to be in good agreement with the values obtained by Scheringer using the 95% interquantile distance (30), and this despite the fact that Scheringer does not use the instant equilibrium approximation, but dynamic exchanges between the phases.

5.1.6 Extension to a two-dimensional, flat geometry

Müller-Herold and Nickel also calculated the spatial range in a two dimensional flat modelling environment (30). The spatial range in the two-dimensional model geometry turns out to be equal to its one-dimensional counterpart up to a constant near one

$$\varrho^{2f} = 1.1\varrho^{1f} \tag{5.30}$$

Thus, the spatial range in the two-dimensional model geometry is slightly *larger* than the spatial range in the one-dimensional geometry. This means that the exposure distribution in the two-dimensional model is a little flatter than in the one-dimensional model.

5.2 One-dimensional circular model

The exposure can be calculated in a topologically more realistic model, consisting of a one-dimensional ring with radius r equal to the earth's radius. The dynamics modifies to a reaction-diffusion problem with periodic boundary conditions:

$$\begin{aligned}
\dot{c}(\varphi,t) &= \frac{D}{r^2}\frac{\partial^2 c(\varphi,t)}{\partial\varphi^2} - kc(\varphi,t) \qquad\qquad -\pi \leq \varphi \leq \pi \\
c(\varphi,0) &= M_0\delta(\varphi) \\
c(\pi,t) &= c(-\pi,t) \\
c'(\pi,t) &= c'(-\pi,t)
\end{aligned} \tag{5.31}$$

Position is now given by $\varphi \in [-\pi, pi]$ where φ is an angle in *rad*. As in the linear one-dimensional model, the quantity M_0 is pulse-released at time $t = 0$ and position $\varphi = 0$, and total degradation occurs after a sufficiently long time:

$$\lim_{t\to\infty} c(\varphi,t) = 0 \tag{5.32}$$

As in the one-dimensional flat geometry, time-integration of the dynamics yields an ordinary differential equation for the exposure, which can be solved by Fourier transformation. The resulting exposure

$$e(\varphi) = \frac{M_0 r}{D}\frac{z}{2}\frac{\cosh\left[(\pi - |\varphi|)r/z\right]}{\sinh[\pi r/z]} \tag{5.33}$$

is plotted in Fig.5.3.

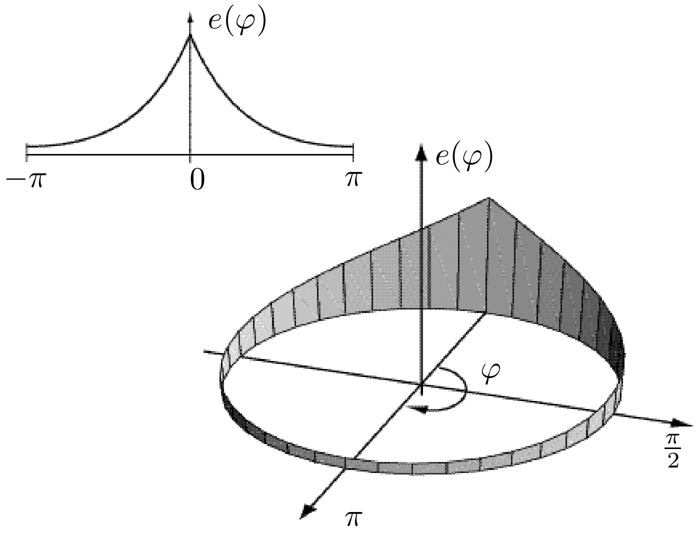


Figure 5.3: Exposure plotted as functions of the angle φ from the emission point of the chemical, located at the origin $\varphi = 0$. Circular and flat representation of the same exposure pattern

The normalization factor $\bar{e}$ is

$$\bar{e} := \int_{-\pi}^{+\pi} e(\varphi)\ d\varphi = \frac{M_0}{k} \tag{5.34}$$

which is identical to the normalization factor found in the one-dimensional flat case. The exposure distribution is given by

$$\varepsilon(\varphi) = \frac{e(\varphi)}{\bar{e}} = \frac{r}{2z}\frac{\cosh\left[(\pi - |\varphi|)r/z\right]}{\sinh[\pi r/z]} \tag{5.35}$$

The spatial range, expressed in kilometers, is equal to

$$\varrho^{1c} = \mathrm{e} \cdot z \cdot \tanh[\pi r/z]\exp[\frac{\frac{\pi}{2} - 2\arctan[\mathrm{e}^{\pi r/z}]}{\sinh[\pi r/z]}] \tag{5.36}$$

5.3 Comparison of results for different model geometries

Each one of the three model geometries yields slightly different characteristic spatial ranges, but all three of them are functions of the parameter $z = \sqrt{D/k}$.

$$\begin{aligned}
\varrho^{1f} &= \mathrm{e} \cdot z \\
\varrho^{2f} &= 1.1 \cdot \mathrm{e} \cdot z \\
\varrho^{1c} &= \mathrm{e} \cdot z \cdot \tanh[\pi r/z] \exp[\frac{\frac{\pi}{2} - 2\arctan[\mathrm{e}^{\pi r/z}]}{\sinh[\pi r/z]}]
\end{aligned}$$

This was to be expected, since the characteristic spatial range is a distance, and a simple dimensional analysis shows that $\sqrt{D/k}$ has units of distance. Moreover, it seems natural that the spatial range should grow with the mobility of the chemical, expressed by its macroscopic diffusion coefficient D, and decrease with its reactivity, expressed by the effective first-rate constant k.

The spatial ranges for the three different model geometry are plotted in Fig.5.4, as a function of the parameter $z = \sqrt{D/k}$. It can be seen on figure 5.4 that, up to $r\frac{\pi}{2} = 10'000km$, ϱ^{1f} can barely be differentiated from its counterpart in the circular geometry, ϱ^{1c}. Hence, one can conclude that the effect of the earth's curvature on the spatial range is only significant for chemicals with a global range ($\varrho^{1f} \geq 10'000km$).

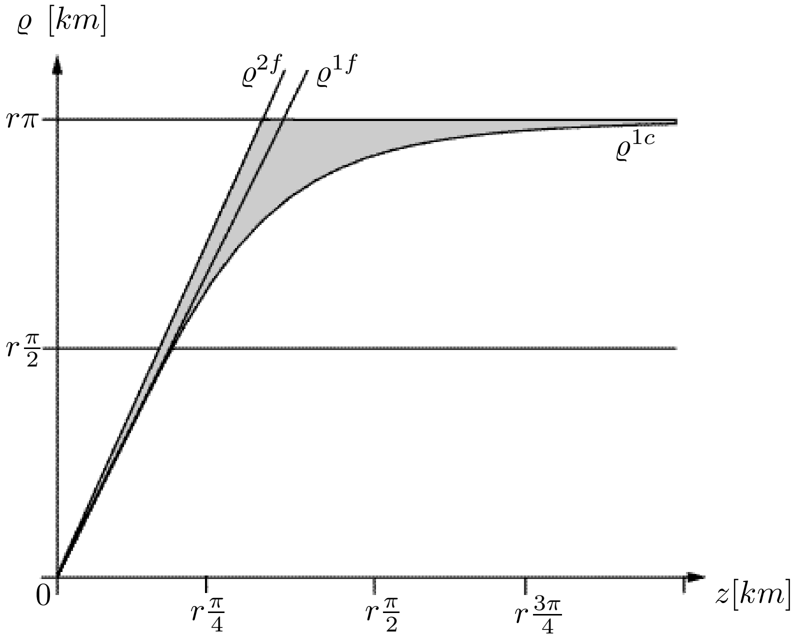


Figure 5.4: Spatial range ϱ as a function of $z = \sqrt{D/k}$ for different model geometries. The letter r stands for the earth radius, and $r\pi$ is equal to 20000 km, which is the maximal range in the circular (or spherical) geometries. (From Müller-Herold and Nickel, (30)).

5.4 Universality of the normalization factor

One can observe that the normalization factor $\bar{e}$ is equal to M_0/k in the one-dimensional flat case as well as in the circular case. In fact, one can easily show that the normalization factor is independent of the geometry of the model. Let us first introduce the decay function $M(t)$, describing the quantity of substance in the model environment as a function of time. In the circular model geometry, it is given by

$$M(t) := \int_{-\pi}^{+\pi} c(\varphi, t) d\varphi \tag{5.37}$$

But, assuming first-order decay, $M(t)$ is simply equal to:

$$M(t) = M_0 e^{-kt} \tag{5.38}$$

which depends on the decay processes only, and not on the model geometry. As shown below, the normalization factor of the exposure is simply the time integral of the decay function $M(t)$:

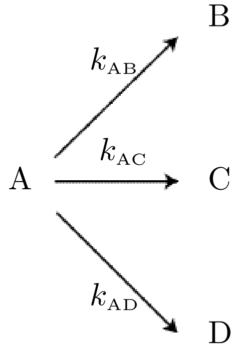
$$\begin{aligned}\bar{e} &:= \int\limits_{-\pi}^{+\pi} e(\varphi)\ d\varphi \\ &= \int\limits_{-\pi}^{+\pi}\int\limits_{0}^{\infty} c(\varphi,t) dt d\varphi = \int\limits_{0}^{\infty}\int\limits_{-\pi}^{+\pi} c(\varphi,t) d\varphi dt \\ &= \int\limits_{0}^{\infty} M(t) dt = \frac{M_0}{k} \qquad (5.39)\end{aligned}$$

Since the decay function $M(t)$ is independant of the geometry of the modelling environment, this also holds for the normalization factor $\bar{e}$.

Chapter 6

Secondary spatial range

Let us assume that a precursor A, released from a point source, transforms to three different transformation products B, C, and D:



Furthermore, let's make the following assumptions on the transformation reactions

1. There are no back reactions.
2. All the reactions obey (pseudo) first-order kinetics, the corresponding effective first-order rate constants being noted k_{AB}, k_{AC} and k_{AD}.

The total degradation rate constant of A is the sum of the three effective rate constants

$$k_{A} = k_{AB} + k_{AC} + k_{AD} \tag{6.1}$$

Let us now focus on transformation product B. It is evident from equation 6.1 that its formation rate k_{AB} cannot exceed the decay rate of its precursor, $k_{\mathrm{AB}} \leq k_{\mathrm{A}}$. Before getting started with the calculation of the exposure to transformation product B, e_{AB}, and of the corresponding spatial range ϱ_{AB}, let us define the terminology and the notation (Fig. 6.1):

- The *primary exposure* is the exposure to a pulse-released chemical as calculated in the preceding chapter. It is denoted by e_{A}, and e_{B} respectively.
- The *characteristic spatial range* is the spatial range calculated from the primary exposure. It is denoted by ϱ_{A} and ϱ_{B} respectively.
- The *secondary exposure* is the exposure to the transformation product of a pulse-released precursor. The secondary exposure is noted with a double index. For example, if B is a transformation product of A, the secondary exposure is noted e_{AB}.
- The *secondary spatial range* calculated from the secondary exposure is ϱ_{AB}

6.1 One-dimensional, flat model

6.1.1 Secondary exposure

In a one-dimensional flat model environment, the concentration c_{AB} of transformation product B of a precursor A is assumed to evolve according to the reaction–diffusion equation

$$\dot{c}_{\mathrm{AB}}(x,t) = D_{\mathrm{B}} \frac{\partial^2 c_{\mathrm{AB}}(x,t)}{\partial^2 x} - k_{\mathrm{B}} c_{\mathrm{AB}}(x,t) + k_{\mathrm{AB}} c_{\mathrm{A}}(x,t) \quad (6.2)$$

With $D_{\mathrm{B}} > 0$ the coefficient of macroscopic (eddy) diffusion, $[D_{\mathrm{B}}] = \mathrm{km}^2\,\mathrm{s}^{-1}$ of the transformation product. The precursor A reacts to B with effective first-order rate constant $0 < k_{\mathrm{AB}} \leq k_{\mathrm{A}}$. Transformation product B is itself degraded with (pseudo-)first-order rate constant $k_{\mathrm{B}} > 0$. As there is no back reaction,

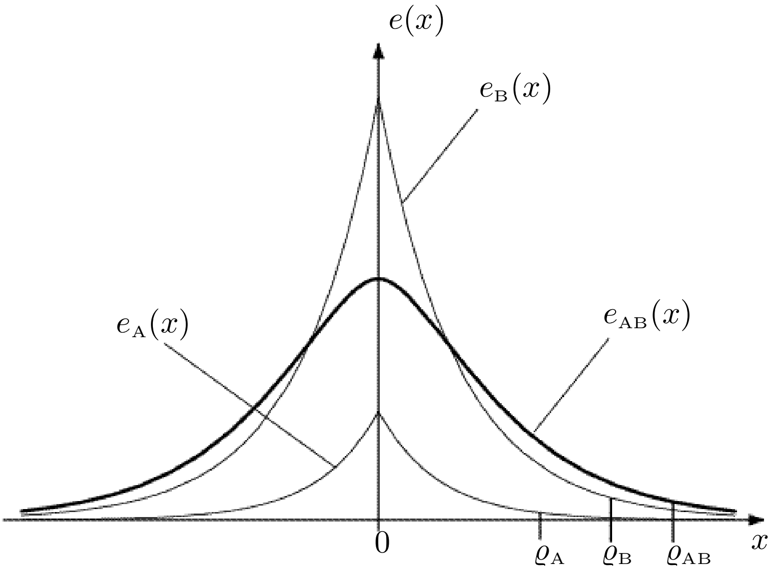


Figure 6.1: The primary exposure to chemical A and B, e_{A} and e_{B}, are plotted as functions of the distance x from the emission point of A located at the origin $x = 0$. The corresponding characteristic spatial ranges are ϱ_{A} and ϱ_{B}. The thick curve with a rounded top is the secondary exposure $e_{\mathrm{AB}}(x)$ to chemical B, in this case a transformation product of A. The corresponding secondary range, ϱ_{AB}, is larger than the two characteristic ranges, ϱ_{A} and ϱ_{B}.

