Modelling the long-range transport and deposition of dioxins; first results for the North Sea and surrounding countries.

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An important aim of describing the atmospheric cycle of contaminants is to relate emissions resulting from human activities to the appearance of the contaminants in eco-systems. For the description of the atmospheric behaviour of PCDDs and PCDFs and other substances which are present in the atmosphere in extremely low concentrations, one has to rely on similarities with other (well known) substances because measurements of atmospheric levels are very scarce. A transport and deposition model can be used to provide such a description; meteorological aspects of the model can be validated on observations of SO_2 or NO_x, for both of which a huge amount of reliable data is available. This paper presents the first results of a study on the dispersion of dioxins on a regional scale using such a model.

Atmospheric processes

The following atmospheric processes can be distinguished: emission, transport, transformation and dry and wet deposition. For some substances an additional process of re-emission can be of importance. The combination of these processes determine what is called the atmospheric residence time of a contaminant. This residence time can be defined as the time after which half of the contaminant mass is deposited or degraded. For a well mixed boundary layer of height H (m) this can be expressed as: $T_{1/2} = log_n 2 / (v_d / H + k_w + k_{ch})$, where v_d is the dry deposition velocity (m s^{-1}), k_w the wet deposition rate (s^{-1}) and k_{ch} the chemical conversion rate (s^{-1}).

Where pollutants are attached to particles, deposition rates are determined by the physical properties of the particles, large particles (> 1 μm) being efficiently removed from the atmosphere by both wet and dry deposition[1]. For particle-bounded PCDDs and PCDFs chemical conversion or photolytic degradation is minor importance compared to the effectivity of the deposition processes[2].

Deposition of pollutants in gaseous form is determined by a number of properties. In general the less reactive and the less water-soluble pollutants have lower deposition rates. For this reason it can be expected that the deposition rates for gaseous PCDF and PCDD congeners will be very low. It is therefore assumed that the deposition of gaseous PCDD/PCDF congeners can be neglected. Probably the main pathway for the removal of gaseous PCDD/PCDF from the atmosphere is photolytic degradation[3,4].

It can be concluded that it is important to know whether the PCDDs and PCDFs are on particles or in gaseous form. The gas/particle ratio is determined mainly by the vapour pressure and the available total particle surface-area[5]. Due to the temperature dependency of the vapour pressure, the gas/particle ratio will show diurnal and seasonal variation. Measurements of atmospheric levels of both phases[6,7] revealed that the highly chlorinated congeners are mainly in the particle phase and the less chlorinated in the gas phase (e.g 2,3,7,8-TCDD/TCDF). Broman et al[8]. measured air concentrations of PCDD/PCDF in Sweden and calculated aerosol fractions for the different congeners. When their concentrations are expressed in toxic equivalents (I-TEF)

it appears that approximately 30% of the PCDDs/PCDFs are in gas phase.

Materials and Methods

The model applied here is the so-called TREND model[9] which is a (Lagrangian) model for the calculation of long term average concentration and deposition. It was developed to describe the deposition of acidifying compounds such as SO_2, NO_y and NH_x[10] but has also been used to calculate the deposition of trace metals to the North Sea[11].

Modelling of particle deposition

Transport and deposition of particle-bounded pollutants is described using 5 particle-size classes where the particle-size distributions of emissions from individual sources can be accounted for. Dry deposition velocities as a function of particle size are taken from the model of Sehmel and Hodgson[12] and for sea surfaces from the model of Williams[13]. Because larger particles are removed faster than smaller particles, the resulting effective removal rate becomes a function of the distance down-wind from the source. Effective dry deposition velocities close to an incinerator can be in the order of 0.02 m/s. For the Netherlands as a whole they are in the order of 0.003 m/s, whereas for the Northern part of the North Sea they will be in the order of only 0.0015 m/s. Table 1 gives the particle size classes as used in the model together with typical deposition velocities and rates. Small particles are removed preferably by wet deposition whereas the very large particles are removed mainly by dry deposition. The size distributions as used in the calculations are obtained from measurements at a number of municipal incinerators in the Netherlands[22]. From these measurements it appears that in some cases more than 50% of the particles have an aerodynamical diameter >20 μm.

