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Environmentally Oriented Design and Assessment of Chemical Products and Processes

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Abstract: In this paper we illustrate our work on integrated process and product design and assessment using three examples: a small calorimeter for quick reaction screening, a multi-criteria process technology assessment method, and a screening tool for exposure-based risk assessment of chemical products. A short introduction is given on our general framework for considering environmental objectives in chemical product and process design.

Keywords: Calorimetry · Environmental product design · Exposure-based assessment · Multi-criteria decision-making · Sustainability

The specialty chemicals industry today is facing the challenge of succeeding with its products and processes in a world of continuously growing economic and ecological requirements. We at the group for 'Environmental and Safety Technology in Chemistry' focus our teaching and research on delivering instruments to improve decision making that considers both economic and environmental objectives in early design stages (Hungerbühler *et al.* [1]). This proactive way of environmentally oriented product and process development is an iterative procedure comprising the generation of design alternatives, performing mass and energy balances for these technology options, analysing the benefits and risks using economic value and ecological impact data, and finally evaluating the results by comparing them with value-based development aims and protection goals (Fig. 1). According to our problem understanding, eco-efficiency, inherent safety and social acceptance are the key principles of this development approach. Special attention has to be given to the problem of model and data uncertainty. We also implement these concepts in our teaching activities using interdisciplinary, teamwork-oriented case studies developed in cooperation with the chemical industry (Fenner *et al.* [2]).

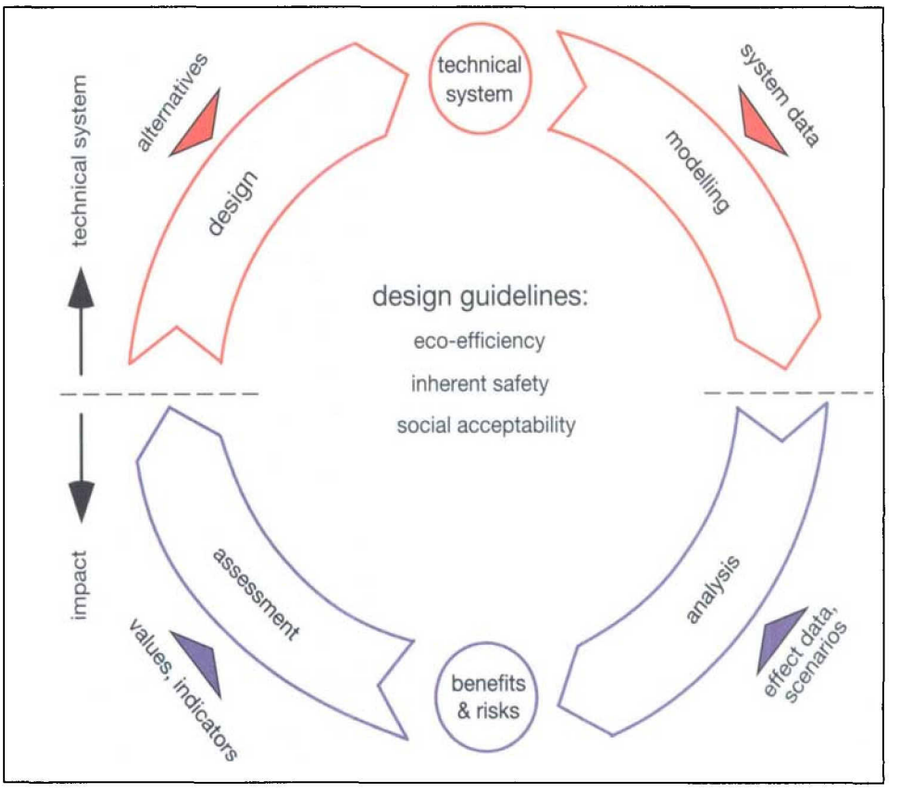

Fig. 1. Framework for integrated process and product design.

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In this paper, three topics of our research are presented: (1) a small calorimeter combined with an FT-IR spectrometer for quick reaction screening, (2) a multi-criteria process technology assessment tool and (3) a screening tool for the exposure-based assessment of chemicals.

1. Reaction Screening Using a Small Calorimeter Combined with a FT-IR Spectrometer

Optimised reaction conditions imply a better environmental performance of a chemical process because raw material utilisation is improved, the energy demand for separations is decreased, and the amount of waste is reduced. To meet this goal, a systematic and quick determination of kinetic and thermodynamic reaction parameters during early process development is needed. For this purpose, a small reaction calorimeter with integrated FT-IR probe has been developed. Such a device is of particular importance for new fine-chemical and pharmaceutical products where generally only small amounts of test substance are available and time-to-market is crucial (Pastre *et al.* [3]).