the dynamics of precursor A remains unchanged, as given in equation 5.1. However, whereas a quantity M_0 of precursor is pulse-released from a point source at position $x = 0$ and time $t = 0$, the initial concentration of the transformation product B at time $t = 0$ can be assumed to be zero everywhere:

$$c_{\mathrm{AB}}(x, 0) = 0 \tag{6.3}$$

Transformation product B is completely degraded after a sufficiently long time:

$$\lim_{t \to \infty} c_{\mathrm{AB}}(x, t) = 0 \tag{6.4}$$

The secondary exposure to degradation product B will now be calculated using the same method as for the calculation of the primary exposure. First, the dynamics described in eq. 6.2 is integrated with respect to time, using boundary conditions

6.3 and 6.4. With the exposure defined as the time-integrated concentration, one gets an ordinary differential equation for secondary exposure e_{AB}:

$$0 = D_{\mathrm{B}} \frac{\partial^2 e_{\mathrm{AB}}(x)}{\partial x^2} - k_{\mathrm{B}} e_{\mathrm{AB}}(x) + k_{\mathrm{AB}} e_{\mathrm{A}}(x) \tag{6.5}$$

This ordinary differential equation can be solved by Fourier transformation. Expressed in the Fourier space, it becomes:

$$0 = -D_{\mathrm{B}} u^2 \hat{e}_{\mathrm{AB}}(u) - k_{\mathrm{B}} \hat{e}_{\mathrm{AB}}(u) + k_{\mathrm{AB}} \hat{e}_{\mathrm{A}}(u) \tag{6.6}$$

which is easily solved for $\hat{e}_{\mathrm{AB}}(u)$

$$\hat{e}_{\mathrm{AB}}(u) = \frac{k_{\mathrm{AB}}}{D_{\mathrm{B}} u^2 + k_{\mathrm{B}}} \hat{e}_{\mathrm{A}}(u) \tag{6.7}$$

Recalling from the preceding chapter (equation 5.12) that

$$\hat{e}_{\mathrm{A}}(u) = \sqrt{\frac{2}{\pi}} \frac{M_0}{D_{\mathrm{A}}} \frac{1}{u^2 + k_{\mathrm{A}}/D_{\mathrm{A}}} \tag{6.8}$$

one can substitute $\hat{e}_{\mathrm{A}}$ in 6.7, and one gets

$$\hat{e}_{\mathrm{AB}}(u) = \sqrt{\frac{2}{\pi}} \frac{k_{\mathrm{AB}} M_0}{D_{\mathrm{A}} D_{\mathrm{B}}} \cdot \frac{1}{u^2 + k_{\mathrm{B}}/D_{\mathrm{B}}} \cdot \frac{1}{u^2 + k_{\mathrm{A}}/D_{\mathrm{A}}} \tag{6.9}$$

The reverse Fourier transform of this expression (ref. (31) p.3) gives the secondary exposure.

$$e_{\mathrm{AB}}(x) = \frac{k_{\mathrm{AB}} M_0}{2 D_{\mathrm{A}} D_{\mathrm{B}}} \frac{z_{\mathrm{A}}^2 z_{\mathrm{B}}^2}{z_{\mathrm{B}}^2 - z_{\mathrm{A}}^2} \left(z_{\mathrm{B}} \mathrm{e}^{-|x|/z_{\mathrm{B}}} - z_{\mathrm{A}} \mathrm{e}^{-|x|/z_{\mathrm{A}}} \right) \tag{6.10}$$

with

$$z_{\mathrm{B}} = \sqrt{D_{\mathrm{B}}/k_{\mathrm{B}}}\,, \quad z_{\mathrm{A}} = \sqrt{D_{\mathrm{A}}/k_{\mathrm{A}}} \tag{6.11}$$

The secondary exposure is plotted together with the primary exposure in Fig. 6.2. The plausibility of expression 6.10 for the secondary exposure will now be demonstrated with the help of a limiting case. Let us consider the limiting case where the precursor transforms into a unique transformation product. This implies $k_{\mathrm{A}} = k_{\mathrm{AB}}$. Introducing this condition in

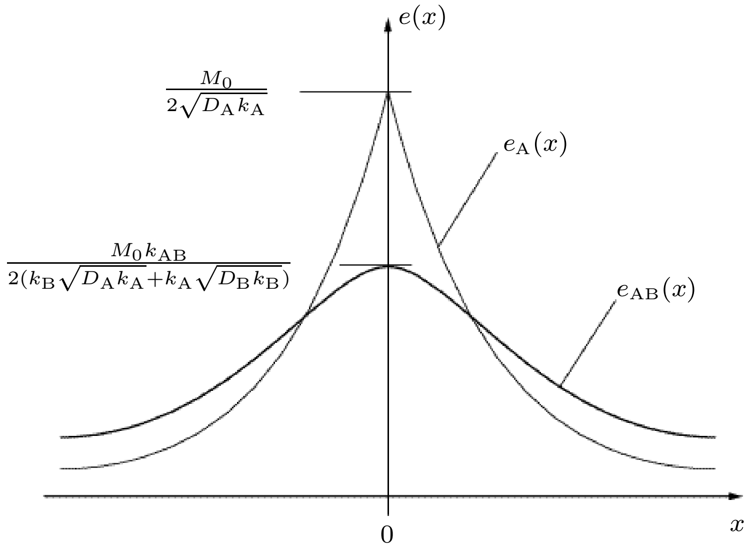


Figure 6.2: Exposure to precursor A (primary exposure e_A) and to its transformation product B (secondary exposure e_{AB}) as functions of the distance x from the emission point of A located at the origin $x = 0$.

6.10 yields the corresponding expression of the secondary exposure:

$$e_{AB}(x) = \frac{M_0}{2(D_B - D_A\frac{k_B}{k_A})}\left(z_B e^{-|x|/z_B} - z_A e^{-|x|/z_A}\right) \qquad (6.12)$$

If the transformation of A to B is not only complete, but also instantaneous, i.e. $k_A \to \infty$, the secondary exposure simplifies to

$$\lim_{k_A \to \infty} e_{AB}(x) = \frac{M_0}{2D_B} z_B e^{-|x|/z_B} \qquad (6.13)$$

which is identical to expression 5.14 of the primary exposure. Indeed, releasing a precursor than instantaneously transforms into a unique transformation product is equivalent to directly releasing the transformation product itself.

6.1.2 Comparison with primary exposure

Under given conditions, the secondary exposure may be larger than the primary exposure at the emission point, $e_{AB}(0) >$

$e_{\mathrm{A}}(0)$. In this situation, the transformation product can be seen as more relevant than the precursor, at least from the point of view of the exposure. The conditions for such a situation to occur will now be made explicit. According to equations 5.13 and 6.10, $e_{\mathrm{AB}}(0) > e_{\mathrm{A}}(0)$ rewrites as:

$$\frac{M_0 k_{\mathrm{AB}}}{2(k_{\mathrm{B}}\sqrt{D_{\mathrm{A}}k_{\mathrm{A}}} + k_{\mathrm{A}}\sqrt{D_{\mathrm{B}}k_{\mathrm{B}}})} > \frac{M_0}{2\sqrt{D_{\mathrm{A}}k_{\mathrm{A}}}} \tag{6.14}$$

The condition for the above inequality to be true is

$$k_{\mathrm{AB}} > k_{\mathrm{B}}\left(1 + \frac{\sqrt{D_{\mathrm{B}}/k_{\mathrm{B}}}}{\sqrt{D_{\mathrm{A}}/k_{\mathrm{A}}}}\right) \tag{6.15}$$

that is, if the transformation product forms significantly faster than it degrades, $k_{\mathrm{AB}} >> k_{\mathrm{B}}$, then the secondary exposure may be larger than the primary exposure, even at the emission point of the precursor. Note that, since $k_{\mathrm{AB}} \leq k_{\mathrm{A}}$, the condition becomes $k_{\mathrm{A}} \geq k_{\mathrm{AB}} >> k_{\mathrm{B}}$. Thus, the secondary exposure may be larger than the primary exposure only if $k_{\mathrm{A}} >> k_{\mathrm{B}}$, i.e. if the transformation product is much more stable than the precursor.

6.1.3 Secondary exposure distribution

The norm of the the secondary exposure is defined as

$$\bar{e}_{\mathrm{AB}} := \int_{-\infty}^{+\infty} e_{\mathrm{AB}}(x)dx = \frac{k_{\mathrm{AB}}M_0}{D_{\mathrm{A}}D_{\mathrm{B}}} z_{\mathrm{A}}^2 z_{\mathrm{B}}^2 \tag{6.16}$$

Dividing the secondary exposure by its norm yields the *secondary exposure distribution* $\varepsilon_{\mathrm{AB}}$, which is required for the calculation of the entropy rank

$$\varepsilon_{\mathrm{AB}}(x) := \frac{e_{\mathrm{AB}}(x)}{\bar{e}_{\mathrm{AB}}} = \frac{1}{2(z_{\mathrm{B}}^2 - z_{\mathrm{A}}^2)}\left(z_{\mathrm{B}}\mathrm{e}^{-|x|/z_{\mathrm{B}}} - z_{\mathrm{A}}\mathrm{e}^{-|x|/z_{\mathrm{A}}}\right) \tag{6.17}$$

Two observations can be made at this point:

1. *Independence on k_{AB}*: As the primary exposure distribution , the secondary exposure distribution $\varepsilon_{\mathrm{AB}}$ is independent of the amount of precursor released M_0. More surprising is the independence of the secondary exposure distribution on the effective first-order transformation rate k_{AB}, which cancels out in the process of normalizing the exposure. In view of the general data situation, it must be regarded as a stroke of luck that a theory of secondary ranges can be developed without numerical values for tranformation rates k_{AB} which, as a rule, are quite difficult to obtain.

2. *Symmetry*: The secondary exposure distribution remains unchanged if one permutes the indexes A and B. This indicates that the precursor and the transformation product both have the same influence on the secondary exposure distribution. As will be shown below, this symmetry holds for the secondary spatial range.

6.1.4 Secondary spatial range

As for the characteristic spatial range, the secondary spatial range of transformation products are calculated via the entropy rank of exposure distribution (see Appendix A). The Shannon-Boltzmann entropy of the secondary exposure distribution is

$$S_{\mathrm{AB}} := -\int_{-\infty}^{+\infty} \varepsilon_{\mathrm{AB}}(x) \ln[\varepsilon_{\mathrm{AB}}(x)]\, dx \qquad (6.18)$$

It is associated with the entropy rank R_{AB}:

$$R_{\mathrm{AB}} := \mathrm{e}^{S_{\mathrm{AB}}} \qquad (6.19)$$

and the spatial range is defined as the half of the entropy rank (see Figure 5.2):

$$\varrho_{\mathrm{AB}} := \frac{1}{2} R_{\mathrm{AB}} \qquad (6.20)$$

The calculation of the Shannon-Boltzmann entropy of the secondary exposure distribution is relatively involved. This is why we shall start with the more simple degenerate case $z_\mathrm{A} = z_\mathrm{B}$, and then solve the general case $z_\mathrm{A} \neq z_\mathrm{B}$.

Degenerate case $z_\mathrm{A} = z_\mathrm{B}$

The degenerate case $z_\mathrm{A} = z_\mathrm{B}$ implies that the two compounds involved have the same characteristic spatial range: $\varrho_\mathrm{A} = \varrho_\mathrm{B}$ (see equation 5.24). The secondary exposure distribution in the degenerate case is equal to

$$\lim_{z_\mathrm{B} \to z_\mathrm{A}} \varepsilon_\mathrm{AB}(x) := \varepsilon_\mathrm{AA}(x) = \frac{1 + |x|/z_\mathrm{A}}{4 z_\mathrm{A}} \cdot \mathrm{e}^{-|x|/z_\mathrm{A}} \tag{6.21}$$

Its Shannon-Boltzmann entropy is (see Appendix B for the detailed calculations).

$$\begin{aligned} S_\mathrm{AA} &= -\int_{-\infty}^{+\infty} \varepsilon_\mathrm{AA}(x) \cdot \ln[\varepsilon_\mathrm{AA}(x)]\, dx \\ &= -\ln\left[\frac{1}{4 z_\mathrm{A}}\right] + 1 - \frac{1}{2}\mathrm{e}\, E_1(1) \end{aligned} \tag{6.22}$$

where $E_1(1)$ is the exponential integral defined by

$$E_1 := -\int_1^{\infty} \frac{\mathrm{e}^{-t}}{t}\; dt \tag{6.23}$$

The associated entropy rank is equal to

$$R_\mathrm{AA} = \mathrm{e}^{S_\mathrm{AA}} = 4 \cdot z_\mathrm{A} \cdot \exp\left[-\tfrac{1}{2}\mathrm{e}\, E_1(1)\right] \tag{6.24}$$

which leads to the secondary spatial range:

$$\varrho_\mathrm{AA} = \tfrac{1}{2} R_\mathrm{AA} = 2 \exp\left[-\tfrac{1}{2}\mathrm{e}\, E_1(1)\right] \cdot \mathrm{e} \cdot z_\mathrm{A} \tag{6.25}$$

Insertion of the numerical value $E_1(1) \approx 0.219384$ (ref. (1), [p. 293]) together with substitution $\mathrm{e} \cdot z_\mathrm{A} = \varrho_\mathrm{A}$ (equation 5.24) yields the (degenerate) secondary spatial range ϱ_AA as a function of the characteristic range ϱ_A:

$$\varrho_\mathrm{AA} \approx 1.4843 \cdot \varrho_\mathrm{A} \tag{6.26}$$

Hence, for precursor and transformation products with identical characteristic spatial range $\varrho_{\mathrm{A}} = \varrho_{\mathrm{B}}$, the secondary range of chemical B as a transformation product of chemical A is about 1.5 times as large as their identical characteristic ranges.

