Appendix 8

Testing PEARL/OPS for volatilization from plant surfaces against experimental field data

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1. Introduction

For registration of plant protection products within the EU, the risk assessment must be done according to the new regulation 1107/2009. This regulation aims to protect humans and the environment against adverse effects of the agricultural use of plant protection products. However, an established methodology for the assessment of this exposure is lacking. The EU FP7 project BROWSE aims to develop the required models and scenarios for assessment of human exposure.

After spraying a pesticide onto the plant or soil surface, various processes influence the subsequent fate of the pesticide. Depending on the physic-chemical properties of the pesticide and the soil and weather conditions, the relative contribution of processes such as leaching, transformation and volatilization to the overall fate will differ. For BROWSE project, volatilization process from plant surfaces are simulated with an improved version of PEARL model (Leistra et al., 2001).

In order to determine vapour concentrations at appropriate locations within a landscape, there is a requirement to couple an emission model such as BROWSE-PEARL to a dispersion model. For this reason BROWSE-PEARL model has been coupled to the atmospheric dispersion model OPS (Van Jaarsveld, 2004). The output of multiple runs using the coupled models will be used in the software tools developed in the BROWSE project for BROWSE-PEARL/OPS regulators to evaluate the exposure of operators, workers, bystanders and residents after volatilization of PPPs from treated areas.

While there has been some validation of the Pearl model for determining the emission rate of vapours from treated fields, this is quite limited to date. OPS has had some validation also, but the linking of the two models is specific to BROWSE and there has been no validation so far of the combined model. The aim of this work is to test the BROWSE-PEARL/OPS modelling tool against experimental field data.

2. Materials and methods

Coupled PEARL/OPS modelling tool

Volatilization from the crop is calculated using the PEARL model (Leistra et al., 2001, Van den Berg and Leistra; 2004).

The PEARL model describes the fate of the plant production product (PPP) in the soil-plant system. The processes considered on the plant canopy are:

- Volatilization
- Photo-transformation (first-order kinetics, dependent on global radiation)
- Penetration into the plant tissue (first-order kinetics)
- Wash-off from the plant leaves to the soil (dependent on water solubility, rainfall intensity)
- At present only volatilization from plant surfaces has been considered.
- OPS (Operational atmospheric transport model of Priority Substances) is a model that simulates the atmospheric process sequence of emission, dispersion, transport, chemical conversion and finally deposition (Van Jaarsveld, 2004). The main processes considered in the OPS model are:
- Transport based on a modified Gaussian plume model (includes, e.g., atmospheric boundary layer mixing and plume depletion concept)
- Dry and wet deposition dependent on properties of the PPP (e.g. Henry coefficient) and the surface (e.g. roughness)

Coupling between emission model PEARL and atmospheric dispersion model OPS (Figure 1) has been done to determine vapour concentrations at appropriate locations within a landscape. OPS model calls PEARL to calculate the PPP emission strength on an hourly basis, using a given set of boundary conditions (e.g. meteorological).

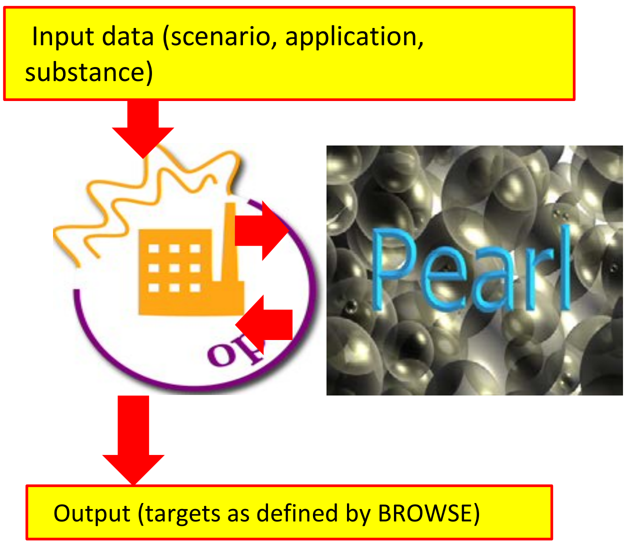

Figure 1. Coupling between emission model PEARL to atmospheric dispersion model OPS

For each BROWSE application scenario, the emissions are computed with PEARL and depend on the combination of application characteristics, substance properties and meteorological conditions, to be provided by the user. An emission file is created as an intermediate product and it's used by OPS model to provide the PPP concentration in air at the giving receptor location and height.

