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Evaluating multimedia/multipathway model intake fraction estimates using POP emission and monitoring data

M. Margni*, D.W. Pennington, C. Amman, O. Jolliet

Industrial Ecology and Life Cycle Systems Group, GECOS, Ecole Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne-EPFL, Switzerland

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''Capsule'': The fraction of PCDD/F Emission which transfers to the human population is assessed for Europe using a novel approach.

Abstract

This paper presents a structured evaluation of a novel multimedia chemical fate and multi-pathway human exposure model for Western Europe, IMPACT 2002, using data for PCDD/F congeners. PCDD/F congeners provide an illustration of the potential use of POPs (Persistent Organic Pollutant) data for the evaluation of such models. Based on available emission estimates, model predictions with and without spatial resolution are evaluated at three different stages against monitored data: at environmental contamination levels, food exposure concentration, and in terms of human intake fractions (iF): the fraction of an emission that is taken in by the population. The iF is $3.5 \cdot 10^{-3}$ for emissions of dioxin in Western Europe. This iF compares well to the traditional non-spatial multi-media/-pathway model predictions of $3.9 \cdot 10^{-3}$ for the same region and to $2 \cdot 10^{-3}$ for the USA. Approximately 95% of the intake from Western European emissions occurs within the same region, 5% being transferred out of the region in terms of food contaminants and atmospheric advective transport.

Keywords: Multimedia models; Intake fraction; Model evaluation; Multi-exposure-pathways; Dioxin

1. Introduction

Multimedia chemical fate and multi-pathway human exposure models like CalTOX (McKone, 1993), EUSES (EC, 1996), and IMPACT 2002 (IMPact Assessment of Chemical Toxics) (Pennington et al., 2003) can be cross compared, but are very difficult to fully evaluate (or validate) in the absence of sufficient field data. Expert panels call for more comparisons of the results of such models with empirical data (Cowan et al., 1994; Hertwich et al., 2002). In this paper we evaluate the recently developed multimedia fate and multipathway exposure model, IMPACT 2002, for a Western European scenario using data for PCDD/F congeners. This helps to illustrate the potential benefits and limitations of using available POPs (Persistent Organic Chemicals) data, which is often more readily available than for many other types of chemicals.

Single-medium models have been subjected to more intense empirical testing, thanks partly to monitoring data studies designed specifically for their evaluation. However, single-medium models such as GREAT-ER (Schroder et al., 2002) or EcoSense (EC, 1999) are usually only evaluated for few chemicals released under specific conditions directly to the medium of interest. Many chemicals are however multimedia in nature, being transported from the medium of emission into another medium that either directly, or indirectly, results in the dominant exposure pathway of a species.

There have also been a few attempts to evaluate and build confidence in multimedia fate models using measurement data for some classic organic pollutants, such as PCBs, PCDDs, and gamma-HCH. A number of evaluations have been published for multimedia chemical fate models that do not provide spatial distinction—distinction between the release location and where chemicals pass into foods, drinking water, or directly into

* Corresponding author. Tel.: +41-21-693-3729; fax: +41-21-693-5760.
E-mail address: manuele.margni@epfl.ch (M. Margni).

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populations via inhalation. (Jager, 1998) published an inventory of experiences and validation activities on EUSES evaluation. EUSES was compared to measured data mostly in the context of chemical fate and with data originating from Germany for PCDDs, some PCBs, DEHP, LAS, EDTA and HHCB (Schwartz, 2000). The ChemCAN fate model was evaluated with monitored benzene and chlorobenzene emissions and concentrations in the southern Ontario region (MacLeod and Mackay, 1999). Similar insights were found by Pederson et al., (2001) for the Louisiana indus−trial corridor testing Simplebox 2.0 model with four organic chemicals (toluene, styrene, trichloroethylene, and metribuzin). Kawamoto et al., (2000) compared EUSES and a modi...ed version of the EQC model to the concentration of 68 organic chemicals in two spatial scales in Japan, also noting that accounting for back−ground contaminants entering such regions was vital in many cases. ChemFRANCE was evaluated with iso−butylene (Devillers et al., 1995) atrazin (Bintein and Devillers, 1996a) and lindane (Bintein and Devillers, 1996b). CalTOX human intake estimations for dioxin were compared to the results of a recent US survey on dioxin risk assessment (Bennett et al., 2002a).

However, spatial di...erentiation could facilitate com−parison with localized monitored data. Evaluation studies using multimedia/multi−pathway models that account for spatial resolution, and particularly cross−comparison with models having such a resolution, remain limited in availability (Fig. 1). Shatalov et al. (2001) published a report comparing predicted fate concentrations to monitored levels of dioxins/furans, B[a]Ps, PCBs, and HBH. The appendix of the study provides a review of further EMEP publications of POPs fate modelling. Koziol and Pudykiewicz (2000) (Liem et al., 2000) and Lammel (2001) (Freijer et al., 2001) similarly published studies evaluating POPs fate models. IMPACT 2002 (Pennington et al., 2003) opens new possibilities by providing for the ...rst time spatial estimates of human intake fractions for Western Europe using a multimedia/multi−pathway model with a spatial resolution. IMPACT 2002 additionally provides a con−sistent model that re...ects more traditional a−spatial multimedia/multi−pathway modelling (see Fig. 2). Both the spatial and a−spatial models are based on the same data and spatial coverage; hence the results can be directly cross−compared in a consistent framework. The spatial and a−spatial models for Western Europe are nested in a global a−spatial model, so contributions to human intakes are estimated accounting for emissions within Western Europe and also for those likely to occur outside. However, the model has still not been used for comparison with measured data.