General case $z_{\mathrm{A}} \neq z_{\mathrm{B}}$

For different characteristic ranges $\varrho_{\mathrm{A}} \neq \varrho_{\mathrm{B}}$, and therefore $z_{\mathrm{A}} \neq z_{\mathrm{B}}$, the Shannon-Boltzmann entropy S_{AB} of secondary exposure distribution $\varepsilon_{\mathrm{AB}}$ (equation 6.17) is given by (for details see Appendix B):

$$\begin{aligned} S_{\mathrm{AB}} &= -\int_{-\infty}^{+\infty} \varepsilon_{\mathrm{AB}}(x) \ln[\varepsilon_{\mathrm{AB}}(x)]\, dx \\ &= \frac{(z_{\mathrm{A}}^2 + z_{\mathrm{B}}^2) - \max\{z_{\mathrm{A}}, z_{\mathrm{B}}\}|z_{\mathrm{A}} - z_{\mathrm{B}}| \cdot F(0)}{\min\{z_{\mathrm{A}}, z_{\mathrm{B}}\}(z_{\mathrm{A}} + z_{\mathrm{B}})} \\ &- \ln[\frac{1}{2(z_{\mathrm{A}} + z_{\mathrm{B}})}] \end{aligned} \tag{6.27}$$

with

$$F(0) := \sum_{n=0}^{\infty} \frac{\min\{z_{\mathrm{A}}, z_{\mathrm{B}}\}}{\min\{z_{\mathrm{A}}, z_{\mathrm{B}}\} + n|z_{\mathrm{A}} - z_{\mathrm{B}}|} \cdot \left(\frac{\min\{z_{\mathrm{A}}, z_{\mathrm{B}}\}}{\max\{z_{\mathrm{A}}, z_{\mathrm{B}}\}}\right)^n \tag{6.28}$$

where $\max\{z_{\mathrm{A}}, z_{\mathrm{B}}\}$ denotes the maximum and $\min\{z_{\mathrm{A}}, z_{\mathrm{B}}\}$ denotes the minimum of z_{A} and z_{B}. The corresponding secondary spatial range is

$$\begin{aligned} \varrho_{\mathrm{AB}} = (z_{\mathrm{A}} + z_{\mathrm{B}}) \cdot \quad & \exp \left[\frac{z_{\mathrm{A}}^2 + z_{\mathrm{B}}^2}{\min\{z_{\mathrm{A}}, z_{\mathrm{B}}\}(z_{\mathrm{A}} + z_{\mathrm{B}})}\right] \\ \cdot \quad & \exp \left[-\frac{\max\{z_{\mathrm{A}}, z_{\mathrm{B}}\}|z_{\mathrm{A}} - z_{\mathrm{B}}| \cdot F(0)}{\min\{z_{\mathrm{A}}, z_{\mathrm{B}}\}(z_{\mathrm{A}} + z_{\mathrm{B}})}\right] \end{aligned} \tag{6.29}$$

Substituting the characteristic ranges $\varrho_{\mathrm{A}}/\mathrm{e}$ for z_{A} and $\varrho_{\mathrm{B}}/\mathrm{e}$ for z_{B} into equation 6.29 yields secondary range ϱ_{AB} as a function of the characteristic ranges:

$$\begin{aligned}\varrho_{\mathrm{AB}} = (\varrho_{\mathrm{A}} + \varrho_{\mathrm{B}}) \cdot \quad &\exp\left[\frac{\varrho_{\mathrm{A}}^2 + \varrho_{\mathrm{B}}^2}{\min\{\varrho_{\mathrm{A}}, \varrho_{\mathrm{B}}\}(\varrho_{\mathrm{A}} + \varrho_{\mathrm{B}})} - 1\right] \\ \cdot \quad &\exp\left[-\frac{\max\{\varrho_{\mathrm{A}}, \varrho_{\mathrm{B}}\}|\varrho_{\mathrm{A}} - \varrho_{\mathrm{B}}| \cdot F(0)}{\min\{\varrho_{\mathrm{A}}, \varrho_{\mathrm{B}}\}(\varrho_{\mathrm{A}} + \varrho_{\mathrm{B}})}\right]\end{aligned} \tag{6.30}$$

Again, we gratefully state that conversion constants of type k_{AB} do not enter the result. As a second important qualitative result, one observes that the secondary range is always smaller than the sum of the respective characteristic ranges,

$$\varrho_{\mathrm{AB}} < (\varrho_{\mathrm{A}} + \varrho_{\mathrm{B}}) \tag{6.31}$$

Indeed, definition 6.28 entails $F(0) > 0$, and it follows that the argument of the exponential in equation 6.30 is negative. This can be sharpened to give the following inequality:

$$\max\{\varrho_{\mathrm{A}}, \varrho_{\mathrm{B}}\} \leq \varrho_{\mathrm{AB}} \leq 1.4843 \cdot \max\{\varrho_{\mathrm{A}}, \varrho_{\mathrm{B}}\} \tag{6.32}$$

The lower limit is attained, if the smaller of the two ranges approaches zero, i. e., if $\min\{\varrho_{\mathrm{A}}, \varrho_{\mathrm{B}}\} = 0$, which is a rather intuitive result. The upper limit is attained in the degenerate case, i. e. for $\varrho_{\mathrm{A}} = \varrho_{\mathrm{B}}$. Hence, the chemical with the larger characteristic range dominates secondary range, regardless of it being the precursor or the transformation product. This is due to the fact that secondary range is a symmetrical function of the two characteristic ranges (equation 6.30).

A simple "rule of thumb" can be deduced from the above: If the characteristic spatial range of the transformation product is larger than the characteristic spatial range of the precursor, then the secondary spatial range of the pair is larger than 1,5 times the characteristic spatial range of the precursor. This can be expressed more clearly as

$$\varrho_{\mathrm{B}} > \varrho_{\mathrm{A}} \qquad \Longrightarrow \qquad \varrho_{\mathrm{AB}} > 1.5 \cdot \varrho_{\mathrm{A}} \tag{6.33}$$

and can be seen at once on Figure 6.3.

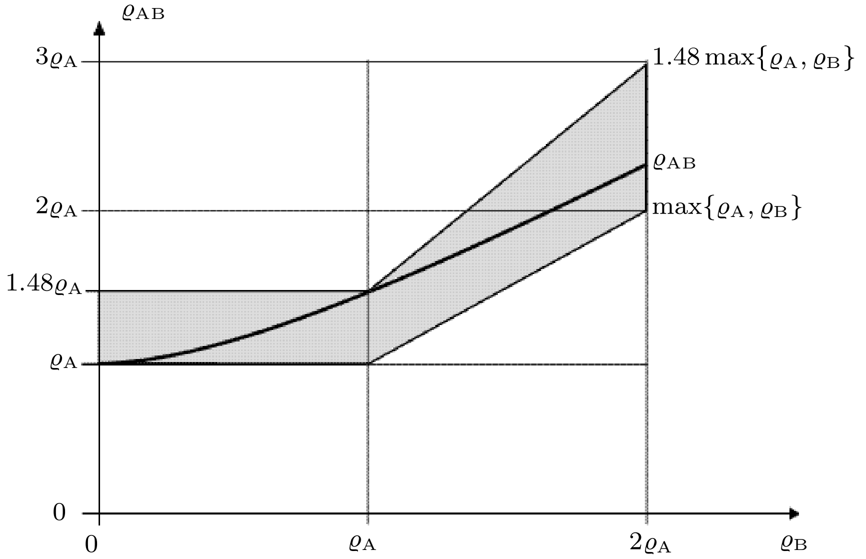


Figure 6.3: Secondary range ϱ_{AB} of B as a transformation product of A. The solid line shows ϱ_{AB} (as a multiple of the characteristic range ϱ_{A} of the precursor A) as a function of the characteristic range ϱ_{B} of B (likewise as a multiple of ϱ_{A}). One observes that $\varrho_{\mathrm{AB}} \leq 1.48\max\{\varrho_{\mathrm{A}},\varrho_{\mathrm{B}}\}$ (see inequality (6.32)), the maximum $\varrho_{\mathrm{AB}} \approx 1.48\max\{\varrho_{\mathrm{A}},\varrho_{\mathrm{B}}\}$ being at $\varrho_{\mathrm{A}} = \varrho_{\mathrm{B}}$.

6.1.5 Analytic approximation of secondary spatial ranges

Although Eq. (6.30) gives the correct numerical results, its form is too complicated to give direct qualitative insight, the main complication being the infinite sum $F(0)$. An essential simplification is achieved if the inequality

$$F(0) < 1 + \frac{\min\{\varrho_{\mathrm{A}},\varrho_{\mathrm{B}}\}}{|\varrho_{\mathrm{A}}-\varrho_{\mathrm{B}}|}\cdot\frac{\min\{\varrho_{\mathrm{A}},\varrho_{\mathrm{B}}\}}{\max\{\varrho_{\mathrm{A}},\varrho_{\mathrm{B}}\}} \tag{6.34}$$

is used as an approximation. (For a proof of inequality 6.34 see Appendix C). Substituting the right-hand side of inequality 6.34 in the expression for the exact secondary range in the one-dimensional, flat case (equation 6.30) yields a simple approximative expression for secondary ranges:

$$\varrho_{\mathrm{AB,app}} = (\varrho_{\mathrm{A}}+\varrho_{\mathrm{B}})\cdot\exp\left[\frac{\max\{\varrho_{\mathrm{A}}\,,\varrho_{\mathrm{B}}\}}{\varrho_{\mathrm{A}}+\varrho_{\mathrm{B}}}-1\right] \tag{6.35}$$

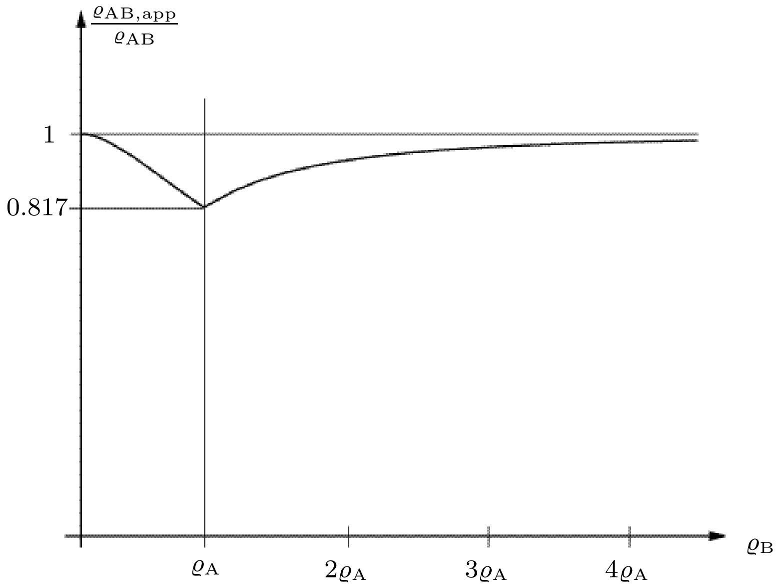


Figure 6.4: Precision of approximation : Approximative secondary range $\varrho_{AB,app}$ (in units of the exact value ϱ_{AB}) as a function of the characteristic range of the transformation product ϱ_B (in units of ϱ_A). The approximative value (equation 6.35) is always smaller than the exact value given in equation 6.30. The largest discrepancy between the approximated and the exact secondary range is 18.3% in the degenerate case $\varrho_A = \varrho_B$.

It can be seen from Figure 6.4 that $\varrho_{AB,app}$ is a fairly good approximation to the exact secondary range, the largest discrepancy of 18.3 % arising in the degenerate case $\varrho_A = \varrho_B$.

6.1.6 A more precise, equally simple fitting formula

One can build a function which is similar to the exact expression of secondary spatial range on a number of critical points. To this end, let us first define the comparison criterion: Using the expression of secondary range as function of the two characteristic ranges ϱ_A and ϱ_B (eq.6.30) one can easily calculate two limits:

$$\lim_{\min\{\varrho_A,\varrho_B\}\to 0} \varrho_{AB}(\varrho_A, \varrho_B) = \max\{\varrho_A, \varrho_B\} \tag{6.36}$$

$$\lim_{\max\{\varrho_A,\varrho_B\}\to \infty} \varrho_{AB}(\varrho_A, \varrho_B) \frac{1}{\max\{\varrho_A, \varrho_B\}} = 1 \tag{6.37}$$

Both limits simply express that the largest characteristic range dominates the secondary range. Furthermore, we know from the degenerate case that

$$\varrho_{\mathrm{AB}}(\varrho_{\mathrm{A}}, \varrho_{\mathrm{A}}) \approx 1.5\varrho_{\mathrm{A}} \tag{6.38}$$

and finally, we know that the secondary range is a symmetric expression with respect to the index A and B:

$$\varrho_{\mathrm{AB}}(\varrho_{\mathrm{A}}, \varrho_{B}) = \varrho_{\mathrm{AB}}(\varrho_{\mathrm{B}}, \varrho_{\mathrm{A}}) \tag{6.39}$$

Now, one can look for an approximation $\varrho_{\mathrm{AB,fit}}(\varrho_{\mathrm{A}}, \varrho_{\mathrm{A}})$ that fulfills conditions 6.36 to 6.39. After testing numerous possibilities, the following expression was retained:

$$\varrho_{\mathrm{AB,fit}}(\varrho_{\mathrm{A}}, \varrho_{\mathrm{A}}) := \frac{\varrho_{\mathrm{A}} + \varrho_{\mathrm{B}}}{2} + \frac{\varrho_{\mathrm{B}}}{2^{1+\varrho_{\mathrm{A}}/\varrho_{\mathrm{B}}}} + \frac{\varrho_{\mathrm{A}}}{2^{1+\varrho_{\mathrm{B}}/\varrho_{\mathrm{A}}}} \tag{6.40}$$

It is as simple as Eq. (6.35) but an even better approximation (Fig. 6.5).The largest discrepancy is 1.06 % (!), and arises in the degenerate case $\varrho_{\mathrm{A}} = \varrho_{\mathrm{B}}$.