The input files needed for OPS are:

- Input file for OPS (setting file with information regarding compound, meteorological data, source and receptor files)
- Input file with compound properties (molar mass, VP, Kom, application)
- Meteorological file (hourly data: global radiation, air temperature, wind speed and direction, relative humidity)
- Source configuration

Source configuration requires a definition of source location, source height and source area in connection with specific application scenarios. Each location is basically treated as a point source. Groups of source locations connected to a specific scenario define a field.

- Receptor configuration

Receptor configuration requires a definition of receptor location, receptor height, and land use and roughness length at the receptor point. The receptor configuration can be set up in a gridded fashion or as a group of individual points.

Experimental data

A series of experimental measurements were made by FERA of vapour concentrations around treated fields. These data were used to validate the Pearl/OPS modelling tool to determine vapour concentrations. This is not the same as validating the BROWSE model as this predicts actual exposures, and no such data is available at the moment. However, the vapour concentration is the most important driver for predictions of actual exposures, and so a validation of the component of BROWSE that predicts vapour concentrations is a vital step in demonstrating the reliability of the BROWSE model. The experimental data have been provided by Richard Glass and a summary of two of the experiments is published in Glass *et al* (2012).

In Figure 2 is given the field plan of the conducted FERA experimental measurements.

Stomp formulated product containing the active substance pendimethalin was applied to winter barley according to the information provided in Table 1.

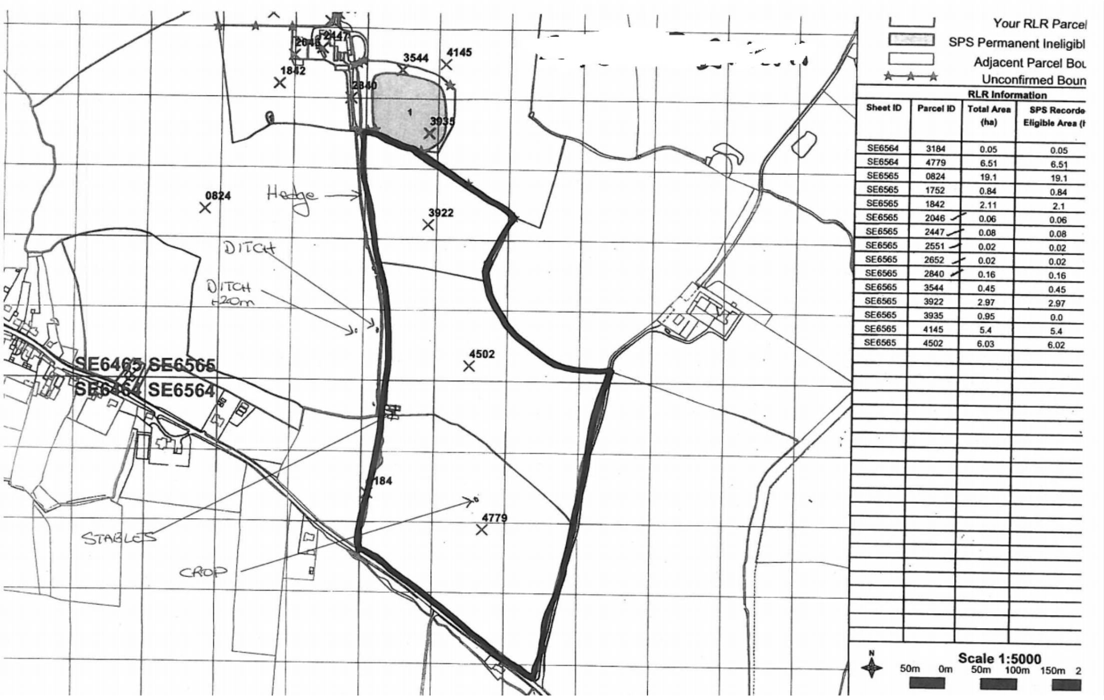

Figure 2. Field plan for the conducted FERA experimental measurements

Table 1. Application information for pendimethalin

Date of application	**21-Oct-11**
Product	Pendimethalin
Dose rate	3L/ha
Volume rate	100 L/ha
Boom height	0.5m
Nozzle	025 BFS
Pressure	3 bar
a.s. Content	400 g/L
a.s. Dose per ha	1.2 kg/ha
Crop growth stage	3 leaf
Crop	Winter barley