Recently POPs like PCDD/Fs have been well studied compounds with regards to widespread monitoring programs in the USA (USEPA, 2000, 2001), Europe (Buckley−Golder et al., 1999; Quass et al., 2000), and throughout the literature (Huwe, 2002), including data in di...erent environmental media and in food. Taking advantage of these recent model developments and data sets, this paper has four objectives:

1. identify criteria to select chemical for a proper model veri...cation of regional and continental multimedia scale,
2. demonstrate the feasibility of a ...rst evaluation of the novel multimedia/multi−pathway exposure model IMPACT 2002 for Western Europe against monitoring data using POPs,
3. analyse the reliability of this model to predict POP fate and exposure, comparing spatial and a−spatial versions,

Fig. 1. Systematic 3−level procedure for evaluating multimedia/multi pathway model intake fractions against monitoring data and risk assessment estimates

Fig. 2. IMPACT 2002 multimedia model. The a−spatial version accounts for the same data and spatial coverage as the spatial di...erentiated version accounting for 136 watersheds zones and 156 air cells. A watershed zone includes air, soil, vegetation water and sediment compartments. Oceanic zones match the air grid.

4. develop the validation approach by comparing both at concentration levels in di...erent media and food, and at population−based intake.

The paper provides a structured framework for evaluating multimedia/multi−pathway models, as shown by Fig. 1. Criteria of the chemical properties to support evaluations of di...erent models are ...rst de...ned. Then an appropriate chemical is selected to evaluate the IMPACT 2002 model. Collected emissions and physical−chemical property data from the literature are used to run IMPACT 2002 (Section 2). The ...rst comparison level is presented at the level of environmental concentrations (Section 3.1). A second comparison is conducted for concentrations in the di...erent human exposure substrates (food) (Section 3.2). The ...nal comparison is at the population intake fraction level (Section 3.3). Obtained results are also compared with exposure estimations found in the literature. Section 4 discusses the ...ndings and the relevance of POPs data for model evaluation.

2. Methods

2.1. Criteria for chemical selection

To evaluate multimedia/multipathway models, ideally one should select a number of su...ciently diverse chemicals to describe, as far as possible, the di...erent combinations of chemical behaviour into the environment. The test−set developed by Margni (2003) (Pennington et al., 2003), for example, helps answer this need by identifying a minimal set of example chemicals and properties for the evaluation of such models. Unfortunately emissions and monitoring data for many of these chemicals are not widely available. In addition, evaluative chemicals have to be appropriate to the scope of the model under consideration. Two extremes are foreseen: (1) use of persistent chemical to evaluate low resolution/large scale models where the assumption of homogeneous well mixed media may be most appropriate, and (2) adoption of rapidly degradable chemicals for high−resolution/local scale.

The choice between strategies (1) and (2) depends on the characteristics of the tested model. The model evaluated in this paper, IMPACT 2002, enables estimation of chemical concentrations in environmental media at a regional and a global scale and multiple exposure pathways that link a chemical concentration in the atmosphere, soil, surface water, and vegetation to human uptake though the inhalation and ingestion. Ingestion pathways include drinking water consumption, incidental soil ingestion, and intake of contaminants in agricultural products (fruits, vegetables, grains,. . .) as well as in animal products, such as beef−, pig−, and poultry−meat, eggs, ...sh, and milk. Two novel scenarios and data are presented for Western Europe; one adopting the typical multimedia approach of no spatial distinction within an environmental medium, the second accounting for spatial resolution (see Fig. 2), i.e. for time−averaged advective ...ows in an atmospheric grid between watersheds (¼600 environmental compartments with a matrix−based solution to instantaneously resolve the associated di...erential mass balance equations). The transfer of contaminants into the human food web is related to spatially distributed agricultural and livestock production levels. Cumulative risk and potential impact per kg of emission are calculated by combining cumulative chemical intake with risk−based e...ect factors. However, human risks remains outside the scope of the present study, focused on fate and exposure.

For such a continental model is clearly the ...rst of the above described strategy that can be retained. Chemicals suitable to evaluate such a multimedia/multipathway model have to satisfy the following characteristics:

- Well studied chemical, with accurate emissions and monitored environmental and exposure concentrations data for all of Europe.
- For models without (or a low degree of) spatial resolution, the chemical must be emitted homogeneously into the compartment to enable a rapid mixing and wide distribution within the spatial cell.
- Long term emissions and concentration monitoring data to estimate long term levels and evaluation.

Long-range transport at continental scale only to avoid high concentrations close to emission locations alone, but also to avoid significant trans-boundary input-output flow rates to the rest of the world. This additionally limits the extent of influence attributable to emissions outside the region of study, as was an important factor in Kawamoto et al. (2000) and Pederson et al. (2001).

Being available in the environment at measurable concentrations, particularly in remote locations. Showing significant transfer to food, low degradation in vegetation and/or metabolism in animals to be found in a wide range of exposure substrates (foods) linked to human exposure and thus important in the evaluation of the food exposure pathways.

2.2. Structured evaluation with selected PCDD/Fs congeners

Among different chemicals it appears that the above mentioned criteria could be met using data for POPs such as Polychlorodibenzo-p-dioxins and -furans (PCDD/Fs) to provide a first empirical evaluation of some multimedia models. These chemicals are not produced specifically, but are found in ubiquitous distribution due to their formation as unwanted by-products in a number of industrial and thermal processes. We can reasonably assume these emissions are spread out over all of Europe, even if differences between and within countries are likely due to heterogeneous anthropogenic activities. PCDD/Fs show continental scale for long-range transport (Pennington et al., 2002), i.e. losses across system boundaries remains limited. Hence, such chemicals are particularly suitable for the evaluation of multimedia models that cover areas such as Western Europe. Exposure to human is due mainly through their diet, which accounts for more than 90% to the total exposure (King et al., 1999; Liem et al., 2000).