Using the equality $\varrho_{\mathrm{A}} = \mathrm{e} \cdot z_{\mathrm{A}}$ and $\varrho_{\mathrm{B}} = \mathrm{e} \cdot z_{\mathrm{B}}$, the approximated form $\varrho_{\mathrm{AB,fit}}$ can also be expressed as

$$\varrho_{\mathrm{AB,fit}} = \mathrm{e} \cdot \left(\frac{z_{\mathrm{B}} + z_{\mathrm{A}}}{2} + z_{\mathrm{B}} \left(\frac{1}{2}\right)^{1+z_{\mathrm{A}}/z_{\mathrm{B}}} + z_{\mathrm{A}} \left(\frac{1}{2}\right)^{1+z_{\mathrm{B}}/z_{\mathrm{A}}} \right) \tag{6.41}$$

If one now defines

$$z_{\mathrm{AB}} := \frac{z_{\mathrm{B}} + z_{\mathrm{A}}}{2} + z_{\mathrm{B}} \cdot \left(\frac{1}{2}\right)^{1+\frac{z_{\mathrm{A}}}{z_{\mathrm{B}}}} + z_{\mathrm{A}} \cdot \left(\frac{1}{2}\right)^{1+\frac{z_{\mathrm{B}}}{z_{\mathrm{A}}}} \tag{6.42}$$

Secondary range can then be expressed in analogy to characteristic range

$$\varrho_{\mathrm{AB,fit}} = \mathrm{e} \cdot z_{\mathrm{AB}} \, . \tag{6.43}$$

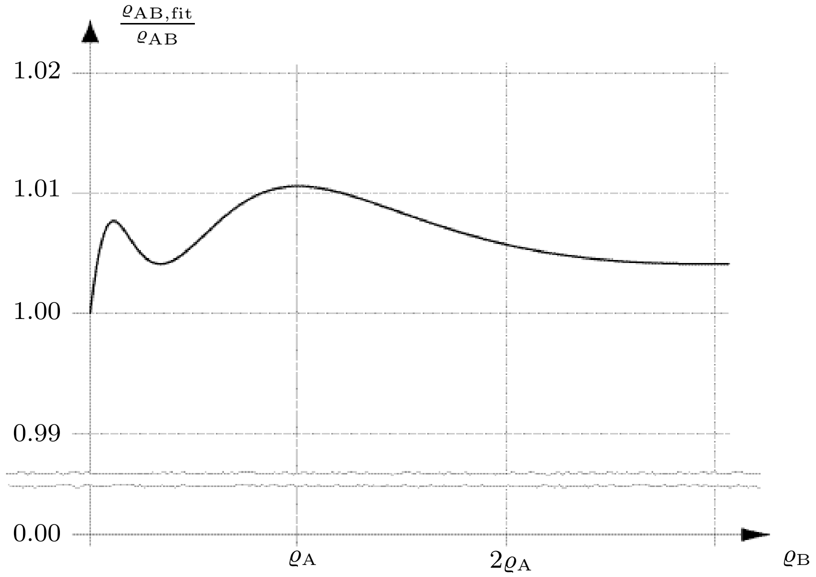


Figure 6.5: The ratio between the approximated secondary range $\varrho_{AB,fit}$ and the exact form ρ_{AB} is plotted as a function of the characteristic range ρ_B of the transformation product B. The approximated secondary range (Eq. (6.40)) is an upper bound for the exact value (Eq. (6.30)), the largest discrepancy being 1.06 % in the degenerate case $\varrho_A = \varrho_B$.

6.2 One-dimensional circular model

6.2.1 Dynamics and exposure

The calculation of secondary exposure in the one-dimensional spherical model is done using the same method as in the one-dimensional linear model. The dynamics for the transformation product is given by the following reaction-diffusion equation with periodic boundary conditions:

$$\begin{aligned} \dot{c_{AB}}(\varphi,t) &= \frac{D_B}{r^2}\frac{\partial^2 c_{AB}(\varphi,t)}{\partial\varphi^2} - k_B c_{AB}(\varphi,t) + k_{AB} c_A(\varphi,t) \\ c_{AB}(0,0) &= 0 \\ c_{AB}(\pi,t) &= c_{AB}(-\pi,t) \\ c'_{AB}(\pi,t) &= c'_{AB}(-\pi,t) \end{aligned} \tag{6.44}$$

The parameters $D_B > 0$, $k_A \geq k_{AB} > 0$ and $k_B > 0$ are the same as in the one-dimensional flat model. Position is now given by $\varphi \in [-\pi, \pi]$ where φ is an angle in *rad*, and r is the earth radius. Total degradation of B occurs after a sufficiently long time:

$$\lim_{t \to \infty} c(\varphi, t) = 0 \tag{6.45}$$

As in the flat model, time-integration of the dynamics yields an ordinary differential equation for the exposure, which can be solved by Fourier transformation. The resulting secondary exposure is

$$\begin{aligned} e_{\mathrm{AB}}(\varphi) = & \frac{k_{\mathrm{AB}} M_0 r}{2 D_{\mathrm{A}} D_{\mathrm{B}}} \frac{z_{\mathrm{A}}^2 z_{\mathrm{B}}^2}{z_{\mathrm{A}}^2 - z_{\mathrm{B}}^2} \\ & \cdot \left(\frac{z_{\mathrm{A}} \cosh\left[(\pi - |\varphi|)\frac{r}{z_{\mathrm{A}}}\right]}{\sinh[\pi \frac{r}{z_{\mathrm{A}}}]} - \frac{z_{\mathrm{B}} \cosh\left[(\pi - |\varphi|)\frac{r}{z_{\mathrm{B}}}\right]}{\sinh[\pi \frac{r}{z_{\mathrm{B}}}]} \right) \end{aligned} \tag{6.46}$$

The secondary exposure is plotted together with the primary exposure in Fig. 6.6. The normalization factor $\bar{e}_{\mathrm{AB}} = \frac{k_{\mathrm{AB}} M_0}{D_{\mathrm{A}} D_{\mathrm{B}}} z_{\mathrm{A}}^2 z_{\mathrm{B}}^2$ being independent of the geometry, one can directly calculate the secondary exposure distribution $\varepsilon_{\mathrm{AB}}(\varphi) = e_{\mathrm{AB}}/\bar{e}_{\mathrm{AB}}$:

$$\begin{aligned} \varepsilon_{\mathrm{AB}}(\varphi) = & \frac{r}{2(z_{\mathrm{A}}^2 - z_{\mathrm{B}}^2)} \\ & \cdot \left(\frac{z_{\mathrm{A}} \cosh\left[(\pi - |\varphi|)\frac{r}{z_{\mathrm{A}}}\right]}{\sinh[\pi \frac{r}{z_{\mathrm{A}}}]} - \frac{z_{\mathrm{B}} \cosh\left[(\pi - |\varphi|)\frac{r}{z_{\mathrm{B}}}\right]}{\sinh[\pi \frac{r}{z_{\mathrm{B}}}]} \right) \end{aligned} \tag{6.47}$$

6.2.2 Approximated secondary spatial range

In the circular case, the calculation of the analytic form of the Shannon-Boltzmann entropy of the secondary exposure distribution is quite difficult. However, a very good analytic approximation of the secondary spatial range can be obtained:

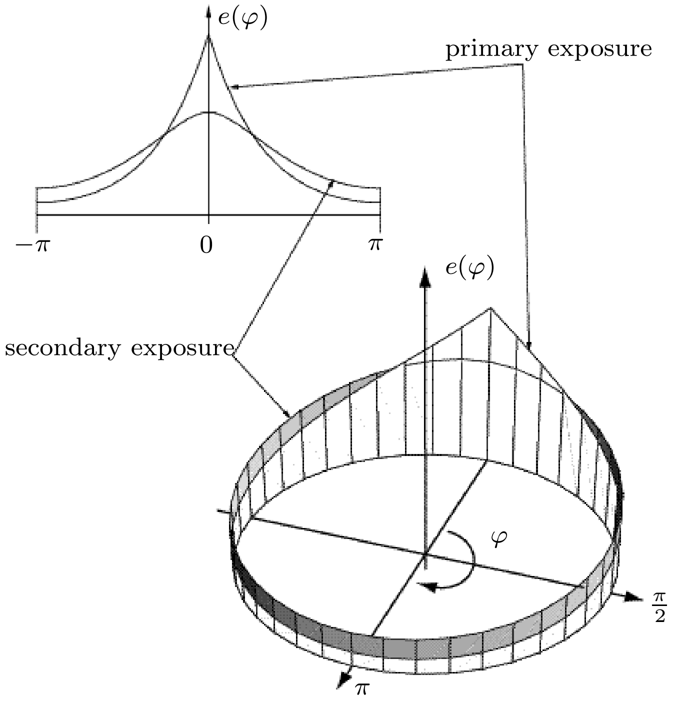


Figure 6.6: Primary exposure and secondary exposure in a one-dimensional ring model geometry: Circular and flat representation of the same exposure pattern

In the expression for the characteristic spatial range (in kilometers) in the ring model calculated by Müller-Herold and Nickel

$$\varrho^{1c} = \mathrm{e} \cdot z \tanh[\pi r/z] \exp[\frac{\frac{\pi}{2} - 2\arctan[e^{\pi r/z}]}{\sinh[\pi r/z]}] \tag{6.48}$$

one substitutes the parameter z_{AB} for z:

$$\varrho^{1c}_{\mathrm{AB,fit}} := \mathrm{e} z_{\mathrm{AB}} \tanh[\pi r/z_{\mathrm{AB}}] \exp[\frac{\frac{\pi}{2} - 2\arctan[e^{\pi r/z_{\mathrm{AB}}}]}{\sinh[\pi r/z_{\mathrm{AB}}]}] \tag{6.49}$$

with z_{AB} as defined in 6.42. The approximation $\varrho^{1c}_{\mathrm{AB,fit}}$ is plotted in Fig. 6.7 against the high-precision numerical value of the secondary range obtained with Mathematica ©. Thus, in both the circular and flat model geometry, secondary spatial range can be expressed as a pseudo-characteristic range. Consequently, in analogy to characteristic spatial range, the

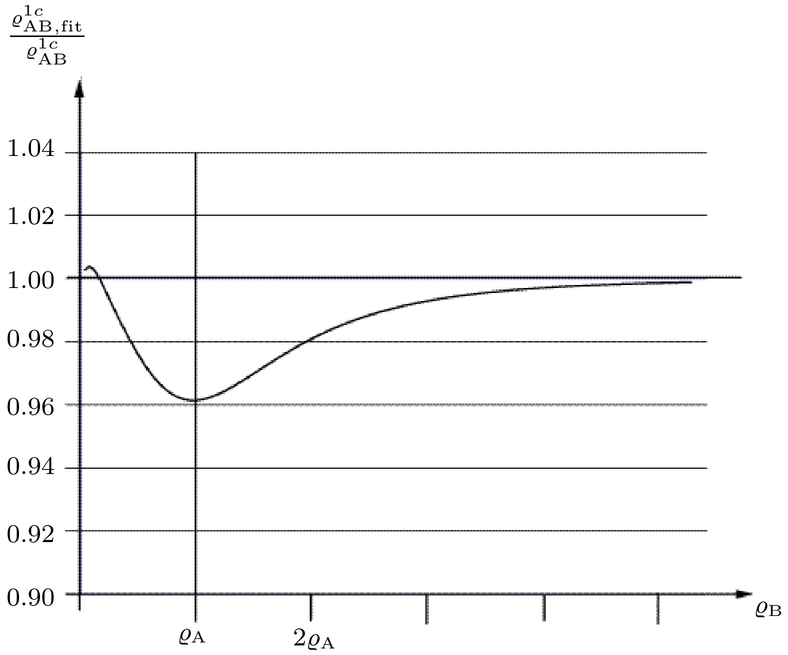


Figure 6.7: Ratio between the approximated secondary range and the exact (numerical) secondary range in the circular case, expressed as a function of ϱ_{B}. The characteristic spatial range ϱ_{A} is considered a fixed parameter. The largest discrepancy, (about 4%) between the approximation $\varrho^{1c}_{\mathrm{AB,fit}}$ and the exact (numerical) secondary range $\varrho^{1c}_{\mathrm{AB}}$ is for $\varrho_{\mathrm{A}} = \varrho_{\mathrm{B}}$.

inclusion of curvature will have no effects on secondary spatial range smaller than 10'000km (See Fig. 5.4)

6.3 Summary

The analytic method proposed by Müller-Herold and Nickel (30) for the calculation of the spatial range of precursors was successfully extended to first-generation transformation products. The result obtained is a closed formula for *secondary spatial range* ϱ_{AB}, expressed as a function of the respective characteristic ranges ϱ_{A} and ϱ_{B} of precursor A and transformation product B. It is proposed as a proxy measure for the spatial extent of the overall impact of a pollutant. Two important features of secondary spatial range can be extracted from the exact expression derived in the one-dimensional, flat model geometry (Eq.6.30):

- Secondary spatial range is bound by the larger of the characteristic ranges

  $$\boxed{\max\{\varrho_{\mathrm{A}}, \varrho_{\mathrm{B}}\} \leq \varrho_{\mathrm{AB}} \leq 1.4843 \cdot \max\{\varrho_{\mathrm{A}}, \varrho_{\mathrm{B}}\}}$$

  As a consequence, the overall impact is significantly larger the direct impact of the precursor if the characteristic spatial range of the transformation product is larger than the characteristic spatial range of the precursor:

  $$\boxed{\varrho_{\mathrm{B}} > \varrho_{\mathrm{A}} \qquad \Longrightarrow \qquad \varrho_{\mathrm{AB}} > 1.5 \cdot \varrho_{\mathrm{A}}}$$

- Secondary spatial range does not depend on the transformation rate k_{AB} of precursor A into transformation product B.