The reaction calorimeter (Fig. 2) has a sample volume of 20–45 ml. To measure the thermokinetic parameters at isothermal conditions, the power compensation principle (internal compensation heating) has been combined with the heat balance approach (external Peltier elements). This combination of two calorimetric measurement principles allows for the direct measurement of the heat evolved during a reaction without a mathematical baseline correction. This new reactor concept and its realization with Peltier elements and a Teflon-coated metal block has been patented and is currently under consideration for commercial use. The calorimeter can be operated at temperatures between –20 and 200 °C and a pressure of 0 up to 10^6 Pa. It is equipped with a magnetic coupling for the stirrer, with pressure and temperature sensors and two inlets and is combined with an FT-IR spectrometer.

For processing the measured data, no tools are currently available for a simultaneous evaluation of both the thermal and the spectroscopic signal (examples see the Scheme and Fig. 3). Therefore we are developing an evaluation algorithm using non-linear optimisation to estimate unknown reaction parameters such as the heat of reaction, the rate constants, and the phase transfer coefficients.

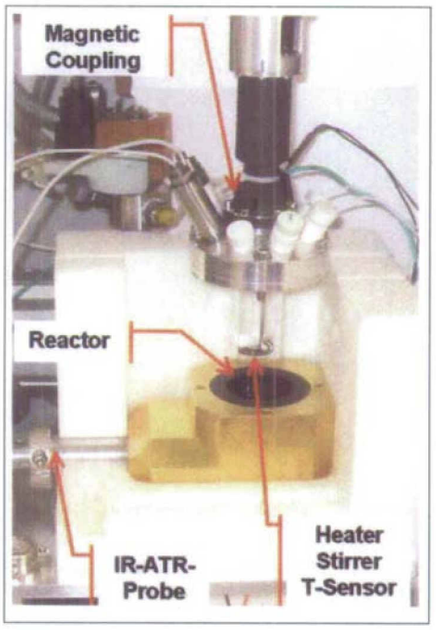
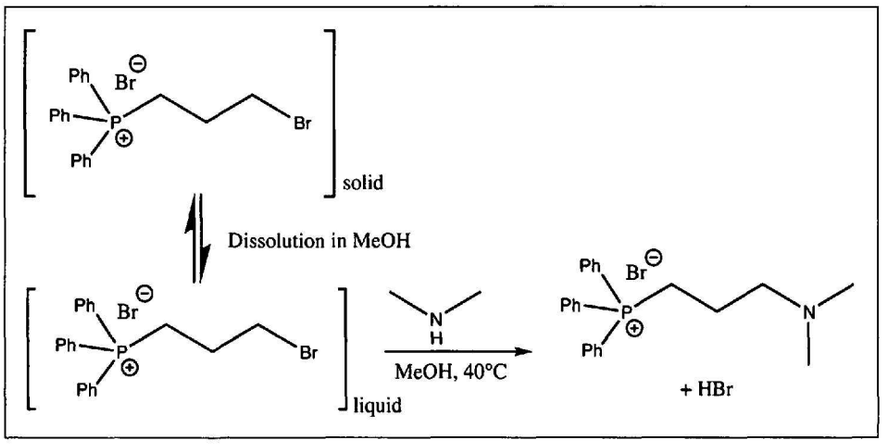


Fig. 2. Small reaction calorimeter with integrated FT-IR probe.

2. Multi-Criteria Process Technology Screening

Multi-criteria process assessment deals with the question of how to evaluate and compare different process technologies in a systematic way. To develop and illustrate the methodology, the well-known HCN production technology with a large number of process alternatives was chosen (Hoffmann [4]). HCN is mostly produced from a carbon feedstock and ammonia according to the reactions shown in Fig. 4.

A general process structure with different system boundaries is indicated in Fig. 5. While a number of standard technologies are currently used in industry, the systematic combination of the literature-known unit operation technologies building up the process superstructure generates more than 70'000 process alternatives (for an example see Fig. 6). By introducing additional constraints such as compatibility between the different unit operation technologies, safety require-



Scheme. The heterogeneous reaction investigated.