Among 75 polychlorodibenzo-p-dioxins and 135 polychlorodibenzofurans, only seven and 10 compounds, respectively, are of high concern in terms of their toxic dose-response effect levels. Data are then commonly available for these 17 congeners of toxicological concern, as listed in Appendix A. All these compounds have chlorine atoms substituted in the 2,3,7,8-position and show a different degree of toxicity. The most toxic congener of PCDD/F family is the 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD), also known as ''Seveso-dioxin''. In order to facilitate comparison of analytical exposure data, analytical results of all 17 congeners of toxicological concern are converted into one summarizing result expressed in toxic equivalents (TEQ). To determine the TEQ, the amounts of each congener are multiplied by their respective toxic equivalency factors (TEF) and obtained results summed as follow:

$$\mathrm{TEQ} = \sum_{i=1}^{17} \mathrm{TEF}_i\, M_i \qquad (1)$$

TEF are assigned to each congener in relation to the most toxic one 2,3,7,8-TCDD, which has the arbitrary value of 1 (Kutz et al., 1990; NATO/CCMS, 1988).

PCDD/F congeners are not only different in their toxicity, but also in terms of their fate and exposure characteristics. Since the behaviour of PCDD/F congeners in the environment is a function of their physical–chemical properties it wouldn't be correct to compare fate and/or exposure model prediction to TEQ measured values. Single congeners therefore have to be considered separately.

Scientific literature has dedicated a large number of publications to dioxin problems. Authors, however, present their results in terms of TEQs, usually stating nothing about PCDD/F mixture composition. Fate and exposure concentrations by single congeners are then estimated according following two-steps procedure.

(1) Based on selected publications, for which information on PCDD/F mixtures is available, the contribution of the specific congener to the TEQ, f_i is determined. For each medium or exposure substrate an average f_i is calculated as follow:

$$f_i = \frac{\sum_n \frac{\mathrm{TEF}_i\, M_i}{\mathrm{TEQ}}}{n} \qquad (2)$$

where f_i is the average contribution of a single congener to the TEQ determined based on n mixture measurements from literature. TEF_i is toxic equivalency factor, M_i the mass (or concentration) of congener i, and TEQ the toxic equivalent of a given PCDD/F mixture.

(2) From available studies reporting TEQ monitored data over all of Western Europe, mass or concentration of single congener i is then estimated by their average contribution f_i to TEQ calculated by Eq. (2) and by their toxic properties, as follow:

$$M_i = \frac{f_i\, \mathrm{TEQ}}{\mathrm{TEF}_i} \qquad (3)$$

Vulykh and Shatalov (2001) investigated PCDD/F composition in emissions and in environmental media for selecting ''indicator congeners'' for fate modelling. This paper builds partly on their work, looking also at congeners contribution to TEQ concentrations in sediment and foods based on an extended survey

European PCDD/F emission estimates and monitoring data for environmental concentrations and exposure levels are obtained from the recent European Commission DG Environment survey (Buckley-Golder et al., 1999; Quass et al., 2000). In this study we consider 5 dioxin congeners. Key criterion for their selection is their contribution to the total equivalent toxicity of the mixture (using the NATO toxic Equivalents System, I-TEQ) in emission estimates, environmental media, and exposure substrates.

Based on emission estimates, IMPACT 2002 predictions are compared to monitored concentrations in environmental media (first level of comparison, see Fig. 1) and exposure substrates (second level). Results of the spatial multimedia model for Western Europe (Pennington et al., 2002) are also included in this comparison in order to look at possible variations between locations. Finally the last comparison is performed at the intake fraction (iF) level, which represents the combined fate and exposure measure for human health (Fig. 1). This fraction is dimensionless and is the fraction of a chemical released that will ultimately results in intake by a human population (Bennett et al., 2002b). This latter measure simplifies discussions of emissions-to-intake relationships, enabling easy intercomparison of the results of many risk investigations as shown in Section 3.3.

The iF for the European population is calculated based on annual emission estimates, monitored exposure substrate concentrations, as well as food intake rates. Results are compared with iFs obtained from risk assessment study estimates at national levels found in the literature.

2.2.1. Emission estimations

Dioxin air emission data for the most relevant source types in Europe [1] are given by an extended review by Quass et al., (2000). We grouped these emission into three major basic sources to the environment, for which Vulykh and Shatalov (2001) investigated the composition: organic fuel combustion (wood, coal and oil product), incineration of waste (municipal, industrial and medical waste) and industrial production, respectively. For the selected congeners, contribution to the PCDD/F mixture toxicity for the overall air emission is calculated looking the specific congener contributions for each source type. The mass of single congener emitted into the environment is then estimated, considering total TEQ emission and the respective TEF data (Table 1). For example according to Vulykh and Shatalov (2001), 2,3,4,7,8-PeCDF represents 47, 28, and 37 percent of the organic fuel combustion, waste incineration, and industrial production sources, respectively. Multiplying these values by the percentage of contribution of each basic source to the total emissions and summing them together, 2,3,4,7,8-PeCDF contributes to 37% of the total TEQ emissions of 5.077 kg_{TEQ}/yr. Dividing this result by that of TEF (0.1), one obtains an emission estimate of 3.725 $kg_{congener}$/yr.

The annual PCDD/F emissions to air, however, do not represent the highest fraction of the total PCDD/F emissions if all environmental media are taken into account (Wenborn et al., 1999). The total is probably several times the emissions to air, but as insufficient data exist input to land can only be estimated with high uncertainty (Table 2). It should also be noted that most of these PCDD/F emissions are ‘‘stored’’ in reservoirs, like disposal sites, and most likely will not enter in the food chain directly. While not quantified, total releases to water are likely to be significantly lower than release to air. Emissions to water and to landfills are therefore neglected in this study. The base year of the dioxin inventory is 1994.