Sampling was made at 0.5m and 2.0m above ground with a sample flow rate 1L/min. Three replicate were taken per sampler at each height. The samplers were (Figure 2):

- In crop sampler >100m from all field boundaries
- Stable sampler at 5m from crop between 2 buildings running east west
- Ditch sampler at 10m west of field
- Ditch sampler at 30m west of field

A tree barrier was present at the running length of ditch at the west of sprayed field (Figure 2).

Setting up of PEARL/OPS modelling tool

PEARL/OPS modelling tool was set up to simulate the experimental conditions for each of the field trials (i.e. field layout, application, meteorological data, measurement location and duration). The aim was to obtain a PEARL/OPS prediction of vapour concentrations at the position and times that measurements were made and finally to compare experimental measurements with model predictions. The experimental field (surrounded by bold black line in Figure 2) was plotted in the receptor configuration file for OPS as described in Figure 3. In Table 2 is given the receptor configuration file with the position of the different samplers.

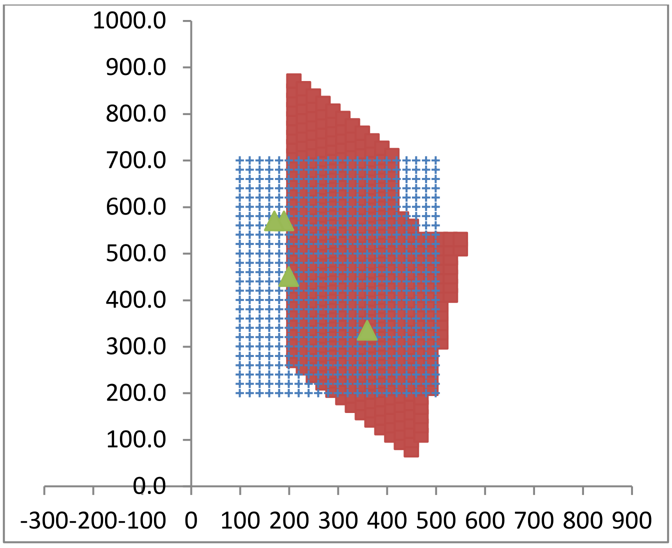

Figure 3. Receptor configuration in OPS model

Table 2. Receptor configuration file with the position of each sampler.

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rcpnr	CODE	POINT_X	POINT_Y	Zrec	Zo
1	**CROP_h**	360.0	335.0	2.0	0.01
2	**CROP_l**	360.0	335.0	0.5	0.01
3	**DIT10_h**	190.0	570.0	2.0	0.01
4	**DIT10_l**	190.0	570.0	0.5	0.01
5	**DIT30_h**	170.0	570.0	2.0	0.01
6	**DIT30_l**	170.0	570.0	0.5	0.01
7	**STAB_h**	200.0	450.0	2.0	0.01
8	**STAB_l**	200.0	450.0	0.5	0.01
9	GRID_h	100.0	200.0	2.0	0.01
10	GRID_h	120.0	200.0	2.0	0.01
11	GRID_h	140.0	200.0	2.0	0.01
12	GRID_h	160.0	200.0	2.0	0.01
13	GRID_h	180.0	200.0	2.0	0.01
14	GRID_h	200.0	200.0	2.0	0.01
15	GRID_h	220.0	200.0	2.0	0.01
16	GRID_h	240.0	200.0	2.0	0.01
17	GRID_h	260.0	200.0	2.0	0.01
18	GRID_h	280.0	200.0	2.0	0.01

Finally in Table 3 is given the source configuration file in OPS for source height set at 0.5m.