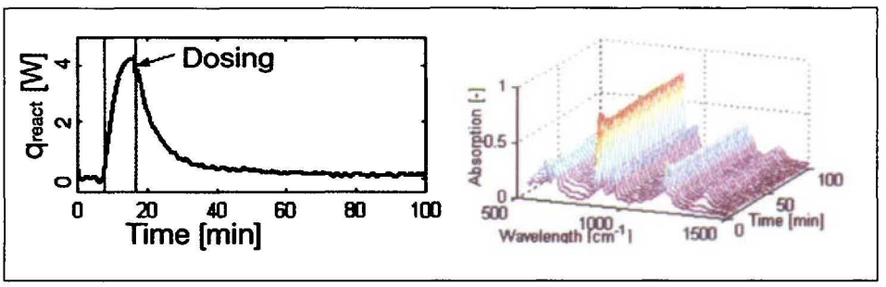


Fig. 3. Heat of the reaction *versus* time course (left) and IR spectra measured online (right).

$CH_4 + NH_3 \rightarrow HCN + 3H_2$	(ΔH_R = 252 kJ/mol)	BMA process
$CH_4 + NH_3 + 1.5\ O_2 \rightarrow HCN + 3H_2O$	(ΔH_R = -474 kJ/mol)	Andrussow process
$C_3H_8 + 3\ NH_3 \rightarrow 3HCN + 7\ H_2$	(ΔH_R = 634 kJ/mol)	Fluohmic process

Fig. 4. Common HCN synthesis reactions.

ments or emission limits, this number can be reduced to about 1200 *feasible* process options. Using a flow-sheeting program, mass and energy balances for each of these alternatives are calculated and are subsequently evaluated using economic and ecological indicators. Fig. 7 shows a two-dimensional plot (Pareto Plot) in which the **T**otal **A**nnualised **P**rofit **P**er **S**ervice unit, *TAPPS*, and the **M**aterial **I**ntensity **P**er **S**ervice unit, *MIPS*, have been chosen to evaluate the different technologies. The *TAPPS* is calculated as the sum of sales, raw material costs and annualised investment cost per kilogram of main product, while the *MIPS* assumes a life-cycle perspective and adds the material use of all upstream products that are necessary to produce one kilogram of main product. Hence, in Fig. 7 a process in the upper left corner – characterized by a high profit and a low material intensity – is preferable to alternatives to the lower right.

Fig. 7 illustrates that alternatives tend to form clusters depending on the key decision of which reactor technology is chosen. Generally, BMA processes seem to exhibit a better performance than Andrussow processes, while Fluohmic processes are environmentally significantly worse than the other two technologies due to the extensive use of electricity to operate the reactor. In other words, if an inferior basic choice is made, *e.g.* to construct a Fluohmic reactor, all other process decisions cannot improve the process in such a way that it becomes comparable to the performance of an Andrussow or even a BMA process. Once the reactor is chosen, a more detailed analysis shows that a second key decision concerns the use of the by-product hydrogen. This

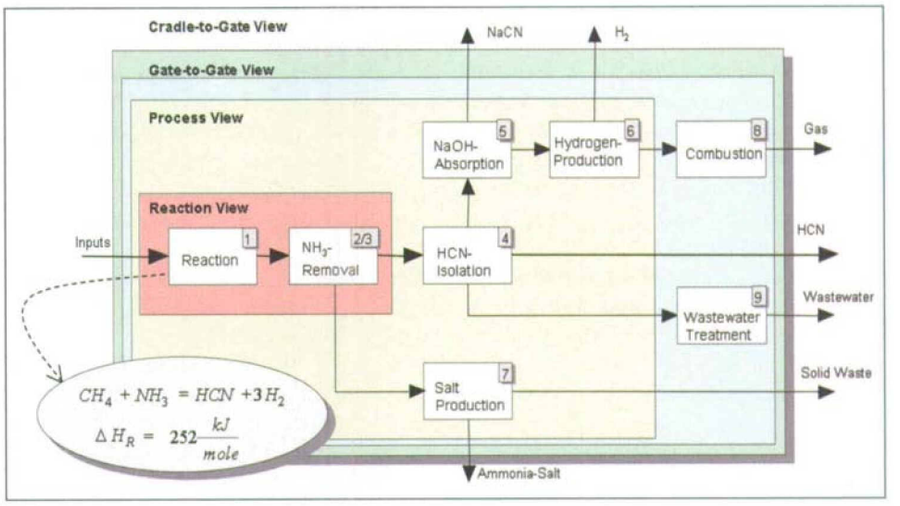


Fig. 5. Block diagram for HCN production with different system boundaries.