Table 1
Emission estimates grouped by: (A) three basic sources contribution to the TEQ (in percent and in kg of toxic equivalent) and (B) by congener contribution to the TEQ of PCDD/F mixture to the overall air emission (in percent and in mass basis)

(A) Basic sources	% to TEQ	Emission to air (kg_{TEQ}/yr) Min.	Mean	Max.
Industrial production	36	1.452	1.803	2.154
Organic fuel combustion	29	0.838	1.48	2.122
Waste incineration	35	1.395	1.794	2.193
Total air emissions	100	3.685	5.077	6.469

(B) Selected congeners	TEF f_i		Emission to air ($kg_{congener}$/yr) Min.	Mean	Max.
2,3,7,8-TCDD	1	4%	0.139	0.206	0.273
1,2,3,7,8-PeCDD	0.5	9%	0.663	0.894	1.126
2,3,4,7,8-PeCDF	0.5	37%	2.638	3.725	4.812
1,2,3,4,7,8-HxCDF	0.1	11%	4.341	5.735	7.13
1,2,3,6,7,8-HxCDF	0.1	7%	2790	3769	4749

Table 2
PCDD/F emissions available from 17 European Countries (EU 15+Norway and Switzerland) at 1994 reference year

Env. compartment	Release (kgTEQ/yr) Min.	Max.	Best estimate
Air	3.685	6.469	5.077[a]
Land[b]	3.85	72.6	38.2

[a] Arithmetic mean from (Quass et al., 2000) estimated values.
[b] Wenborn et al. (1999).

[1] Information on dioxin emissions are available from 17 European Countries (EU 15 + Norway and Switzerland).

2.2.2. Estimating monitored environmental concentrations

Fiedler et al. (1999) provided an overview of monitored values of dioxin contamination in Europe, as summarized in Table 3 (A). The sign " < " for soil, air and sediment measured concentrations indicate that samples below detection limit were collected. Dioxin concentrations in air in a given location might vary within a fairly broad range (up to 1 order of magnitude), due to the rapid transport and fast mixing of pollutants in air (quick reaction to pulse emissions), meteorological condition (inversion layers) and seasonal trends. More stable conditions are expected for soil, vegetation and sediment—the homogeneity of the samples should therefore be carefully evaluated.

Based on a wide literature survey and their measurements Vulykh and Shatalov (2001) determined the average congener contribution to TEQ concentrations in soil, air, and vegetation (see Table 3B). We estimated the mean congener contribution to sediment toxicity mixture, f_i based on the values obtained by Cole et al. (1999), Green et al. (2001) and Jimenez et al. (1998).

No signi...cant di...erences are observed in the congener distributions between air in European cities and in rural areas (remote from emission sources). Similar trends are observed in vegetation. Di...erences are observed in forest soil samples, which might have a slightly di...erent pro...le compared to rural and urban zone soils. These di...erences are especially noted for TCDD (up to a factor 5 in the percentage of TEQ contribution). According to the cited references, di...erences between single congeners contribution to total TEQ toxicity in sediment remains within a factor 5.

2.2.3. Estimating monitored exposure substrate concentrations

A similar approach was adopted to determine congener concentrations in exposure substrates. Data on dioxin concentration levels in milk, meat, eggs, vegetables, and ...sh were obtained from European exposure and human health data compilation King et al. (1999) [! see monitored values in Table 4A]. We calculated the mean congener contribution to TEQ concentration, f_i through the arithmetic mean of data obtained in MAFF (1997), Freijer et al. (2001) and Domingo et al. (1999) as reported in Table 4B.

The ...ve selected congeners contribute between 67% (meat) and 80% (milk) of the total TEQ in food, with 1,2,3,7,8−PeCDD alone representing up to 42% of the total contribution in fruits and vegetable. Poultry meat shows similar congener distributions as in meat. A recent survey of dioxin levels in ...sh and ...shery products on the German market observed dioxin concentrations as a function of dependence of the ...shing area: measured dioxin concentration in herring ...sh in the Western Baltic Sea are up to a factor 7 higher than those in the Irish Sea (Karl et al., 2002).

In general restricted variations are observed in the contribution of selected congeners to the total TEQ, unless for milk, where in a sample the minimum measured outlier of 1,2,3,7,8−PeCDD was a factor 7 higher than the arithmetic mean value.

2.2.4. Estimating intake fraction

A summary of the total exposure data available from risk assessment studies in several EU countries are provided by King et al. (1999). The estimates range from 0.93 to 3.0 pg_{TEQ}/kg_{BW}/day, with Spain having the highest risk exposure estimate and the Netherlands the lowest. Fig. 3 shows large variations in the food exposure pathways between countries, as a result of their respective diet and concentrations of dioxin in the consumed foods.

Based on these exposure data, iF for Western Europe can be estimated as follow: each exposure estimate is ...rst multiplied by the population of each single country

Table 3
(A) Overview of dioxin measured concentration in Europe by type of location and (B) contribution of selected congeners to environmental concentrations of dioxin toxic mixture (in % TEQ)

(A) Monitored values	Concentration of dioxin in environmental media (TEQ−based)			
	Air (fg_{TEQ}/m^3)	Soil (ng_{TEQ}/kg_{DM})	Vegetation (ng_{TEQ}/kg_{DM})	Sediment (ng_{TEQ}/kg_{DM})
Min. rural areas	<1	<1	0.3	<1
Max. rural areas	64	125	1.9	208
Max. industrial areas	252	810	86	1500

(B) Congeners contribution	Contribution to dioxin f_i (% of TEQ)			
	Air	Soil	Vegetation	Sediment
2,3,7,8−TCDD	8	14	19	3
1,2,3,7,8−PeCDD	11	12	13	6
2,3,4,7,8−PeCDF	33	23	12	21
1,2,3,4,7,8−HxCDF	7	6	3	27
1,2,3,6,7,8−HxCDF	6	6	3	6

and summed over all countries. The result is then divided by the sum of the total population over all countries. Total intake over all Western Europe is then obtained assuming an average body weight of 70 kg, and a Western European population of 431 million inhabitants. iF is then calculated by dividing the total intake from risk assessment estimates by the emitted quantity. This is termed iF(estimated).