The exact form of secondary spatial range in the one-dimensional, flat model geometry is quite complicated, but a simple but yet precise approximation was constructed:

$$\boxed{\varrho_{\mathrm{AB,fit}} = \frac{\varrho_{\mathrm{A}} + \varrho_{\mathrm{B}}}{2} + \frac{\varrho_{\mathrm{B}}}{2^{1+\varrho_{\mathrm{A}}/\varrho_{\mathrm{B}}}} + \frac{\varrho_{\mathrm{A}}}{2^{1+\varrho_{\mathrm{B}}/\varrho_{\mathrm{A}}}}}$$

Finally, it was shown that secondary spatial range can be expressed in the same form as characteristic spatial range (Equ.6.43 and 6.49). Thus, as for characteristic spatial ranges, the results obtained in the flat model geometry will hold for the circular geometry for spatial ranges up to 10'000km.

Chapter 7

Illustrative examples

The pair benzene/ phenol was chosen to illustrate the case $\varrho_{\mathrm{A}} > \varrho_{\mathrm{B}}$. Emissions of benzene are connected with its presence in gasoline. Benzene shows no direct photolysis, but reacts with photochemically produced OH radicals in the troposphere, with phenol as its main degradation product in clean air (22). Besides being a degradation product of benzene, phenol is also a high-production volume chemical used as an intermediate in the production of various chemicals, such as phenolic resins, caprolactam, and bisphenol A.

The pair Methyl *tert*-butyl ether (MTBE)/*tert*-butyl alcohol (TBA) was taken as representative example of the case $\varrho_{\mathrm{A}} \approx \varrho_{\mathrm{B}}$. MTBE is used as gasoline oxygenate and therefore produced in huge amounts. It has been detected in urban air, surface water, and groundwater. Because of its resistance to biodegradation and high water solubility, it is a designated groundwater contaminant (23). Its most thoroughly investigated degradation path yields *tert*-butyl alcohol (TBA), which is quite persistent (6).

The third case, $\varrho_{\mathrm{A}} < \varrho_{\mathrm{B}}$, is illustrated by the pair heptachlor/ heptachlor epoxide. Heptachlor was widely used as a non-agricultural insecticide. Now that it is officially listed as a Persistent Organic Pollutant (33), the only permitted commercial use is for fire ant control in buried electric power transformers, and in underground cable television and telephone cable boxes. Heptachlor degrades to heptachlor epoxide in the environment. Heptachlor epoxide is neither produced commercially nor is it normally present as an impurity in commercial heptachlor, so that the only source of heptachlor epoxide is from the degradation of heptachlor. Both heptachlor and heptachlor epoxide are potential human carcinogens and bioaccumulate extensively (22).

First, characteristic spatial range will be calculated for each of these six chemicals. This will be followed by the calculation of secondary spatial range for the three precursor/transformation product pairs. All calculations are done in a three-compartment model with one-dimensional, flat model geometry. As it will turn out, all the spatial ranges calculated in this chapter are smaller than 10'000km. Accordingly, calculation in the circular model geometry would yield similar results.

7.1 Characteristic spatial range

The model environment is constituted of the three compartment air, water and soil, indicated by the corresponding indices $i = a, w, s$. The corresponding (relative) volume and macroscopic transport coefficient were taken in accordance with Scheringer (ref. (43) p.114 and 117):

Compartment	D_i ($\mathrm{km}^2\,\mathrm{s}^{-1}$)	$V_i[-]$
water	0.01	233
air	2	200 000
soil	0	1

The temperature T of the system is set to 298K.

Using the effective (eddy) diffusion coefficient D (Equ.4.22) and the effective reaction constant k (Equ.4.23), following from the instant equilibrium assumption (Chapt.4), one can directly calculate the ratio D/k from the macroscopic transport coefficients D_a, D_s, D_w and the (pseudo) first-order degradation rates k_a, k_s and k_w :

$$D/k = \sqrt{\frac{D_a V_a + D_w V_w K_{wa} + D_s V_s K_{sa}}{k_a V_a + k_w V_w K_{wa} + k_s V_s K_{sa}}} \tag{7.1}$$

with

$$K_{wa} = \mathrm{R}T/K_H \quad \text{and} \quad K_{sa} = f_{oc} 0.41 K_{ow} \cdot K_{wa} \tag{7.2}$$

Hence, in a three-compartments model, one only needs five measurable parameters to calculate the effective macroscopic transport coefficient and the effective first-order degradation rate of a chemical. These substance-specific parameters are:

1. the Henry's law constant K_H, $[K_H] = \mathrm{atm}\,\mathrm{m}^3\,\mathrm{mol}^{-1}$
2. the octanol/water partition coefficient K_{ow}, usually given as a decimal logarithm, $\log[K_{ow}] = [-]$
3. the (pseudo) first-order degradation rates k_a, k_w and k_s in each compartment i, $[k_i] = s^{-1}$

They are listed in table D.1 and D.2. Once the effective macroscopic transport coefficient and the effective first-order degradation rates are known, the characteristic spatial range in the one-dimensional, flat model geometry is easily calculated using relation 5.26

$$\varrho = \mathrm{e} \cdot \sqrt{D/k}$$

The characteristic spatial ranges of the six chemicals considered here can be found in the first column of table 7.2.

7.2 Secondary spatial range

Phenol, TBA and heptachlor epoxide are assumed to be first-generation transformation products, as defined in section 4.4. Secondary spatial ranges are calculated using the exact form for the one-dimensional flat geometry Equ. (6.30), and its best approximation Equ. (6.40). The results are compiled in Table 7.2 and plotted in Fig. 7.1.

Secondary spatial range is most influenced by the chemical with the largest characteristic spatial range. Thus, the

Table 7.1: Effective eddy diffusion coefficients and effective degradation rates in a three-compartment model environment.

Compound	D [km^2 s^{-1}]	k [s^{-1}]
Methyl *tert*-butyl ether	1.9	$6.93 \cdot 10^{-7}$
tert-Butyl alcohol	$6.44 \cdot 10^{-1}$	$1.34 \cdot 10^{-7}$
Benzene	1.99	$3.85 \cdot 10^{-7}$
Phenol	$3.13 \cdot 10^{-2}$	$3.46 \cdot 10^{-6}$
Heptachlor	1.62	$1.61 \cdot 10^{-5}$
Heptachlor epoxide	$4.04 \cdot 10^{-1}$	$6.57 \cdot 10^{-7}$

Table 7.2: For a three-compartment model environment with flat, one-dimensional geometry: characteristic spatial ranges ϱ_A, ϱ_B, exact secondary spatial range ϱ_{AB} and approximated secondary spatial range $\varrho_{\mathrm{AB\ fit}}$ for three precursors/transformation products pairs.

		ϱ_{A}, ϱ_{B}	ϱ_{AB}	$\varrho_{\mathrm{AB\ fit}}$
Pair 1	Heptachlor Heptachlor epoxide	860km 2140km	**2370km**	**2380km**
Pair 2	Methyl *tert*-butyl ether *tert*-Butyl alcohol	4500km 6000km	**7850km**	**7930km**
Pair 3	Benzene Phenol	6140km 270km	**6190km**	**6230km**

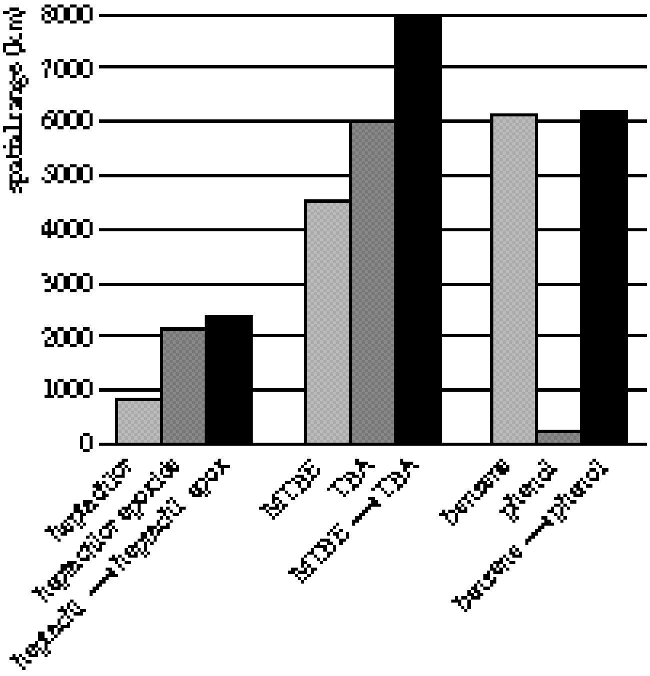


Figure 7.1: Characteristic and secondary spatial ranges for three precursor/transformation product pairs. It clearly appears that secondary spatial range is most influenced by the chemical with the larger characteristic spatial range. Consequently, the secondary spatial range of a pair is significantly higher than the characteristic spatial range of the precursor if the transformation product has the largest characteristic range (see the pair heptachlor/heptachlor epoxide).

secondary spatial range of the pair benzene/phenol is dominated by the precursor. The opposite is true of the pair heptachlor/heptachlor epoxide, where secondary spatial range is clearly dominated by the transformation product. The pair methyl *tert*-butyl ether/*tert*-butyl alcohol is close to the degenerate case (the secondary range of 7850 km being about 1.5 times the average characteristic range of 5250 km of the two compounds) and both chemicals contribute significantly to secondary spatial range.

Chapter 8

Conclusions and Outlook

8.1 Conclusions

The analytic method developed by Müller-Herold and Nickel for estimating the spatial extent of the direct impact was successfully extended to first-generation transformation products. The result obtained, called secondary spatial range, is a proxy measure for the spatial extent of the *overall* (chemical) impact.

The utility of secondary spatial range as a proxy measure of the spatial extent of the overall impact is illustrated by the following example: Measurements show that the transformation product heptachlor epoxide is one of the major chlorinated contaminant in snow samples from the Canadian arctic (18), whereas its precursor, heptachlor, is not. This indicates that the spatial extent of the overall impact of heptachlor is significantly larger than the spatial extent of its direct impact. This is well accounted for by the model presented here, which gives a secondary range of 2370km for heptachlor epoxide, and a characteristic range of 860km for heptachlor. The difference of a factor 3 between the two ranges is reflected in the experimental findings that the epoxide reaches the arctic, whereas its precursor does not. According to Müller-Herold and Nickel (30), 860 km corresponds to local ranges, whereas 2370km is regarded as hemispherical. Thus, heptachlor appears as a local chemical if one considers only its direct impact, but it is an hemispherical chemical if one takes its transformation product heptachlor epoxide into account (See Fig. 8.1). In conclusion, it turns out that the integration of transformation products in

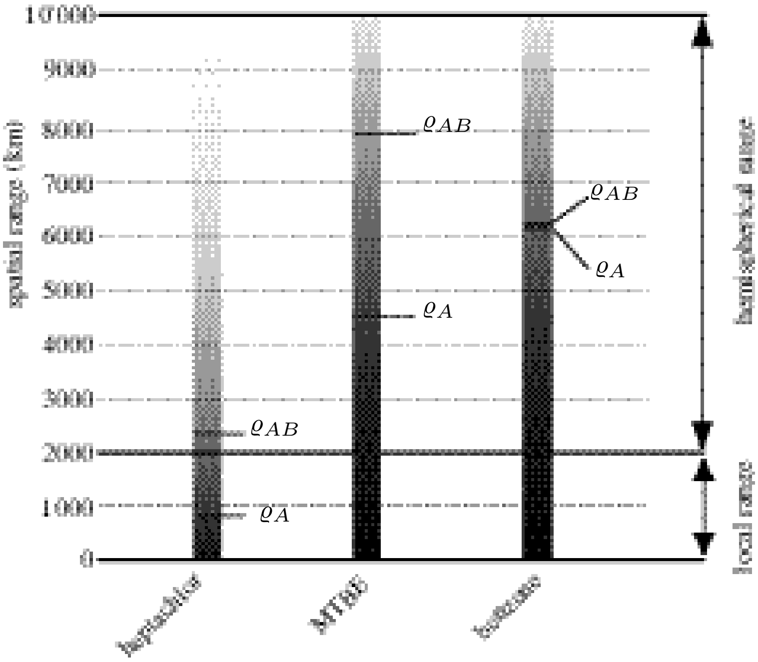


Figure 8.1: Characteristic spatial range ϱ_A appears as a lower bound for the spatial extent ϱ_{AB} of the overall impact of a pollutant, symbolized by the graded column.

an assessment based on spatial range is not only technically feasible, but also necessary.