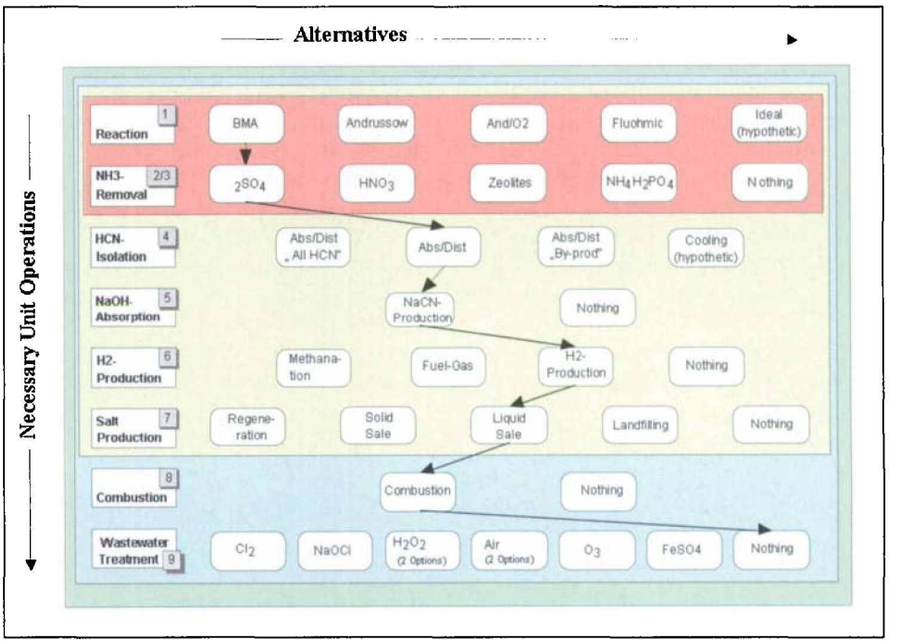


Fig. 6. Unit operations network for HCN production.

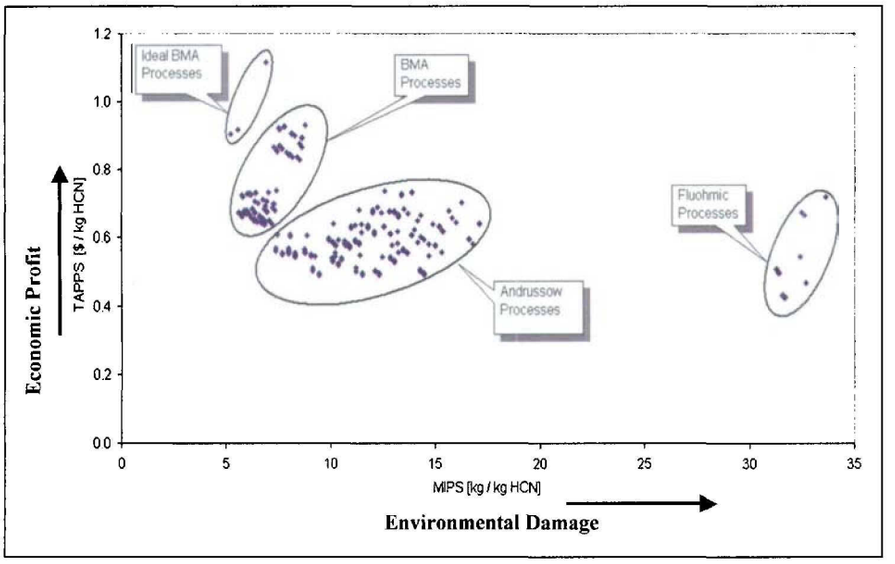


Fig. 7. Pareto plot of the environmental and economic assessment of 1244 HCN production technologies.

suggests that, for technology screening, a proper analysis of potential uses for hydrogen has a higher priority than, for example, the design of the purification system. In order to direct research and development efforts and to allocate financial resources to the most promising processes, key decisions of this type need to be identified and inferior processes have to be excluded as early as possible (Heinzle *et al.* [5]).

Unfortunately, it is an inherent characteristic of technology assessment in early development stages that decisions

have to be made with incomplete information. A probabilistic approach based on Monte-Carlo simulations has been developed allowing to efficiently propagate parameter uncertainties through complex process models and to identify key uncertainties (Hoffmann [4]). While the *absolute* uncertainty intervals of different technologies might partly overlap, a *relative* analysis can enable the decision maker to make a ranking according to the economic and environmental performance.