Table 3. Source configuration file for source height set at 0.5m

1	210.0	270.0	400	1
2	210.0	290.0	400	1
3	210.0	310.0	400	1
4	210.0	330.0	400	1
5	210.0	350.0	400	1
6	210.0	370.0	400	1
7	210.0	390.0	400	1
8	210.0	410.0	400	1
9	210.0	430.0	400	1
10	210.0	450.0	400	1

11	210.0	470.0	400	1
12	210.0	490.0	400	1
13	210.0	510.0	400	1
14	210.0	530.0	400	1
15	210.0	550.0	400	1
16	210.0	570.0	400	1
17	210.0	590.0	400	1
18	210.0	610.0	400	1
19	210.0	630.0	400	1
20	210.0	650.0	400	1
21	210.0	670.0	400	1
22	210.0	690.0	400	1
23	210.0	710.0	400	1
24	210.0	730.0	400	1

3. Results and Discussion

PEARL/OPS simulations against experimental results

In Figure 4 is given the comparison between model predictions (series 1) and experimental data (series 2) for pendimethalin concentration in air (ug/m^3)

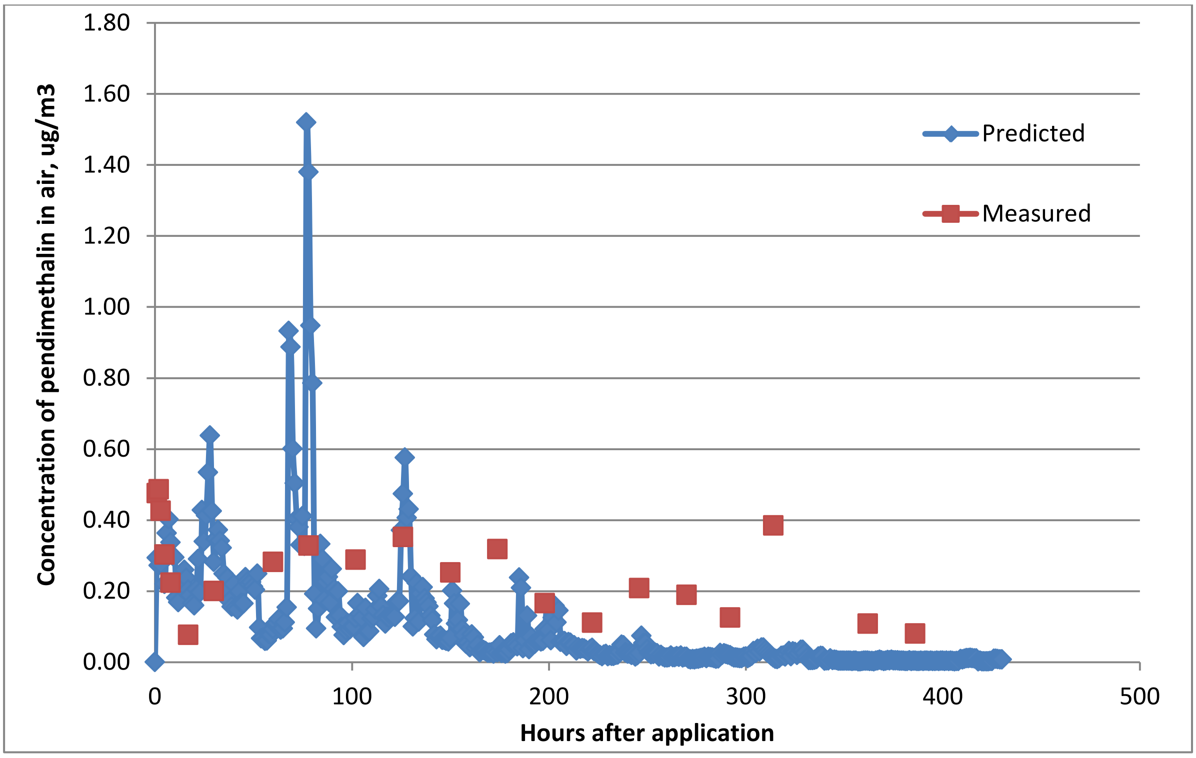

Figure 4. Comparison between model predictions and experimental data for pendimethalin concentration in air, measured at 0.5 m above the ground

The peaks predicted in the model simulations between 70 and 75 hours after pendimethalin application but not detected in the experimental trials (Figure 4) are the results of the sudden drop of wind speed after the 70th hour after application (Table 4).