There is no specific approach to transformation products in the current assessment practice: Relevant transformation products of pesticides are treated like their precursors, but transformation products of non-pesticides are generally not assessed at all. However, it is stated in the Dangerous Substance Directive that:

> "If it can be shown to be necessary for the evaluation of risks which may be caused by the substance, the competent authorities may ask for further information, verification and/or confirmatory

> tests concerning the substances *or their transformation products*". (art. 16, Directive 67/548/EC)

The Directive and the corresponding technical guidance document are rather vague on how to demonstrate the relevance of a transformation product for the risk evaluation. Consequently, a criterion based on spatial range is proposed here: It is shown in the present work that the spatial extent of the overall impact is significantly larger than the spatial extent of the direct impact if a transformation product has a larger characteristic spatial range than its precursor (See section 6.3). Moreover, approximations for each of the five substance-specific parameters necessary for the calculation of characteristic spatial ranges can be generated by computer models (4). Finally, the calculation of spatial ranges can easily be done in any commercial spreadsheet software. Thus, a simple comparison of the characteristic spatial ranges of precursor and transformation products could be a powerful tool for sorting out transformation products deserving a more comprehensive assessment.

8.2 Outlook

Only first-generation transformation products are considered in the present work. Preliminary calculations show that the method can be extended to later-generation transformation products with only minor changes For example, assuming the reaction path $A \longrightarrow B \longrightarrow C$, the complete dynamics would be:

$$\begin{aligned}
\dot{c}_{\mathrm{A}}(x,t) &= D_{\mathrm{A}}\frac{\partial^2 c_{\mathrm{A}}(x,t)}{\partial^2 x} - k_{\mathrm{A}}c_{\mathrm{A}}(x,t)\\
\dot{c}_{\mathrm{B}}(x,t) &= D_{\mathrm{B}}\frac{\partial^2 c_{\mathrm{B}}(x,t)}{\partial^2 x} - k_{\mathrm{B}}c_{\mathrm{B}}(x,t) + k_{\mathrm{AB}}c_{\mathrm{A}}(x,t)\\
\dot{c}_{\mathrm{C}}(x,t) &= D_{\mathrm{C}}\frac{\partial^2 c_{\mathrm{C}}(x,t)}{\partial^2 x} - k_{\mathrm{C}}c_{\mathrm{C}}(x,t) + k_{\mathrm{BC}}c_{B}(x,t)
\end{aligned} \tag{8.1}$$

with the limiting conditions

$$\begin{aligned} c_{\mathrm{A}}(x,0) &= M_0\delta(x) \\ c_{\mathrm{B}}(x,0) &= c_{\mathrm{C}}(x,0)=0 \end{aligned} \tag{8.2}$$

One can then easily calculate the exposure distribution for the second-generation transformation product C. Taking the entropy rank of this "ternary exposure distribution" might be difficult, but one could choose another way to define an equivalent equipartition, based for example on the equivalent width or the expected value of the exposure distribution. However, the spatial range will grow with each additional generation. If one goes as far as including CO_2, all organic chemicals will ultimately have the same maximal spatial range of 20'000km. This reflects the fact that all organic chemicals contribute to the global rise of the CO_2 level, but spatial range, being identical for all chemicals, would be totally useless as an assessment tool. Therefore, further investigations should aim at finding criterion for determining how many generations of transformation products are relevant and should be included in the calculation of the spatial extent of the impact.

Appendix A

Entropy rank and Spatial Range

The entropy S of a material system consisting of $1/w$ $(0 < w \leq 1)$ states with the same energy, is given by the Boltzmann formula

$$S = -k \ln w \tag{A.1}$$

According to the rules of statistical mechanics, these states occure with the same probability. Due to the normalization of total probability to 1, the probability of each state is w.

The Boltzmann formula can be regarded as a special case of the more general Shannon-Boltzmann entropy

$$S = -k \sum_{i=1}^{N} p_i \ln p_i \tag{A.2}$$

Indeed, if all probabilities p_i are identical: $p_i = 1/N$, one becomes

$$\begin{aligned} S &= -k \sum_{i=1}^{N} p_i \ln p_i \\ &= -kN(\frac{1}{N} \ln \frac{1}{N}) \\ &= -k \ln \frac{1}{N} \qquad , \omega = \frac{1}{N} \end{aligned} \tag{A.3}$$

Thus, the Boltzmann formula is the special case of the Shannon-Boltzmann entropy A.2 adapted to equipartition, i.e. to equally probable events. It was Einstein[1] (16) who proposed to invert Boltzmann's formula and to use the fact that the exponential of entropy is a probability.

$$w = e^{-S/k} \tag{A.4}$$

The same applies to the exponential $e^{-S/k}$ of any Shannon-Boltzmann entropy $S = -k\sum_{i=1}^{\infty} p_i \ln p_i$, with $\sum_{i=1}^{\infty} p_i = 1$. Its reciproke

$$R := e^{S/k} \tag{A.5}$$

is called the *entropy rank* of the probability distribution $p_i \geq 0 \quad i = 1, 2, ...$(Note that i may go to infinity. If only a finite number $M < \infty$ of events is to be considered, the probabilities $p_{i>M}$ are taken as zero). $1/R$ is a probability. It is associated with the probability distribution $\{p_i\}$ used to calculate R. The relation between $1/R$ and the p_i clearly appears if one applies the Boltzmann formula A.1 for $w = 1/R$.

$$\begin{aligned} -k \cdot \ln\left(\frac{1}{R}\right) &= -k \ln\left(e^{-S/k}\right) \\ &= S = -k\sum_{i=1}^{N} p_i \ln p_i \end{aligned} \tag{A.6}$$

Thus, $1/R$ is the probability of R events with equal probability $1/R$ such that the equipartition distribution has the same Shannon-Boltzmann entropy as the original distribution $\{p_i\}$. The entropy rank R, accordingly, gives the number i of events one has to consider if the p_i are replaced by an isoentropic equipartition distribution.

---

[1] On page 188 of his paper *"Zum gegenwärtigen Stand des Strahlungsproblems"*, Einstein proposes to use the Boltzmann formula, um "aus den mit Hilfe der Erfahrung ermittelten Entropiewerten die statistische Wahrscheinlichkeit der einzelnen Zustände eines nach aussen abgeschlossenen systems zu ermitteln."

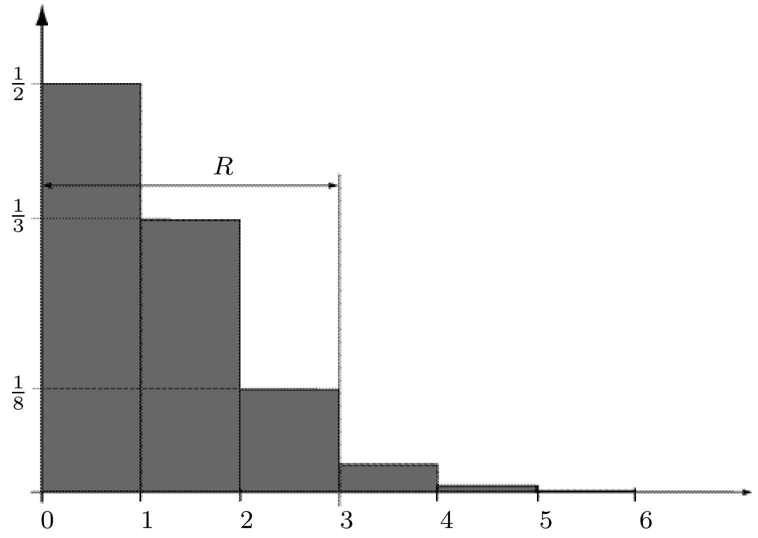


Figure A.1: Plot of the normed probability distribution $p_n = n/(n+1)!$. This distribution rapidly decreases with n. Its entropy rank R is approximately equal to 3.

A.1 Example

The sequence $p_n = n/(n+1)!$, $n = 1, 2, ...$ is a normed probability distribution: $p_n > 0$, $\sum_{n=1}^{\infty} p_n = 1$, which rapidly decays with n. The first three terms already contributes 95% to the infinite sum. Its entropy is defined as

$$S = -k \sum_{n=1}^{\infty} \{n/(n+1)!\} \ln \{n/(n+1)!\} \approx k \cdot 1.1303 \quad \text{(A.7)}$$

gives an entropy rank of $R = e^{S/k} = 3.09685 \approx 3$. The corresponding equipartiton distribution q_k with the same entropy rank is given by

$$q_k = \begin{cases} 1/3 & n = 1, 2, 3 \\ 0 & n \geq 4 \end{cases} \quad \text{(A.8)}$$

(See Figure A.1)

A.2 Entropy rank and chemical assessment

In this short digression we want to give an argument presented informally by Müller-Herold for the distinguished role of entropy in chemical assessment. Due to transport processes, such as eddy diffusion, a point-released molecule can appear at any place on the globe with, however, highly different probability. The concept of spatial range can be used to divide the world into two regions: An inner region where the chemical is likely to appear and an outer region where this is unlikely. Within the two regions, no further distinctions are made, which corresponds to equipartition. The equipartition probability of the outer "safe" region is idealized to zero. The equipartition probability of the inner region is fixed only by its size (because of normalization). In our approach we take advantage of the fact that entropy rank directly fixes the equipartition probability as well as the size of the endangered domain. In addition, when passing from the "real" distribution to equipartition, the Shannon-Boltzmann entropy remains constant and thus plays the role of a controlling invariant.

A.3 Remark

Although entropy ranks of Shannon-Boltzmann entropies plays a distinguished role its choice is not uniquely fixed. There are other entropies than the Shannon-Boltzmann entropy, which is actually a special case of Renyi entropy. In case of N events with probability q_k, $k = 1, 2, \ldots, N$ the Renyi entropy of degree α is given by (36):

$$S_\alpha = \log_2 N - \frac{1}{1-\alpha} \log_2 \left\{ \sum_{k=1}^{N} (q_k)^\alpha / \sum_{k=1}^{N} q_k \right\} \quad , \alpha \neq 1 \quad \text{(A.9)}$$

Each of these Renyi entropies defines an entropy rank $R_\alpha = e^{S_\alpha}$ that could be used for a definition of spatial ranges. The Shannon-Boltzmann entropy is obtained as the limiting case for $\alpha \to 1$.

Appendix B

Entropy of secondary exposure

B.1 Degenerate case

The secondary exposure distribution in the degenerate case is equal to

$$\lim_{z_B \to z_A} \varepsilon_{AB}(x) := \varepsilon_{AA}(x) = \frac{1 + \frac{|x|}{z_A}}{4z_A} \exp[-\frac{|x|}{z_A}] \tag{B.1}$$

Its entropy is

$$\begin{aligned} S_{AA} &:= -\int_{-\infty}^{+\infty} \varepsilon_{AA}(x) \cdot \ln[\varepsilon_{AA}(x)]\, dx \\ &= -2 \cdot \int_0^{+\infty} z_A \frac{1 + z_A x}{4} \mathrm{e}^{-z_A x} \\ &\quad \cdot (\ln[z_A/4] - z_A x + \ln[1 + z_A x])\ dx \end{aligned} \tag{B.2}$$

Substituting $y = z_B x$ and re-arranging yields

$$\begin{aligned} S_{AA} = -\frac{1}{2} \int_0^{+\infty} &\underbrace{\mathrm{e}^{-y}(1+y)\ln[z_B/4]}_{A} - \underbrace{\mathrm{e}^{-y}(y+y^2)}_{B} \\ + &\underbrace{\mathrm{e}^{-y}(1+y)\ln[1+y]}_{C}\ dy \end{aligned} \tag{B.3}$$

Integration yields

$$A = \int_0^{+\infty} \mathrm{e}^{-y}(1+y)\ln[z_A/4]\, dy = 2\ln[z_A/4] \tag{B.4}$$

$$
\begin{aligned}
B &= \int_0^{+\infty} \mathrm{e}^{-y}(y+y^2)\,dy \\
&= -\mathrm{e}^{-y}(y^2+3y+3)\Big|_0^{+\infty} = 3
\end{aligned}
\tag{B.5}
$$

$$
\begin{aligned}
C &= \int_0^{+\infty} \mathrm{e}^{-y}(1+y)\ln[1+y]\,dy \\
&= \int_0^{+\infty} \mathrm{e}^{-y}(1+\ln[1+y])\,dy \\
&= 1+\int_0^{+\infty} \frac{\mathrm{e}^{-y}}{1+y}\,dy \\
&= 1+\mathrm{e}\cdot\int_1^{+\infty} \frac{\mathrm{e}^{-v}}{v}\,dv \ \ ,v=1+y
\end{aligned}
\tag{B.6}
$$

The numerical value of the exponential integral is

$$
\int_1^{+\infty} \frac{\mathrm{e}^{-v}}{v}\,dv = E_1(1) \approx 0.219384 \tag{B.7}
$$

Substituting A, B and C into equation B.3, one obtains

$$
S_{AA} = -\ln[z_A/4] + 1 - \frac{\mathrm{e}}{2}\cdot E_1(1) \tag{B.8}
$$

B.2 General case

Starting from secondary exposure distribution ε_{AB} (equation 6.17) we first calculate the indefinite integral

$$
\begin{aligned}
s_{AB}(x) \ &:= -\int \varepsilon_{AB}(x)\ln[\varepsilon_{AB}(x)]\,dx = \\
- \ & \frac{\mathrm{e}^{-\min\{z_A,z_B\}x}(z_A z_B^2 - z_A^2 z_B) - z_B^3\mathrm{e}^{-z_A x} + z_A^3\mathrm{e}^{-z_B x}}{2\min\{z_A,z_B\}(z_A^2-z_B^2)} \\
+ \ & \frac{|z_A-z_B|\max\{z_A,z_B\}\mathrm{e}^{-\min\{z_A,z_B\}x}}{2\min\{z_A,z_B\}(z_A+z_B)}\cdot F(x) \\
+ \ & \frac{z_A^2\mathrm{e}^{-z_B x} - z_B^2\mathrm{e}^{-z_A x}}{2(z_A^2-z_B^2)}\cdot\ln[\varepsilon_{AB}(x)]
\end{aligned}
\tag{B.9}
$$

with $F(x)$ defined as:

$$\begin{aligned} F(x) = \sum_{n=0}^{\infty} \qquad & \frac{\min\{z_A, z_B\}}{\min\{z_A, z_B\} + n|z_A - z_B|} \\ & \cdot \left(\frac{\min\{z_A, z_B\}}{\max\{z_A, z_B\}} \mathrm{e}^{-|z_A - z_B|x} \right)^n \end{aligned} \tag{B.10}$$

