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**EMECAP**  
**Deliverable 5.2**  
**First report on mercury dispersion**

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## EMECAP Deliverable 5.2

### 1 Introduction

As part of Work Package 5 of the EMECAP project, dispersion model calculations have been carried out in order to determine the concentration and deposition of Mercury in the region surrounding the selected MCCA plants. The 3 plants under study are the Bohus plant in Sweden, the Rosignano Solvay plant in Italy and the Tarnow plant in Poland. Measurements campaigns at all 3 plants during the EMECAP project have provided essential data to allow validation and verification of dispersion model results.

The dispersion and deposition of Mercury around MCCA plants is a three fold problem. The first is the dispersion itself, which is dependant on local meteorology and emissions from the plant. The second is the Mercury chemistry and the third is the deposition rate for varying Mercury species. Mercury can be found in several forms and chemically react with other gases, in particular Chlorine, to transform into more reactive species. The deposition rates of these different forms can differ by up to 2 orders of magnitude and so a more precise description of the chemistry may be needed in order to access the total deposition of elemental Mercury.

This report details the dispersion and chemistry modelling that has been carried out on the Rosignano Solvay plant. A previous report (D5.1) has dealt with the preliminary studies at the Bohus plant. The approach in the current study is similar to the previous one in that the meteorology/dispersion model TAPM has been used to calculate concentrations of Gaseous Elemental Mercury (GEM) around the MCCA plant. However, in addition to this a separate off-line chemistry and dispersion model, EPISODE, has been applied that allows chemical transformations and differing deposition rates to be taken into account. Comparisons are made with measurements made during the EMECAP campaigns and average concentration and deposition fields are calculated.

In addition a ventilated box chemistry model has been applied to simulate reactions within the MCCA plants themselves. The aim being to determine if simple homogenous gas phase chemistry can explain the measured concentrations of Reactive Gaseous Mercury (RGM) in the plants.

### 2 Description of the models

Two models are employed in the current study. The first is ‘The Atmospheric Pollution Model’ (TAPM) from CSIRO in Australia, which is used for meteorological and dispersion calculations. The second model is an off-line dispersion chemistry model called EPISODE. This model has been adapted to include a Mercury-Chlorine chemistry scheme and is used to calculate deposition and concentration fields of both GEM and RGM.

## 2.1 The meteorology and dispersion model TAPM

TAPM has been developed by CSIRO in Australia as a complete pollution model that includes meteorology, dispersion and a limited photochemistry scheme (Hurley, 2002). The heart of TAPM is the meteorological model. This can be nested into a regional scale model, in this case the LAPS model (Puri et al. 1998), starting at a resolution of 10's of kilometres and reducing down with each nest to a grid spacing of around 1 km. In the current study 4 nestings have been implemented down to a resolution of 500m. Within TAPM are worldwide land use and sea surface temperature data sets that can be used for surface exchange calculations. In addition to the boundary conditions set by the regional scale model, input of local wind measurements can be used to 'nudge' the local wind field towards local observations.

In addition to meteorology, TAPM also calculates the transport and dispersion of pollutants on a pollution grid. This does not have to be the same as the meteorology grid and is set to a horizontal resolution of 250 m for this study. For the case of MCCA plants, emissions from these sources are placed into the grid as volume sources. Currently the chemistry within TAPM does not allow for Mercury reactions or for deposition so these must be calculated using an off-line model as described in the following section.

## 2.2 The chemistry/transport model EPISODE

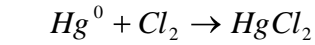
In order to calculate Mercury chemistry and deposition an off-line model, using TAPM meteorology fields, has been used. This is the EPISODE model (Slørdal et al., 2003), especially adapted to calculate Mercury chemistry and deposition. It consists of a transport and dispersion scheme, similar to TAPM and a Mercury/Chlorine/Ozone chemistry scheme. Dry deposition is calculated by using predefined deposition velocities and wet deposition occurs during precipitation events using a wet scavenging parameterisation. No aqueous phase or heterogeneous chemistry is included in the model.