We also de...ne a monitored intake fraction, iF(monitored). This fraction is calculated assuming median concentrations of monitored dioxin levels in foodstu...s (see Table 4) and using European food production data, as reported in the IMPACT 2002 exposure module (Margini, 2003; Pennington et al., 2003).

The predicted intake fraction, iF(predicted), is the estimate from the model for the ...ve selected congeners. Results are then multiplied to their respective TEF and summed over a single TEQ value. The iF(predicted) is determined by accounting for the single congener contribution to the overall air emission. A comparison

Table 4
Measured Dioxin concentration in exposure substrate in Western Europe and congeners contribution to TEQ in %

(A) Monitored values	Concentration of dioxin in foods (ng_{TEQ}/kg_{fat})				
	Milk	Meat [a]	Eggs	Fruits and vegetables [b]	Fish
I−TEQmin	0.2	0.1 (0.7)	1.2	0.01 (0.1)	2.4
I−TEQmedian	1.3	1.3 (1.6)	1.5	0.02 (0.9)	21.2
I−TEQ max	2.6	16.7 (2.2)	4.6	0.2 (2.4)	214
(B) Congeners contribution	**Contribution to dioxin mixture f_i (% of TEQ)**				
	Milk	Meat [a]	Eggs	Fruits and vegetables [b]	Fish
2,3,7,8−TCDD	9	19	22	17	12
1,2,3,7,8−PeCDD	21	15	18	12	11
2,3,4,7,8−PeCDF	40	24	20	42	37
1,2,3,4,7,8−HxCDF	6	6	6	2	9
1,2,3,6,7,8−HxCDF	4	3	2	1	4

[a] In parentheses are reported values for poultry.
[b] Units are in ng/kg fresh weight, in parentheses are reported values for bread and cereals.

Fig. 3. Breakdown of total dietary exposure to dioxin by food type for several Western European countries (King et al., 1999). Total dietary risk assessment exposure estimates in $pg_{TEQ}/kg_{BW}/day$ are in parentheses.

between the three iFs on the single TEQ value is then made as an overall fate and exposure model evaluation (level 3 of the comparison).

3. Results

3.1. Fate evaluation

For the ...ve selected congeners, 2,3,7,8−TCDD, 1,2,3,7,8−PeCDD, 2,3,4,7,8−PeCDF, 1,2,3,4,7,8−HxCDF and 1,2,3,6,7,8−HxCDF, model parameterization was performed on the basis of expert reviewed data from (Mackay et al., 1995; Sinkkonen and Paasivirta, 2000; Vulykh and Shatalov, 2001), as summarized in Table 5. Degradation half−lives in vegetation were assumed to be equal to those in soil (generally slower than in air). Emission estimates to air from Table 1 were used as source data for the a−spatial version of the IMPACT 2002 model. For the spatial version emission data are from (Pacyna, 1999). The sum of the releases to each spatial cell from (Pacyna, 1999) is similar to the estimations reported in Table 1.

Fig. 4 presents fate concentrations in (a) sediment, (b) vegetation, (c) soil and (d) air. Monitoring values are compared to a−spatial (or single zone) and spatial model outcomes. The range between spatial cells is given together with the mean value (total mass in the system divided the total volume), which is directly comparable with the a−spatial predictions.

The monitoring concentrations range over about two orders of magnitude and spatial model outcomes up to three. Model predictions are in a good agreement with the monitoring values. This is particularly the case for the sediment, air and vegetation compartments. Predicted chemical concentrations in soil are slightly under predicted compared to the monitored results.

Based on the uncertainty approach in Hofstetter (1998), the estimated square geometric standard deviations for fate factors is approximately 12. The 95th percentile con...dence interval model results are estimated by multiplying and dividing the model output by this value of 12 (not plotted). One should also be aware that the lower limit of monitored concentrations in soil, sediments, and in air correspond to the detection limit. Minimum concentrations might actually be lower than the reported ones.

3.1.1. Sediment compartment

The results for the sediment compartment, together with those for air, show the best ...t compared to monitored data. Note that monitored values refer to inland sediment including coastal regions. A−spatial model sediment concentrations lie within the min–max of the monitored range. Ranges in predicted results in the spatial model vary up to a factor 760. Such good predictions might be explained by a reasonable description of the sedimentation processes (dominant input pathway into sediment), accurate estimation of degradation half−lives in sediment (dominant removal rate process compared to resuspension and burial rate), and the homogeneous distribution of the pollutant in the sediment. Input to sediment is controlled by water loss processes, for which advection to sea still remains the dominant removal process controlling the concentration in most water bodies.

3.1.2. Air compartment

Good agreement exists between predicted and monitored air concentrations. A−spatial model results fall within monitored ranges. Chemical concentrations in air spatial cells show variations up to 3 orders of magnitude between continental and west oceanic zones, mainly because dioxin is emitted on the continent and the wind is predominantly from west to east. Minimum values estimated by the model refer to air spatial cells over the ocean, where essentially no emissions occur. Lower limits of monitored values are much higher, primarily because they are measured on continental spatial scales and secondly because the lower limits

Table 5
Physical–chemical properties for selected congeners used for model parameterisation

Congeners	H [a]	$\log(k_{0w})$ [b]	Haif−lifes [h] [c]			
	(Pa/m^3/mol)	( )	Air	Soil	Water	Sediments
2,3,7,8−TCDD	3.34E+00	6.8	200	900,000	4000	900,000
1,2,3,7,8−PeCDD	2.66E 01	7.4	360	1,000,000	7200	1,000,000
2,3,4,7,8−PeCDF	5.05E 01	6.8	660	550,000	13,200	550,000
1,2,3,4,7,8−HxCDF	1.45E+00	7.5	1400	600,000	28,000	600,000
1,2,3,6,7,8−HxCDF	7.41E 01	7.6	1400	700,000	28,000	700,000

[a] Mackay et al. (1995).
[b] Mackay et al. (1995) and Vulykh and Shatalov (2001).
[c] Sinkkonen and Paasivirta (2000).

correspond to the detection limit. Maximal concentrations in spatial cells are about 5 times higher than the mean results.