Derivation of equation B.9 with respect to x allows for a verification of the indefinite integral. Entropy is now given as the corresponding definite integral

$$\begin{aligned} S_{AB} \quad &:= \quad -\int_{-\infty}^{+\infty} \varepsilon_{AB}(x) \ln[\varepsilon_{AB}(x)]\, dx \\ &= \quad -2 \cdot \int_{0}^{+\infty} \varepsilon_{AB}(x) \ln[\varepsilon_{AB}(x)]\, dx \\ &= \quad 2 \cdot s_{AB}(x) \Big|_{0}^{+\infty} \end{aligned} \tag{B.11}$$

First we show that the upper bound is equal to zero. The function $F(x)$ is clearly majorated by a geometric series:

$$F(x) < \sum_{n=0}^{\infty} \left(\frac{\min\{z_A, z_B\}}{\max\{z_A, z_B\}} \mathrm{e}^{-|z_A - z_B|x} \right)^n \tag{B.12}$$

The geometric series on the right-hand side of equation B.12 can be summed

$$\sum_{n=0}^{\infty} \left(\frac{\min\{z_A, z_B\}}{\max\{z_A, z_B\}} \mathrm{e}^{-|z_A - z_B|x} \right)^n = \frac{1}{1 - \frac{\min\{z_A, z_B\}}{\max\{z_A, z_B\}} e^{-|z_A - z_B|x}} \tag{B.13}$$

and the upper limit of $F(x)$ is thus

$$\lim_{x \to \infty} F(x) \leq 1 \tag{B.14}$$

It now follows from equations B.9 and B.14 that

$$\lim_{x \to \infty} s_{AB}(x) = 0 \tag{B.15}$$

For x going to zero s_{AB} is given by

$$\begin{aligned}\lim_{x\to 0} s_{AB}(x) = & - \frac{(z_A^2 + z_B^2) - \max\{z_A, z_B\}|z_A - z_B|F(0)}{2\min\{z_A, z_B\}(z_A + z_B)} \\ & + \frac{1}{2}\ln\left[\frac{z_A z_B}{2(z_A + z_B)}\right] \end{aligned} \tag{B.16}$$

where

$$F(0) = \sum_{n=0}^{\infty} \frac{\min\{z_A, z_B\}}{\min\{z_A, z_B\} + n|z_A - z_B|} \cdot \left(\frac{\min\{z_A, z_B\}}{\max\{z_A, z_B\}}\right)^n \tag{B.17}$$

Thus, introducing the limits found in B.15 and B.16 into equation B.11, one gets the entropy in the non-degenerate general case:

$$\begin{aligned} S_{AB} = & \frac{(z_A^2 + z_B^2) - \max\{z_A, z_B\}|z_A - z_B|F(0)}{\min\{z_A, z_B\}(z_A + z_B)} \\ & - \ln\left[\frac{z_A z_B}{2(z_A + z_B)}\right] \end{aligned} \tag{B.18}$$

Appendix C

Majoration of $F(0)$

The goal is to demonstrate that

$$F(0) < 1 + \frac{\min\{z_A, z_B\}}{|z_A - z_B|} \cdot \frac{\min\{z_A, z_B\}}{\max\{z_A, z_B\}} \tag{C.1}$$

is a correct majoration for $F(0)$ in the case $z_A \neq z_B$. Substituting definition 6.28 of the function $F(0)$ in inequality C.1 yields

$$\sum_{n=0}^{\infty} \frac{\min\{z_A, z_B\}}{\min\{z_A, z_B\} + n|z_A - z_B|} \cdot \left(\frac{\min\{z_A, z_B\}}{\max\{z_A, z_B\}}\right)^n < 1 + \frac{\min\{z_A, z_B\}}{|z_A - z_B|} \cdot \frac{\min\{z_A, z_B\}}{\max\{z_A, z_B\}} \tag{C.2}$$

Extracting the term $n = 0$ from the infinite sum, one becomes

$$1 + \sum_{n=1}^{\infty} \frac{\min\{z_A, z_B\}}{\min\{z_A, z_B\} + n|z_A - z_B|} \cdot \left(\frac{\min\{z_A, z_B\}}{\max\{z_A, z_B\}}\right)^n < 1 + \frac{\min\{z_A, z_B\}}{|z_A - z_B|} \cdot \frac{\min\{z_A, z_B\}}{\max\{z_A, z_B\}}$$

Substracting 1 on both sides and dividing by $\frac{\min\{z_A,z_B\}}{\max\{z_A,z_B\}}$ yields

$$\sum_{n=1}^{\infty}\frac{\min\{z_A,z_B\}}{\min\{z_A,z_B\}+n|z_A-z_B|}\cdot\left(\frac{\min\{z_A,z_B\}}{\max\{z_A,z_B\}}\right)^{n-1} < \frac{\min\{z_A,z_B\}}{|z_A-z_B|}$$

after re-arranging one becomes

$$\sum_{n=1}^{\infty}\frac{\min\{z_A,z_B\}}{\min\{z_A,z_B\}+n|z_A-z_B|}\cdot\left(\frac{\min\{z_A,z_B\}}{\max\{z_A,z_B\}}\right)^{n-1} < \frac{1}{1-\frac{\min\{z_A,z_B\}}{\max\{z_A,z_B\}}}-1$$

The next inequality is simply obtained by adding 1 on both sides

$$1+\sum_{n=1}^{\infty}\frac{\min\{z_A,z_B\}}{\min\{z_A,z_B\}+n|z_A-z_B|}\cdot\left(\frac{\min\{z_A,z_B\}}{\max\{z_A,z_B\}}\right)^{n-1} < \frac{1}{1-\frac{\min\{z_A,z_B\}}{\max\{z_A,z_B\}}} \tag{C.3}$$

Inequality C.3 will now be demonstrated: The term inside the sum can be rewritten as:

$$\frac{\min\{z_A,z_B\}}{\min\{z_A,z_B\}+n|z_A-z_B|}\cdot\left(\frac{\min\{z_A,z_B\}}{\max\{z_A,z_B\}}\right)^{n-1} = \frac{1}{\frac{\min\{z_A,z_B\}}{\max\{z_A,z_B\}}+\frac{n}{\max\{z_A,z_B\}}|z_A-z_B|}\cdot\left(\frac{\min\{z_A,z_B\}}{\max\{z_A,z_B\}}\right)^{n} \tag{C.4}$$

We will now prove that

$$\frac{1}{\frac{\min\{z_A,z_B\}}{\max\{z_A,z_B\}}+\frac{n}{\max\{z_A,z_B\}}|z_A-z_B|} < 1 \tag{C.5}$$

which of course implies

$$\frac{\min\{z_A, z_B\}}{\max\{z_A, z_B\}} + \frac{n}{\max\{z_A, z_B\}}|z_A - z_B| > 1 \tag{C.6}$$

Since $|z_A - z_B| = \max\{z_A, z_B\} - \min\{z_A, z_B\}$, inequality C.6 rewrites as

$$n - \frac{\min\{z_A, z_B\}}{\max\{z_A, z_B\}}(n-1) > 1 \tag{C.7}$$

which is true, and inequality C.5 is thus proved. This allows the following majoration

$$\sum_{n=1}^{\infty} \frac{1}{n - \frac{\min\{z_A, z_B\}}{\max\{z_A, z_B\}}(n-1)} \cdot \left(\frac{\min\{z_A, z_B\}}{\max\{z_A, z_B\}}\right)^n < \sum_{n=1}^{\infty} \left(\frac{\min\{z_A, z_B\}}{\max\{z_A, z_B\}}\right)^n \tag{C.8}$$

adding 1 on both sides one becomes

$$1 + \sum_{n=1}^{\infty} \frac{1}{n - \frac{\min\{z_A, z_B\}}{\max\{z_A, z_B\}}(n-1)} \cdot \left(\frac{\min\{z_A, z_B\}}{\max\{z_A, z_B\}}\right)^n < \sum_{n=0}^{\infty} \left(\frac{\min\{z_A, z_B\}}{\max\{z_A, z_B\}}\right)^n \tag{C.9}$$

The sum on the right-hand side converges for $z_A \neq z_B$,

$$\sum_{n=0}^{\infty} \left(\frac{\min\{z_A, z_B\}}{\max\{z_A, z_B\}}\right)^n = \frac{1}{1 - \frac{\min\{z_A, z_B\}}{\max\{z_A, z_B\}}} \tag{C.10}$$

and one can re-write inequality C.9 as

$$1 + \sum_{n=1}^{\infty} \frac{1}{n - \frac{\min\{z_A, z_B\}}{\max\{z_A, z_B\}}(n-1)} \cdot \left(\frac{\min\{z_A, z_B\}}{\max\{z_A, z_B\}}\right)^n < \frac{1}{1 - \frac{\min\{z_A, z_B\}}{\max\{z_A, z_B\}}} \tag{C.11}$$

which, according to inequality C.4, implies

$$1 + \sum_{n=1}^{\infty} \frac{\min\{z_A, z_B\}}{\min\{z_A, z_B\} + n|z_A - z_B|} \cdot \left(\frac{\min\{z_A, z_B\}}{\max\{z_A, z_B\}}\right)^{n-1} < \frac{1}{1 - \frac{\min\{z_A, z_B\}}{\max\{z_A, z_B\}}} \tag{C.12}$$

Inequality C.3 is thus verified, and one can write

$$F(0) < 1 + \frac{\min\{z_A, z_B\}}{|z_A - z_B|} \cdot \frac{\min\{z_A, z_B\}}{\max\{z_A, z_B\}} \tag{C.13}$$

of $z = \mathrm{e}\varrho$ according to equation 5.26 gives an expression in terms of the intrinsic spatial ranges of the precursor and the transformation product

$$F(0) < 1 + \frac{\min\{\varrho_A, \varrho_B\}}{|\varrho_A - \varrho_B|} \cdot \frac{\min\{\varrho_A, \varrho_B\}}{\max\{\varrho_A, \varrho_B\}} \tag{C.14}$$

which is the desired result.

Appendix D

Data

Table D.1: Degradation rates calculated from Howard et al. (20).

Compound	CAS	k_s s^{-1}	k_a s^{-1}	k_w s^{-1}
Methyl *tert*-butyl ether	1634-04-4	$4.46 \cdot 10^{-8}$	$7.27 \cdot 10^{-7}$	$4.46 \cdot 10^{-8}$
tert-Butyl alcohol	75-65-0	$4.01 \cdot 10^{-8}$	$3.26 \cdot 10^{-7}$	$4.46 \cdot 10^{-8}$
Benzene	71-43-2	$5.01 \cdot 10^{-7}$	$3.84 \cdot 10^{-7}$	$5.01 \cdot 10^{-7}$
Phenol	108-95-2	$8.02 \cdot 10^{-7}$	$8.37 \cdot 10^{-6}$	$3.41 \cdot 10^{-6}$
Heptachlor	76-44-8	$1.49 \cdot 10^{-6}$	$1.97 \cdot 10^{-5}$	$1.49 \cdot 10^{-6}$
Heptachlor epoxide	1024-57-3	$1.45 \cdot 10^{-8}$	$3.2 \cdot 10^{-6}$	$1.45 \cdot 10^{-8}$

Table D.2: Henry's law constants and $\log K_\mathrm{ow}$ values according to Howard and Meylan (21)

Compound	K_H atm m^3 mol^{-1}	$\log K_\mathrm{ow}$
Methyl *tert*-butyl ether	$5.87 \cdot 10^{-4}$	0.940
tert-Butyl alcohol	$1.44 \cdot 10^{-5}$	0.350
Benzene	$5.55 \cdot 10^{-3}$	2.13
Phenol	$3.33 \cdot 10^{-7}$	1.46
Heptachlor	$1.48 \cdot 10^{-3}$	5.5
Heptachlor epoxide	$3.2 \cdot 10^{-5}$	4.98

Appendix E

List of symbols

Model parameters

Symbole	Value	Units	Description
R	$8.21 \cdot 10^{-5}$	$\mathrm{atm m^3 mol^{-1} K^{-1}}$	Gas constant
T	298	K	Temperature
D_a	2	$\mathrm{km^2 s^{-1}}$	Eddy diffusion coefficient in air
D_w	0.01	$\mathrm{km^2 s^{-1}}$	Eddy diffusion coefficient in water
D_s	0	$\mathrm{km^2 s^{-1}}$	Eddy diffusion coefficient in soil
D_i		$\mathrm{km^2 s^{-1}}$	Eddy diffusion coefficient in compartment i
V_a	$2 \cdot 10^5$	[−]	Relative volume of the air compartment
V_w	233	[−]	Relative volume of the water compartment
V_s	1	[−]	Relative volume of the soil compartment
V_i		[−]	Relative volume of compartment i
f_{oc}	0.02	[−]	Fraction organic carbon in soil
ρ_s	1	[−]	Relative density of soil
r	6320	km	Radius of the earth

Substance parameters

Symbole	Units	Description
K_H	$\mathrm{atm\,m^3 mol^{-1}}$	Henry's law constant
K_{wa}	$[-]$	Water/air partition coefficient
K_{sa}	$[-]$	Soil/air partition coefficient
K_{sw}	$[-]$	Soil/water partition coefficient
K_{oc}	$[-]$	Organic carbon/water partition coefficient
K_{ow}	$[-]$	Octanol/water partition coefficient
K_{ij}	$[-]$	Partition coefficient between compartments i and j
k_a	$\mathrm{s^{-1}}$	(pseudo) first-order degradation rate in air
k_w	$\mathrm{s^{-1}}$	(pseudo) first-order degradation rate in water
k_s	$\mathrm{s^{-1}}$	(pseudo) first-order degradation rate in soil
k_i	$\mathrm{s^{-1}}$	(pseudo) first-order degradation rate in compartment i
D	$\mathrm{km^2 s^{-1}}$	Effective eddy diffusion coefficient
k	$\mathrm{s^{-1}}$	Effective first-order degradation rate
z	km	$z := \sqrt{D/k}$

Functions of time t and/or position x [1]

Symbole	Units	Description
$m_i(x,t)$	mol	Amount of chemical in compartment i
$M(t)$	mol	Total amount of chemical in the model environment
$c_i(x,t)$	$\mathrm{mol\ m^{-1}}$	Concentration in compartment i
$c(x,t)$	$\mathrm{mol\ m^{-1}}$	Total amount of chemical at position x and time t
$e(x)$	$\mathrm{mol\,m^{-1}s}$	Exposure
$\varepsilon(x)$	$\mathrm{m^{-1}}$	Normalized exposure

Others

Symbole	Units	Description
M_0	mol	Quantity of chemical released
$\bar{e}$	mol s	Normalisation factor of exposure
S	$[-]$	Entropy of normalized exposure
R	km	Entropy rank of normalized exposure

---

[1] Concentrations, exposures, and normalized exposures are not given in their natural units, but in the units corresponding to the one-dimensional, flat model geometry.