Table 4. OPS meteorological input file

2011102303	0	12	0	0	129	7	84	0
2011102304	0	11.6	0	0	138	5.3	84	0
2011102305	0	11.2	0	0	119	5.4	85	0
2011102306	0	11.3	0	0	190	5.4	86	0
2011102307	0	11.5	0	0	126	4.8	85	0
2011102308	0	11.5	0	0	139	6.5	85	0
2011102309	7	11.2	0	0	108	4.1	88	0
2011102310	72	11.4	0	0	113	3.9	89	0
2011102311	110	12.1	0	0	105	4.2	88	0
2011102312	150	12.6	0	0	110	4.7	87	0
2011102313	257	13.9	0	0	110	5.5	82	0
2011102314	321	15	0	0	113	6.8	76	0
2011102315	305	15.2	0	0	109	7	75	0
2011102316	189	14.7	0	0	129	6.4	77	0
2011102317	112	13.3	0	0	96	7.7	82	0
2011102318	62	12.1	0	0	98	9.3	87	0
2011102319	9	11.3	0	0	92	8.4	90	0
2011102320	0	11.1	0	0	109	9.2	90	0
2011102321	0	11.3	0	0	101	8.9	87	0
2011102322	0	11.7	0	0	115	8.1	84	0
2011102323	0	11.7	0	0	111	7.7	86	0
2011102324	0	11.6	0	0	111	6.3	88	0
2011102401	0	11.5	0	0	119	6	89	0
2011102402	0	11.7	0	0	113	5.5	89	0
2011102403	0	11.9	0	0	120	5.6	90	0
2011102404	0	11.8	0	0	104	5.9	93	0
2011102405	0	11.5	0.13	1	104	5.4	99	0
2011102406	0	11.7	0.03	0.5	114	5.2	100	0
2011102407	0	11.9	0.07	1	107	**5.0**	100	0
2011102408	0	12	0.03	0.5	111	**0.3**	100	0
2011102409	1	12.3	0	0	133	0.3	100	0
2011102410	17	12.6	0	0	116	0.3	100	0
2011102411	63	13	0	0	182	0.3	100	0
2011102412	136	13.5	0	0	157	0.3	96	0
2011102413	154	13.5	0	0	159	0.3	91	0
2011102414	219	14.1	0	0	180	0.3	82	0
2011102415	117	13.7	0	0	122	0.3	84	0
2011102416	168	14.3	0	0	139	0.3	78	0
2011102417	204	15.3	0	0	151	0.3	72	0
2011102418	89	14.6	0	0	164	0.3	77	0
2011102419	11	13.4	0.03	0.5	113	0.3	84	0
2011102420	0	12.1	0	0	104	0.9	95	0

Indeed, as it can been seen in Table 4, the wind blows with a speed of more than 5m/h for several hours and the wind speed drops suddenly to 0.3m/h. This cause the sudden increase in concentration of pendimethalin in air predicted by the modelling tool (Figure 4) but this increase has not been observed in the experimental data.

OPS/PEARL optimisation

In the experimental field there is a tree barrier at the running length of ditch at the west of sprayed field (Figure 2). This tree barrier will lower the pendimethalin concentration in the air because of the crop interception at the time of application. However, the real effect that the tree barrier will have in the pendimethalin concentration in the air at different receptor heights cannot be evaluated by the modelling tool because the receptor configuration (Figure 3) does not involve the tree barrier. To test indirectly the effect of the tree barrier in the results OPS/PEARL was coupled to PEST software (Model-Independent Parameter Estimation and Uncertainty Analysis, Doherty; 2010) in order to estimate (calibrate) some input parameters. The parameters to estimate were application rate (to indirectly simulate the effect of crop interception the tree barrier and the vapour pressure of pendimethalin that is the main parameter that drives the substance volatilization. PEST runs OPS/PEARL changing the parameters we need to optimize, comparing model outputs with observation (experimental) data, until optimization is reached.

In Figure 5 is given the comparison between model predictions (series 1) and experimental data (series 2) for pendimethalin concentration in air (ug/m^3) after optimization with PEST software.