3.1.3. Vegetation

The range of chemical concentrations in vegetation predicted with the spatial model is larger compared to the monitoring values. However the mean spatial result, together with the a-spatial model prediction, fall within the measured range with the exception of 2,3,7,8-TCDD. Leaf–air transfer accounts for 100% of the total leaf removal rate for all chemicals. Since degradation rates within vegetation play a marginal role, chemical properties like octanol-water partitioning coe...cient and Henry's law constant in...uence discrepancies in transfer rate estimates.

3.1.4. Soil compartment

Dioxin congeners are highly lipophilic and have the tendency to accumulate in the top-soil layer. The monitored concentrations were collected in the ...rst 30 cm of soil on arable land and ...rst 2–10 cm elsewhere (Fiedler et al., 1999), the predicted model concentrations were calculated as averages in the ...rst 30 cm. This corrected by about a factor of 10 preliminary results that accounted for a 230 cm soil depth (both root-soil and vadose-soil layers).

The soil module in IMPACT 2002 is adopted from the vertical concentration-pro...le model of McKone and Bennett (2003). The model shows a high gradient in concentration decrease with increasing soil depth. In the ...rst 1cm the concentration decreases by more than 1 order of magnitude. Apart from 2,3,7,8-TCDD, the a-spatial predicted chemical concentrations in the ...rst 30 cm of soil are 2–3 times below monitored lower limits. This di...erence is slightly higher for the mean spatial results. As samples below the lower monitoring limit were collected, these values are feasible. The soil–air transfer rate is the dominant removal process from soils, about 2–4 times faster than degradation—hence provide a focus for future studies.

3.2. Exposure evaluation

Concentrations in exposure substrate were estimated for the selected congeners in several foods and compared with monitored values from Western Europe, as summarised in Table 4. Monitored min/max food concentration ratios range between 4 (eggs) and 167 (meat), and between 2 and 4 orders of magnitude for predicted concentrations among spatial cells (see Fig. 5a–g).

From spatial outcomes a weighted concentration is calculated by dividing the chemical intake rate for a given pathway by the corresponding food intake at the population level. This latter is directly comparable with the a-spatial model estimations. Overall the model predictions are in good agreement with monitored concentrations in exposure substrates, except for wheat and bread and to a lesser extent for sea ...sh.

3.2.1. Meat

Modelled concentrations fall within monitored ranges for all congeners. Biotransfer factors (BTF) for meat are estimated based on the (Travis and Arms, 1988) correlation, with a max threshold value for dioxin set at 0.1 as stated Bennet et al. (2002a). For the selected dioxin congeners this threshold reduces the theoretical chemical transfer into meat by up to 1 order of magnitude (because of their high K_{ow} that would otherwise result in an unrealistically high BTF estimation).

In addition to beef, the model also estimates chemical concentrations in poultry and pigs (results are given for the a-spatial model only). BTF for these two animal species is based on the same (Travis and Arms, 1988) correlation as for beef, but is modi...ed to account for the speci...c feed intake rate and fat content in the meat (Margni, 2003). These two factors partly explain the reduced congener transfer to pig and poultry meat. In addition, animals in IMPACT 2002 are assumed to be fed with pasture, which is a combination between roughage and industrial feeds for diary cattle and beef, but predominantly with industrial feed for poultry and pigs. Pollutant concentrations in roughage are assumed to be equal to those in leaves in the model (exposed produce) and industrial feed contaminants equal to those in stems (unexposed produce). The concentration levels in stems are 2–4 orders of magnitude lower than those in the leaf (see Fig. 5e and f). From these results, the assumption of considering industrial feed residue levels equal to those in stems is therefore questionable for high lipophilic chemicals. However, this issue should be further evaluated on additional chemicals with diverse properties using improved agricultural vegetation models.

3.2.2. Milk

The model slightly overestimates congener concentrations in milk for at least the two HxCDFs. However, results still fall within the 95th percentile con...dence interval, which is estimated at approximately plus/minus one order of magnitude.

Similarly to meat, a threshold of 0.1 was set for BTF_{milk}, reducing by a factor of 3 the original predicted values suggested by Travis and Arms (1988). This threshold appears to be con...rmed by the data collected by the two Authors, where no BTF data higher than 0.035 were observed. McLachlan et al. (1990), in a mass balance study of dioxins in lactating cows, similarly noted that these empirical K_{ow} relationships are not appropriate for dioxins. They overestimate the transfer into milk. McLachlan et al. (1990) measured biotransfer

Fig. 4. Comparison between model predictions and monitored concentration for Western Europe for (a) sediment (b) vegetation (c) soil and (d) air environmental compartment. Modelled results are given for a−spatial and spatial versions of IMPACT 2002.

factors [2] between 0.005 (1,2,3,7,8−PeCDF) and 0.016 (2,3,7,8−TCDD) for the ...ve congeners under considera− tion, i.e. between a factor 6–20 below the proposed maximum threshold of 0.1. Our studies with IMPACT 2002 were parameterised with empirical BTF data from McLachlen et al. (1990).

3.2.3. Fish

From the consulted sources (King et al., 1999) we could not distinguish between monitored congener con− centrations in seawater and fresh water ...sh. The model appears to predict accurate concentrations in ...sh for fresh water systems, but to slightly underestimate con− centrations in seawater ...sh, by a factor 2 (for HxCDFs) to 100 (2,3,7,8−TCDD).