Precursor A and transformation product B

Symbole	Units	Description
D_{A}	$\mathrm{km^2 s^{-1}}$	Effective eddy diffusion coefficient of chemical A
D_{B}	$\mathrm{km^2 s^{-1}}$	Effective eddy diffusion coefficient of chemical B
k_{A}	$\mathrm{s^{-1}}$	Effective first-order degradation rate of A
k_{B}	$\mathrm{s^{-1}}$	Effective first-order degradation rate of B
z_{A}	km	$z_{\mathrm{A}} := \sqrt{\frac{D_{\mathrm{A}}}{k_{\mathrm{A}}}}$
z_{B}	km	$z_{\mathrm{B}} := \sqrt{\frac{D_{\mathrm{B}}}{k_{\mathrm{B}}}}$
z_{AB}	km	$z_{\mathrm{AB}} := \frac{z_{\mathrm{B}}+z_{\mathrm{A}}}{2} + z_{\mathrm{B}} \left(\frac{1}{2}\right)^{1+\frac{z_{\mathrm{A}}}{z_{\mathrm{B}}}} + z_{\mathrm{A}} \left(\frac{1}{2}\right)^{1+\frac{z_{\mathrm{B}}}{z_{\mathrm{A}}}}$
$c_{\mathrm{A}}(x,t)$	$\mathrm{mol\,m^{-1}}$	Total concentration of chemical A at position x and time t
$c_{\mathrm{B}}(x,t)$	$\mathrm{mol\,m^{-1}}$	Total concentration of chemical B at position x and time t
$e_{\mathrm{A}}(x)$	$\mathrm{mol\,m^{-1}s}$	Primary exposure to chemical A at position x
$e_{\mathrm{B}}(x)$	$\mathrm{mol\,m^{-1}s}$	Primary exposure to chemical B at position x
$\varepsilon_{\mathrm{A}}(x)$	$\mathrm{m^{-1}s}$	Normalized primary exposure of A at position x
$\varepsilon_{\mathrm{B}}(x)$	$\mathrm{m^{-1}s}$	Normalized primary exposure of B at position x
ϱ_{A}	km	Characteristic spatial range of chemical A
ϱ_{B}	km	Characteristic spatial range of chemical B
k_{AB}	$\mathrm{s^{-1}}$	Effective first-order transformation rate of precursor A into transformation product B
$c_{\mathrm{AB}}(x,t)$	$\mathrm{mol\,m^{-1}}$	Concentration of B as a transformation product of A at position x and time t
$e_{\mathrm{AB}}(x)$	$\mathrm{mol\,m^{-1}s}$	Secondary exposure to B as a transformation product of A at position x
$\varepsilon_{\mathrm{AB}}(x)$	$\mathrm{m^{-1}}$	Normalized secondary exposure at position x
S_{AB}	[−]	Entropy of normalized secondary exposure $\varepsilon_{\mathrm{AB}}(x)$
ϱ_{AB}	km	Secondary spatial range of B as a transformation product of A
ϱ_{AA}	km	Secondary spatial range in the degenerate case $z_{\mathrm{A}} = z_{\mathrm{B}}$
$\varrho_{\mathrm{AB},app}$	km	Analytic approximation of ϱ_{AB}
$\varrho_{\mathrm{AB},fit}$	km	Fitting approximation of ϱ_{AB}

Bibliography

[1] Abramowitz, M., and Stegun, I. (Eds) (1970) *Handbook of Mathematical Functions.* Dover Publications, New York

[2] Ballschmiter, K., (1998) Persistent, ecotoxic and bioaccumulative compounds *Pure & applied chemistry* 68: 1771-1780

[3] Bennett, D. H., McKone, T. E., Matthies, M., Kastenberg, W. E. (1998) General formulation of characteristic travel distance for semivolatile organic chemicals in a multimedia environment *Envion. Sci. Technol.* 32: 4023–4030

[4] Boethling, R. S., Mackay, D., (2000) *Handbook of property estimation methods for environmental and health sciences* Lewis Publishers; Boca Raton.

[5] Bunce, N. J., Liu, L., Zhu, J. and Lane, D. A., (1997) Reaction of Naphtalene and its derivatives with Hydroxyl radicals in the gas phase. *Envion. Sci. Technol.* 31: 2252–2258

[6] Church, C. D., Isabelle, L. M., Pankow, J. F., Rose, D. L., Tratnyek, P. G.,(1997) Method for determination of Methyl-*tert*-Butyl Ether and its degradation products in water *Envion. Sci. Technol.* 31: 3273–3276

[7] Convention on Long-Range Transboundary Air Pollutants, www.unece.org/env/lrtap/pdfbrochure/brochuree.htm United Nation Economic Commision for Europe, Geneva

[8] College voor de toelating van bestrijdingsmiddelen (1999)
Guidance document on relevant metabolites; Draft working document, Wageningen, The Netherlands

[9] Dr. Egly, Novartis Crop Protection
personal communication

[10] Directive 67/548/EEC on the approximation of the laws, regulations and administrative provisions relating to the classification, packaging and labelling of dangerous substances.

[11] Directive 91/414/EEC of 15 July 1991 concerning the placing of plant protection products on the market.

[12] Directive 92/32/EEC of 30 April 1992 amending for the seventh time Directive 67/548/EEC

[13] Directive 97/57/EC of 22 September 1997 establishing Annex VI to Directive 91/414/EEC concerning the placing of plant protection products on the market

[14] European Communities (1997)
Technical Guidance Document in support of Commission directive 93/67/EEC on risk assessment for new notified substances and Commission regulation (EC) No 1488/94 On risk assessment for exisiting substances
Luxembourg Office for Official Publications of the European Communities

[15] European Communities, (1997)
Technical guidance document for the completion of summary notification dossier for a new chemical substance utilising the structured notification interchange format (SNIF), European Commission
Luxembourg Office for Official Publications of the European Communities

[16] Einstein, A. (1909)
Zum gegenwärtigen Stand des Strahlungsproblems
Physikalische Zeitschrift, 10: 185–193

[17] Fenner, K., Scheringer, M. and Hungerbühler, K. (2000)
Persistence of parent compounds and transformation products in a level IV multimedia model.
Envion. Sci. Technol., in press.

[18] Gregor, D. J., (1990)
Deposition and accumulation of selected agricultural

pesticides in Canadian arctic snow in *Long Range Transport of Pesticides*, Kurz , D. A., (Ed.),
Lewis Publishers, Chelsea, 1990, pp 373-86

[19] Hickey, J. J., Anderson, D. W. (1968)
Chlorinated hydrocarbons and eggshell changes in raptorial and fish-eating birds
Science 162:271–273

[20] Howard, P. H., Boethling, R. S., Jarvis F. W., Meylan, M. W., and Michalenko, E. M. (1991).
Handbook of Environmental Degradation Rates.
Lewis Publishers, Chelsea

[21] Howard, P. H. and Meylan M. W. (Eds.) 1997.
Handbook of Physical Properties of Organic Chemicals.
Lewis Publishers, Boca Raton

[22] Howard, P. H. (Ed.) (1989)
Handbook of Environmental Fate and Exposure Data for Organic Chemicals.
Lewis Publishers, Chelsea

[23] Johnson, R., Pankow, J., Bender, D., Price, C., Zogorski, J. (2000)
MTBE: To what Extent Will Past Releases Contaminate Community Water Supply Wells?
Envion. Sci. Technol. 34:210.A–217.A

[24] Karickhoff, S. W., (1981).
Semi-empirical estimation of sorption of hydrophobic pollutants on natural sediments and soils.
Chemosphere 10: 833–846

[25] Kelce, W.R., C.R. Stone, S.C. Laws, L.E. Gray, J.A. Kemppainen and E.M. Wilson. (1995).
Persistent DDT metabolite p,p'-DDE is a potent androgen receptor antagonist.
Nature 375:581-585.

[26] Key, B. D., Howell, R. D., Criddle, C. S. (1997)
Fluorinated organics in the biosphere
Envion. Sci. Technol. 31:2445–2454

[27] La Clair, J.J.; Bantle, J.A.; Dumont, J. (1998)
Photoproducts and metabolites of a common insect growth regulator produce developmental deformities in Xenopus.
Envion. Sci. Technol. 32: 1453-1461

[28] Mackay, D., Paterson, S. (1991)
Evaluating the multimedia fate of organic chemicals: A level III fugacity model.
Envion. Sci. Technol. 25: 427-436

[29] Müller-Herold, U. (1996)
Measures of endangerment
The Geneva Papers on Risk and Insurance 80: 383-392

[30] Müller-Herold, U. and Nickel, G.(2000)
A closed analytical formula for the characteristic spatial range of persistent organic pollutants.
Ecological Modelling 126: 191-200

[31] Oberhettinger, F. (1990)
Tables of Fourier Transforms and Fourier Transforms of Distributions
Springer, Berlin.

[32] OECD (1981)
Guidelines for testing of chemicals
OECD, Paris

[33] Protocol on Persistent Organic Pollutants (POPs)
http://www.unece.org/env/lrtap/
United Nation Economic Condition for Europe, Geneva

[34] van Pul, W. A. J., de Leeuw, F. A. A. M., van Jaarsveld, J. A., van der Gaag, M. A., and Sliggers, C. J. (1998).
The potential of long-range trans-boundary atmospheric transport.
Chemosphere 37: 113–141

[35] Regulation (EC) No 1488/94 of 28 June 1994 laying down the principles for the assessment of risks to man and the environment of existing substances in accordance with Council Regulation (EEC) No 793/93.

[36] Rényi, A. (1973)
Wahrscheinlichkeitsrechnung,
VEB deutscher Verlag der Wissenschaften, Berlin. (Anhang 6, §6 and 7.)

[37] Risenbrough, S. (1990).
Beyond Long-Range Transport: A model of a global gas chromatographic system.
in Kurz, D.A (ed) *Long Range Transport of Pesticides*, Lewis Publishers, Chelsea.

[38] Scheringer, M., Berg, M., Müller-Herold, U., (1994).
Jenseits der Schadensfrage: Umweltschutz durch Gefährdungsbegrenzung,
in: Berg, M et al. (eds): *Was ist ein Schaden? Zur normativen Dimension des Schadensbegriffs in der Risikowissenschaft.*
Verlag der Fachvereine Zürich

[39] Scheringer, M., Berg, M., (1994).
Spatial and temporal range as measures of environmental threat.
Fresenius Envir. Bull. 3: 493–498

[40] Scheringer, M., (1996).
Persistence and spatial range as endpoints of an exposure-based assessment of organic chemicals.
Envion. Sci. Technol. 30 (5): 1652–1659

[41] Scheringer, M., (1996).
Räumliche und zeitliche Reichweite als Indikatoren zur Bewertung von Umweltchemikalien.
Dissertation No 11746, ETH Zürich

[42] Scheringer, M., Mathes, K., Weidemann, G., Winter, G. (1998)
Für einen Paradigmenwechsel bei der Bewertung ökologischer Risiken durch Chemikalien im Rahmen der staatlichen Chemikalienregulierung,
Zeitschrift für Angewandte Umweltforschung 11: 227-233.

[43] Scheringer, M., (1999)
Persistenz und Reichweite von Umweltchemikalien,
Wiley-VCH, Weinheim.

[44] Sidebottom, H., Franklin, J., (1998)
Atmospheric fate and impact of HCFCs and chlorinated sovents
Pure & applied chemistry 68: 1757-1769

[45] Somasundaram, L., Coats, J. R., (1991)
Pesticide transformation products: Fate and significance in the environment,
American Chemical Society; Washington, D.C

[46] Soto, A.M., Justitia, H., Wray,J. W., and Sonnenschein, C. (1991)
p-Nonylphenol, an estrogenic xenobiotic released from modified polystyrene
Environ. Health Persp. , 92: 167-163

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