3. A Screening Tool for Exposure-Based Assessment of Chemicals

In the design of chemicals, the assessment of the environmental fate and toxicity is required to ensure a good environmental performance. However, a complete understanding of a chemical's behaviour in the environment including its eco-toxicity requires tremendous efforts (testing for degradability, bioaccumulation, and toxicity to different species and ecosystems). For this reason, it is helpful to assess the environmental fate (chemical reactivity; transport with wind and water currents; exchange between the environmental media) and the eco-toxicity of a chemical in two subsequent steps. Especially on a screening level, when toxicity data are scarce, it is appropriate to investigate the exposure potential of a chemical as a clearly defined first assessment step (exposure-based assessment). If a chemical exhibits an unwanted exposure potential (high persistence and mobility such as chlorofluorocarbons), it can be concluded - even without knowledge of its toxicity - that the chemical is likely to cause environmental problems.

Measures of the exposure potential of a chemical are its persistence, τ, and spatial range, R, which describe the temporal and spatial extent of environmental exposure patterns (Fig. 8). For screening purposes, it is most useful to determine R and τ with generic multimedia fate models (Van de Meent *et al.* [6]). The Chemrange model (Scheringer *et al.* [7]) is a simple model of the global circulation that calculates R and τ for organic chemicals from their Henry's law constants, octanol-water partitioning coefficients and average degradation rates in soil, water, and air. The model results can be used for the ranking and classification of chemicals. Fig. 9 shows model results for different substances, some of which are Persistent Organic Pollutants (POPs) with high uncertainty in their atmospheric degradability and, therefore, also in the spatial range. Within the possibilities of a generic model, the model results agree quite well with experimental findings on the global dispersion of chemicals (Scheringer [8]).

Recently, Fenner *et al.* [9] developed a methodology to include transformation products together with the parent compound into the exposure-based assessment. To this end, the *joint persistence* covering the entire cascade of the parent compound and a selection of relevant metabolites has been introduced. Application to different chemicals such as atrazine, perchloroethylene, methyl-t-butylether, and nonylphenol ethoxylates revealed that the inclusion of transformation products can cause considerable changes to the ranking of chemicals according to their persistence.

The approach of exposure-based assessment introduces a new perspective into chemicals assessment. In contrast to toxicity indicators, which do not provide any information on the location and time