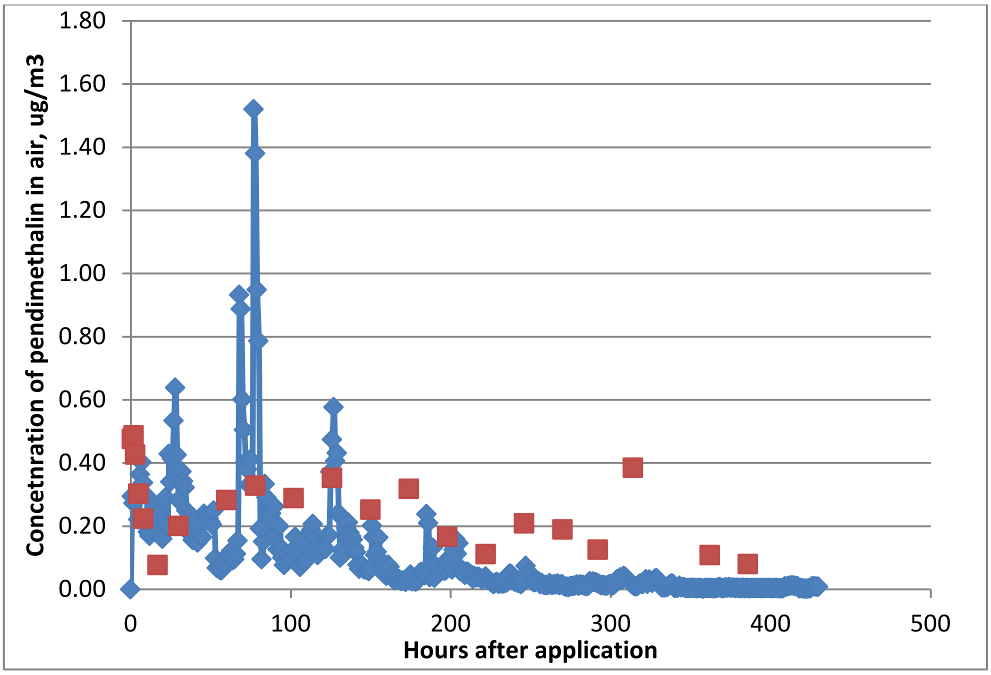

Figure 5. Comparison between model predictions and experimental data for pendimethalin concentration in air after optimization with PEST software.

Finally in Figure 6 are given the results for the optimized input parameters (pendimethalin vapour pressure and application rate) after optimization with PEST software.

- OPTIMISATION RESULTS
- Parameters ----->
- Parameter Estimated 95% percent confidence limits
- value lower limit upper limit
- **vp** **1.426930E-03** -1.080240E-03 3.934100E-03
- **ap.rate** **0.296535** -8.539690E-02 0.678467
- Note: confidence limits provide only an indication of parameter uncertainty.
- They rely on a linearity assumption which may not extend as far in
- parameter space as the confidence limits themselves - see PEST manual.
- See file stomp.sen for parameter sensitivities.
- Observations ----->

Observation	Measured value	Calculated value	Residual	Weight	Group
o1	0.476000	0.215000	0.261000	1.000	obsgroup
o2	0.487000	0.201000	0.286000	1.000	obsgroup
o3	0.426000	0.207000	0.219000	1.000	obsgroup
o4	0.303000	0.167000	0.136000	1.000	obsgroup
o5	0.224000	0.260000	-3.600000E-02	1.000	obsgroup
o6	7.700000E-02	0.190000	-0.113000	1.000	obsgroup
o7	0.200000	0.548000	-0.348000	1.000	obsgroup
o8	0.282000	0.203000	7.900000E-02	1.000	obsgroup
o9	0.328000	0.255000	7.300000E-02	1.000	obsgroup
o10	0.288000	0.386000	-9.800000E-02	1.000	obsgroup
o11	0.352000	0.136000	0.216000	1.000	obsgroup
o12	0.252000	0.263000	-1.100000E-02	1.000	obsgroup

Figure 6. Optimized input parameters after optimization with PEST software

4. Conclusions

The aim of this work was to test the BROWSE-PEARL/OPS modelling tool against experimental field data. This first evaluation of the coupled modelling tool has shown that the BROWSE-PEARL/OPS model can be used as a first tier assessment from regulators to evaluate the exposure of operators, workers, bystanders and residents after volatilization of PPPs from treated areas. Further work is needed (inclusion of possibility to simulate the effect of other crops present in the treated field in volatilization, possibility to simulate volatilization from bare soil) in order to use BROWSE-PEARL/OPS model in higher tier assessments.

The vapour pressure has a large effect on the vapour concentrations in air, so attention should be paid to the reliability of the value introduced in the model.

References

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