As no relevant monitored concentration data are available, it is not possible to determine whether the model underestimates seawater concentration or bio− concentration factors in sea...sh. Seawater concentra− tions in northern Europe might also be signi...cantly in...uenced by external imports associated with emissions outside Western European system, e.g. emissions trans− ported by the Gulf Stream into the region. For 2,3,7,8− TCDD, the larger discrepancies might also be explained by overestimation of monitored values, due to limi− tations in analytical detection and assuming the mon− itored concentration equals the detection limit. Unfortunately we don't have any information about the number of positive samples over the total to evaluate the extent of this potential overestimation.

3.2.4. Fruit and vegetables+wheat and bread

Fruits and vegetables in the model are considered exposed produce, for which concentrations are assumed to be equal to those in the generic agricultural vegeta− tion leaf compartment. Model estimations are in a good

[2] BTF are obtained by dividing carry−over factors measured by McLachlan et al. (1990) by the reported daily milk production rate of 28 l/day. Please note that the carry−over rate is expressed as the dimension− less ratio between input/output ...uxes and BTF the ratio between chemi− cal concentration in milk divided by chemical input ...ux.

agreement with monitoring levels. This is also the case for the spatial model results, for which the range is broader compared to the monitored values.

Monitored concentrations in wheat and bread are much higher compared to those in fruits and vegetables and close to model prediction for leaf. Stems under-estimate congener concentrations between 3 and 4 orders of magnitude—suggesting wheat should be associated to exposed produce rather than unexposed produce.

Fig. 5. Comparison between model predictions and monitored concentration for Western Europe for (a) meat, (b) milk, (c) fresh water ...sh, (d) sea ...sh, (e) fruits and vegetable, (f) wheat and bread concentration, and (g) eggs.Modelled results are given for a-spatial and spatial versions of IMPACT 2002

3.2.5. Eggs

Mean concentrations predicted by the spatial model fall within the range of monitored values. This is not the case for the a−spatial model prediction, in particular for 2,3,7,8−TCDD and to a lesser extent also for 1,2,3,7,8−PeCDD and 1,2,3,7,8−PeCDF.

3.3. Intake fraction

Fig. 6 compares 1) the intake fractions predicted by the model, iF(a−spatial) and iF(spatial) with 2) those based on median values of monitored concentrations combined with the food production statistics, iF(moni−tored), and 3) those extrapolated by estimations from risk assessment studies in several European countries, iF(estimated).

Estimation of 95th percentile interval for the model results is based on the approach/values of (Hofstetter, 1998). Uncertainties for estimated and monitored iF re...ect minimum and maximum values from literature.

Fig. 6 presents the iF(estimated) from risk assessment studies for Western Europe (King et al., 1999) of 3.5.10 3, implying that 3.5 parts per thousand of dioxin released into the environment are likely to pass into the western European population. This estimate is in the same order of magnitude as that for the USA (iF=2.10 3), as cal−culated Bennet et al. (2002a) based on a recent survey of dioxin exposure in the US (USEPA, 2001). IMPACT 2002 predicts intake fractions of 3.9.10 3 and 1.1.10 2 for the a−spatial and the spatial version, respectively.

Note that only emissions to air are taken into con−sideration. However, since most of the emissions to land are ''stored'' in reservoirs—like disposal sites—they are unlikely to enter the food chain in signi...cant quantities on an overall European or US population basis.

The iF(predicted) based on the empirical BTF values for milk from McLachlan et al. (1990), are comparable to the iF(estimated), see Figs. 6 and 7. The iF from monitored data are about 4 times higher than the esti−mates but still remain within the con...dence intervals.

Fig. 7 provides a breakdown of the results into single exposure pathway contributions. Milk, exposed produce and meat are the dominant exposure pathways. Since the iF(monitored) accounts for the same production statistics as adopted in IMPACT 2002, the concentra−tions in food only in...uence the resulting di...erences.

Chemical intake via milk based on empirical BTF predicts iF close to monitored values. The opposite is observed for unexposed produce, as explained earlier by the discrepancies between the model predictions and the observed concentrations.

IMPACT 2002 determines dioxin intake through sea−water ...sh (iF−...sh=7.7.10 7) about 1 order of magnitude below that through fresh water ...sh−related intake, and about a factor 700 below the intake estimated by in risk assessment studies (iF ¼5.25.10 4) (King et al., 1999) 3.

4. Discussion

In this evaluation of IMPACT 2002 only con−taminants from Western European sources are con−sidered, so predicted concentrations are not absolute values but re...ect the contributions from these sources. As dioxins are a ''continental scale'' chemical (the lar−gest part of these emissions remains withing in Western Europe) they generally will not contribute to relevant discrepancies between model predictions and monitored values. Obvious discrepancies include near border areas of the modelled region and for sea ...sh that may be caught in remote areas more in...uenced by other sources.

Dioxins congeners were identi...ed as suitable chemi−cals for a ...rst empirical evaluation of the IMPACT 2002 multimedia/multi−pathway model. The literature provide a large amount of monitoring data, collected over all of Europe, as well as air emissions inventory estimates. As emission and monitoring data are usually published in terms of TEQs, usually stating nothing about the exact PCDD/F mixture composition, we had to nevertheless estimate the contribution of each selec−ted congener to the overall TEQ based on selected pub−lications, for which information on PCDD/F mixtures is available. This introduces additional uncertainty in respect to the monitored values, but this remains smal−ler than the min./max. range of these data. Secondary emissions from land...lls into the environment are per−haps another source of uncertainty and should still be carefully evaluated in terms of their potential importance.

The presented procedure provides a useful way of systematically conducting an evaluation of multimedia/ multi−pathway models. This facilitates interpretation at di...erent stages against empirical observations and against the results of many other existing risk investi−gations.