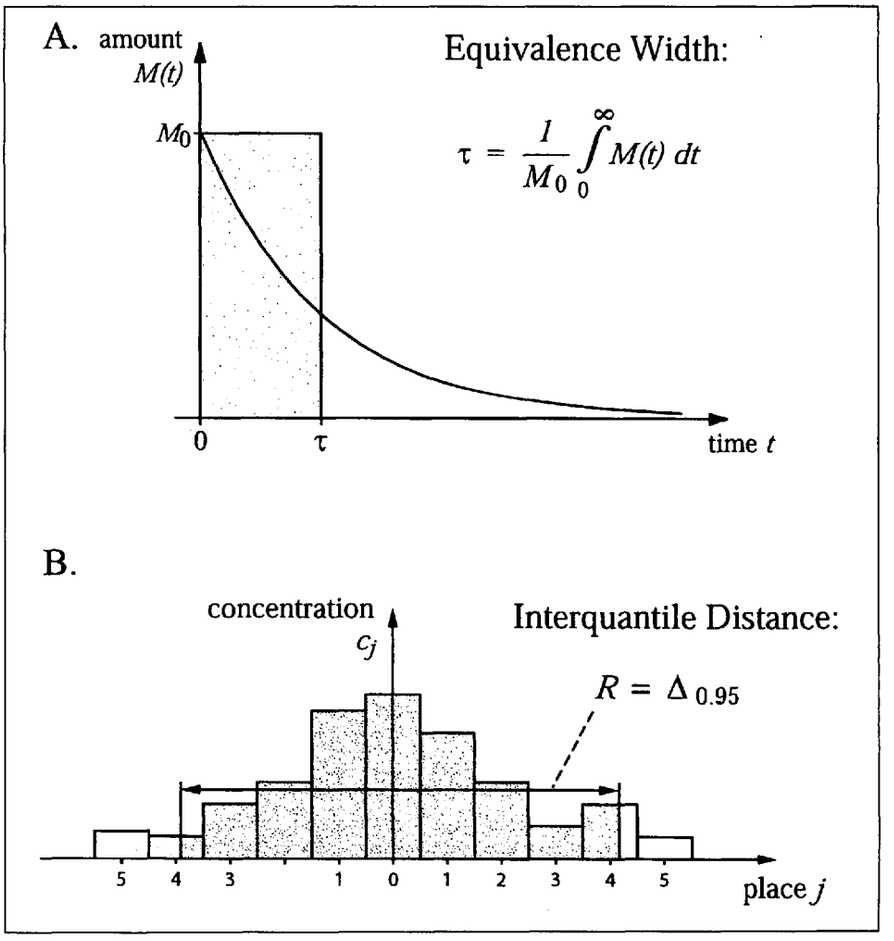


Fig. 8. Calculation of the environmental persistence τ of a chemical [A] from the function $M(t)$ describing the decrease of the chemical's overall mass in time and calculation of its environmental spatial range R [B] as the 95% interquantile distance of the concentration distribution. Reprinted with permission from M. Scheringer, *Env. Sci. Technol.* **1996**, *30*, 1652–1659. Copyright (1996) American Chemical Society.

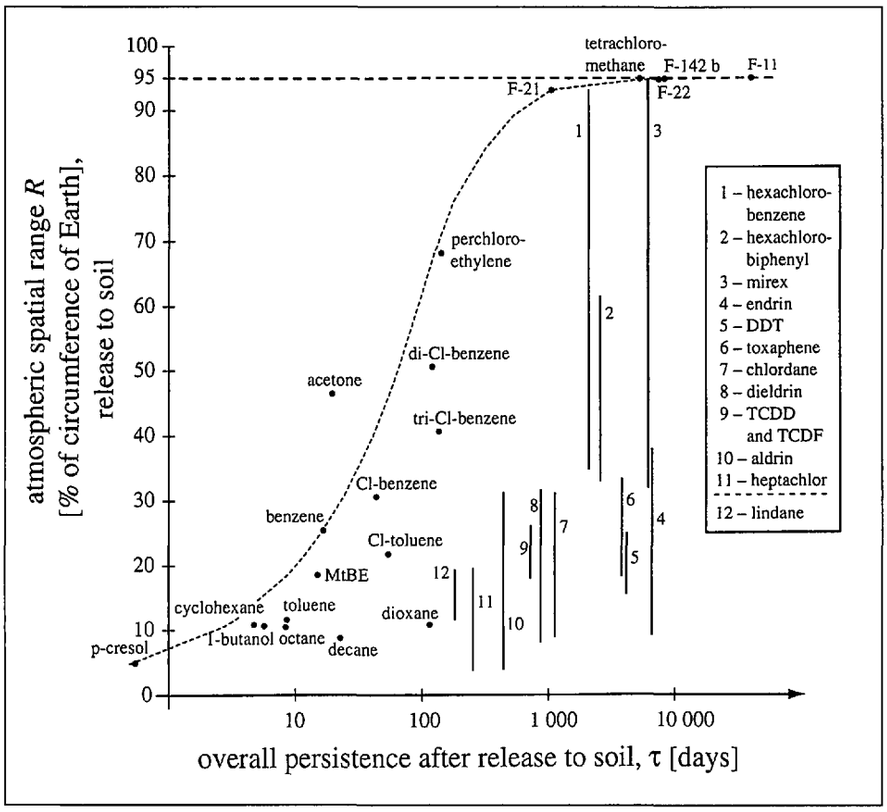


Fig. 9. Spatial range in air, *R*, vs. overall persistence t as calculated with the Chemrange model. All chemicals are released to the soil. Persistent Organic Pollutants exhibit high uncertainties in *R* due to their unknown atmospheric degradability. Reprinted with permission from R.L. Lipnick et al. (eds.) 'Persistent, Bioaccumulative, and Toxic Chemicals II', American Chemical Society **2001**, p. 59. Copyright (2001) American Chemical Society.

of the occurrence of effects, it explicitly focuses on the temporal and spatial distribution of benefits and burdens associated with the production and use of chemicals. If, in the future, exposure patterns could be restricted to the surroundings of the users of a chemical, it is more likely that the users and those who are exposed to the chemical are in similar political, economic, and legal contexts, which would make negotiations much easier than on the global level. In this sense, we suggest that the chemical product technology should be directed towards a 'chemistry of low ranges'.

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