Table 1. Atmospheric residence time $T_{1/2}$ and transport range $R_{1/2}$ for the 5 particle-size classes as used in the TREND model. The ratio between dry and wet deposition is also given. Values are based on average climatological conditions in the Netherlands.

particle-size class (μm)	v_d (m s^{-1})	k_w (% h^{-1})	k_{ch} (% h^{-1})	dry/wet ratio	$T_{1/2}$ (h)	$R_{1/2}$ (km)
<0.95	0.00065	0.8	0.1	0.36	63	1800
0.95 - 4.0	0.0025	5.0	0.1	0.23	11	320
4.0 - 10.0	0.0071	5.0	0.1	0.64	8	230
10.0 - 20.0	0.013	5.0	0.1	1.2	6	170
>20.0	0.067	5.0	0.1	6.0	2	50

Modelling of gaseous PCDD/PCDF

For these first calculations it is assumed that all PCDDs/PCDFs are attached to particles. This leads to an overestimation of the deposition by probably not more than 30%. Concentrations will be underestimated by a much smaller percentage. We felt that at this stage the errors were acceptable.

Emissions

The emissions used in the calculations are based on available data as much as possible while missing data are estimated on the basis of emission factors and figures on production and use quantities[23]. Emission estimates were available for some countries[14,15,16,17]; most of these estimates are based on measurements at municipal incinerators and other major point sources (e.g. base-metal industry). Locations of incinerators and their capacity were available for the

Netherlands, Belgium, Western Germany and Denmark. The geographical distribution of diffuse sources (use of wood preservatives, burning of wood, metal reclamation, traffic) was assumed to be proportional to population density in the various regions. Emissions calculated for a part of Europe are given in Table 2.

Table 2. Estimated emissions of PCDD/PCDF in some countries in g I-TEQ yr^{-1}

Belgium	680	Denmark	120
F.R. Germany	890	France	2100
The Netherlands	870	Norway	60
Sweden	210	United Kingdom	1700
Poland	2400	GDR	1100

Results

Figure 1 shows the deposition distribution of PCDDs and PCDFs over a part of Europe. The deposition is expressed in ng I-TEQ m^{-2} yr^{-1}. High deposition values are calculated in the western part of the Netherlands and Belgium. The results suggest a rather steep deposition gradient over the North Sea. Average concentration and deposition values for the different areas are given in Table 3. The importance of long-range transport may be illustrated by the calculation that more than 80% of the dioxin concentration levels in Central Sweden was due to non-Swedish sources.

Table 3. Calculated average concentration and deposition for some areas. Minimum and maximum values for 30x30 km grid cells from these areas are given within brackets.

area	air concentration (fg I-TEQ m^{-3})		deposition (ng I-TEQ m^{-2} yr^{-1})	
Belgium	23.0	(12-67)	8.7	(3.2-48)
Denmark	4.9	(2.8-6.6)	1.3	(0.63-2.0)
W. Germany	14.0	(6.9-41)	3.6	(1.5-10)
Netherlands	25.0	(12-62)	8.1	(3.3-28)
UK	8.2	(0.9-21)	2.5	(0.21-6.0)
North Sea	4.9	(0.9-58)	1.3	(0.19-27)

Table 4. Comparison of predicted and measured air concentrations of dioxins.

location	predicted (1989)	measured	year	period	ref.
	fg I-TEQ m^{-3}	fg I-TEQ m^{-3}		days	
Eifel/Egge (FRG)	19	13[a]	1985	18	18
Hamburg (sub-urban) (FRG)	21	40[a]	1986	3	19
Rörvik (S)	5.0	3.6-85[b]	1986	8	20
85 km NE of Stockholm (S)	2.8	2.6	1989	64	8
130 km SW of Stockholm (S)	4.0	4.4	1989	37	8