A number of general insights can be drawn from the results of this IMPACT 2002 evaluation in respect to using POPs data, and speci...cally data for PCDD/F congeners:

- The soil module slightly underestimates mon−itored concentrations, probably due to an over−estimation of volatilisation losses. The processes and mixing mechanisms leading to high vertical concentration gradients for lypophilic chemicals should be reviewed.
- The vegetation module, designed for agricultural crops, predicts accurate concentrations for lypo−philic chemicals thanks to the introduction of a loss rate, which is determined assuming 1 yr

3 Calculated assuming ...sh exposure is contributing on average to 15% of the total dioxin exposure (see Fig. 4) and a iF(estimanted)=3.5.10 3

Fig. 6. Intake fraction (iF) for dioxin emissions in Western Europe (in TEQ basis): IMPACT 2002 model predictions (spatial and a-spatial scenarios) vs. estimation from available risk assessment studies vs. results based on monitored data combined with production statistics.

Fig. 7. Break-down of intake fraction per exposure pathway for model predictions and monitored values. iF(a-spatial)* estimates milk concentration based on Travis and Arms (1988) K_{ow}-correlation; iF(a-spatial) and iF(spatial) use empirical values from McLachlan et al. (1990). iF(monitored) is based on a-spatial predicted concentrations and European food production statistics.

residence time between harvests. Assuming a chemical degradation half-life in a leaf equals that in soil appears a reasonable hypothesis for dioxin congeners, as this loss pathway appears to be negligible.

It is questionable how the model should best distinguish between exposed and unexposed produce (at least for dioxin-like compounds), with the current model basis assuming concentrations equal those in leaves and stems, respectively. Monitored concentrations in wheat (the grains being an unexposed crop) are better predicted by the leaf than the stem model. Due to likely large uncertainties and the high importance of this human exposure medium, current models may omit this distinction—as a ...rst approximation, a homogeneous concentration for the entire agricultural crop compartment only is adopted. Further modelling improvements for agricultural crops are then recommended.

The Travis and Arms (1988) method to estimate concentrations in meat and milk does not correctly predict biotransfer factors for many dioxin compounds. IMPACT 2002 accounts for a limited BTF at high K_{ow} values by setting a maximal theoretical threshold of BTF of 0.1. However, this is not su...cient, because BTFs in milk for dioxins still remain overestimated, according to measurements from (McLachlan et al., 1990).

Low dioxin concentrations in sea ...sh can be explained by two reasons. (1) The model, as run in this study, considers only contaminants in ...sh from European emissions. (2) It is also likely that concentrations in seawater is underestimated by a poor description of removal mechanisms, as the transfer rate to deep sea dominates for more than 99% the overall removal rate in surface sea.

Overall, the model accounting for spatial resolution estimates slightly higher iF compared to the one without spatial capabilities (factor 2.8). As the production rates in both models are exactly the same, i.e. the sum of the production rate of each spatial cell equals the total production of the a-spatial version, concentrations are the key parameter to look at—more speci...cally concentrations in exposed produce. The spatial model better accounts for emission locations, chemical distributions patterns, and the relative locations of agricultural production. Figs. 4 and 5 shows that some environmental or exposure concentrations are likely to vary up to 1 order of magnitude. Hence, depending on where a product is grown relative to a source in...uences the results but the extent of this in...uence is limited in terms of the overall intake fractions for the dioxins studied.

5. Conclusions

This project demonstrates that it is feasible to evaluate multimedia models in a consistent way within a structured framework using data for POPs.

Only carefully selected and well−studied chemicals, satisfying speci...c characteristics related to the system to evaluate, are appropriate to evaluate multimedia fate and multi−pathway exposure models. Four dioxin con−geners were identi...ed as suitable chemicals for a ...rst evaluation of models that provide continental scale insights (''continental chemicals''). Characteristics that need to be taken into consideration include the amount of emission/monitoring data available, the resolution and scope of the model, as well as the di...erent chemical characteristics that ensure full cover of all key fate and exposure pathways.

Given the uncertainties, the model IMPACT 2002 predicts reasonably accurate results when compared to empirical data for the POPs considered and may serve as a provisional basis for evaluating European dioxin emissions (with the reservations for the soil compartment and the sea...sh ingestion pathway). This evaluation pro−vided important insights, identifying areas where improvements have to be undertaken in priority in the model, particularly for volatilisation rate estimates from soil to air, the sea ...sh ingestion pathway/oceanic model, and for di...erent types of agricultural vegetation.

Further evaluations with additional chemicals have to be undertaken to improve the acceptance and robust−ness of multimedia/multi−pathway models, but this also requires careful planning of monitoring programs, more interaction between modellers and such monitoring programs, and an increased public right to have chemi−cal emissions data.

Appendix A. International toxic equivalency factors (I−TEFs) for 17 toxic TCDD/F congeners

Congeners	I−TEF
2,3,7,8−Cl_4DD	1
1,2,3,7,8−Cl_5DD	0.5
1,2,3,4,7,8−Cl_6DD	0.1
1,2,3,7,8,9−Cl_6DD	0.1
1,2,3,6,7,8−Cl_6DD	0.1
1,2,3,4,6,7,8−Cl_7DD	0.01
Cl_8DD	0.001
2,3,7,8−Cl_4DF	0.1
1,2,3,7,8−Cl_5DF	0.05
2,3,4,7,8−Cl_5DF	0.5
1,2,3,4,7,8−Cl_6DF	0.1
1,2,3,7,8,9−Cl_6DF	0.1
1,2,3,6,7,8−Cl_6DF	0.1
2,3,4,6,7,8−Cl_6DF	0.1
1,2,3,4,6,7,8−Cl_7DF	0.01
1 ,2,3,4,7,8,9−Cl_7DF	0.01
Cl_8DF	0.001

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