[a] estimated, using (sum PCDD-F)/(sum TEQ) = 80.
[b] episodic situations during january 1986

Comparison with measurements

There are, unfortunately, only a few measurements available to date. Most of these measurements represent only a short period of sampling. Table 4 gives an overview of measured and predicted air concentrations. It can be concluded that calculated concentrations at the remote locations in Sweden compare rather well with the observations. The high concentrations in the Hamburg sub-urban area are underpredicted. Such local influences cannot be resolved with the current grid resolution (approx. 30 km). A more detailed comparison of calculated deposition near municipal incinerators in the Netherlands with deposition derived from soil samples revealed that also on a local scale the agreement is satisfactory[22]. In addition, concentrations in cow's milk could be accurately predicted by a chain model of which the TREND model was one of the constituents[21].

Conclusions

In this paper the deposition distribution of PCDD/PCDF over a part of Europe is calculated using the TREND model. It was assumed that all PCDD/PCDF deposition occurred in the form of particles. Both theoretical considerations and measurements suggest that this leads to an overestimation of the deposition (in I-TEQ), but probably by not more than 30%. Inherent uncertainties in the model concept at the scale as applied here are in the order of 30%[9]. The main uncertainty in the approach followed is probably the limited knowledge on emission data and emission processes. In this view the current results can be qualified as encouraging. Regardless of the uncertainties mentioned it can also be concluded that dioxins in whatever phase are transported over very large distances where the deposition load of remote areas is mostly due to fine particles (< 1 μm), while local pollution is caused mainly by large particles (> 10 μm).
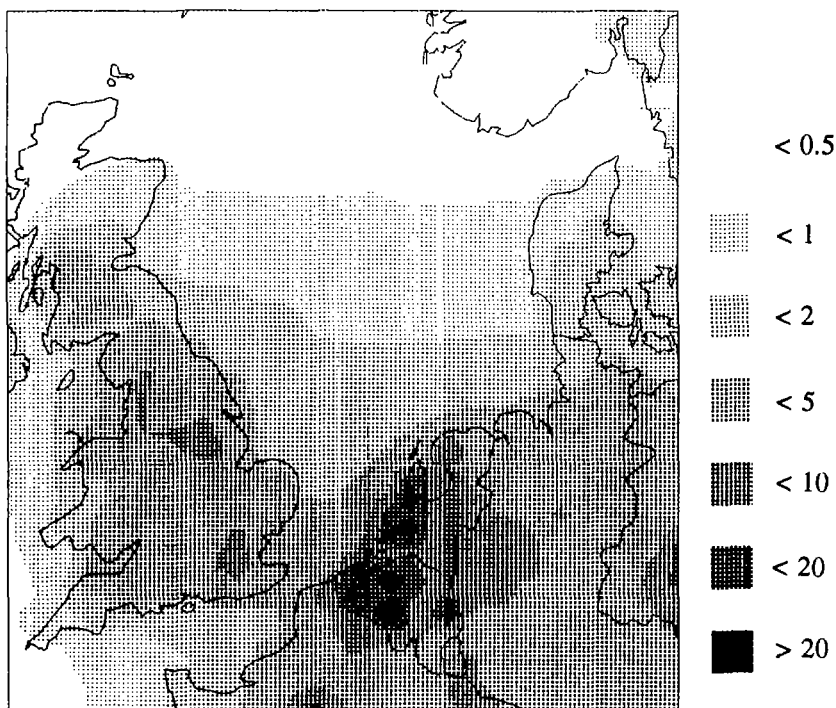

Fig. 1. Calculated deposition of PCDDs and PCDFs for the year 1989. Units: ng I-TEQ m^{-2} yr^{-1}

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