### 2.2.1 Chemistry scheme

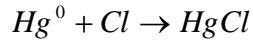
The Mercury chemistry mechanism applied in the model is based on 2 important points. Firstly that we are interested only in short time scale chemistry, as advection of the emitted plumes and ventilation of the MCCA plants occurs within a time scale of minutes. Secondly, the emission of Chlorine from MCCA plants is sufficiently high as to make the chlorine chemistry the most likely source of reactions with Mercury. Most studies of atmospheric Mercury have focused on the reaction of Mercury with Ozone (long time scales) as reactions with the Halogens, Chlorine and Bromide, are generally too low as a result of their low concentrations. However this study focuses on the chlorine reactions with Mercury.

The following gaseous phase scheme has been implemented.

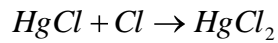
### *Mercury chemistry*



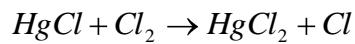
(R1)



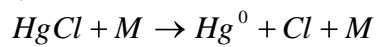
(R2)



(R3)

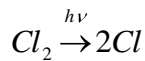


(R4)

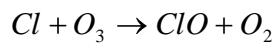


(R5)

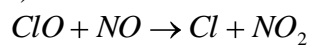
### *Chlorine chemistry*



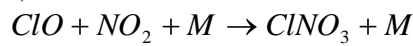
(R6)



(R7)

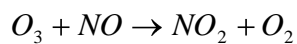


(R8)

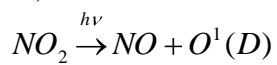


(R9)

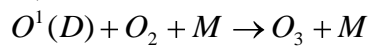
### *Ozone chemistry*



(R10)



(R11)



(R12)

The reaction and photolysis rates for these reactions are listed in Table 1

Table 1. List of reaction rates for the Mercury Chlorine chemistry scheme R1 – R12

Reaction	Reaction or photolysis rate (cm <sup>3</sup> /molecule/s)	Comments	Reference
R1	$3.0 \times 10^{-18}$		Ariya et al. 2002
R2	$1.0 \times 10^{-11}$		Ariya et al. 2002
R3	$1.0 \times 10^{-11}$		Ariya et al. 2002 Sliger et al. 2000
R4	(?)	Unknown	
R5	$1.0 \times 10^{-1} \text{ (s}^{-1}\text{)}$	Estimated	
R6	$4.03 \times 10^{-3} e^{(-0.53/\cos(\theta))}$	Photolysis rate based on radiation transfer model	
R7	$2.8 \times 10^{-11} e^{(-250/T)}$		Atkinson et al. 2000
R8	$6.2 \times 10^{-12} e^{(+295/T)}$		Atkinson et al. 2000
R9	$2.3 \times 10^{-12}$		Sander et al. 1996
R10	$1.4 \times 10^{-12} e^{(-1310/T)}$		Atkinson et al. 2000
R11,R12*	$1.45 \times 10^{-2} e^{(-0.4/\cos(\theta))}$	Combined photolysis rate	Atkinson et al. 2000

Reactions R1, R3 and R4 lead to the formation of HgCl<sub>2</sub>, which is the expected form of RGM. Of these, R1 is likely to be dominant under night time or shaded conditions since the other 2 reactions require the formation of the Cl radical by photolysis, R6. Cl is quickly produced under day time conditions but is also highly reactive. It reacts fastest with the O<sub>3</sub> molecule, and can be cycled through reactions R8 and R9 to produce the relatively stable ClNO<sub>3</sub>. As a result, the amount of Cl available to react with Hg is limited by the presence of O<sub>3</sub> and the amount of HgCl available to form RGM is also limited by its thermal decomposition, R5.

Reaction rates are available for most of these reactions however reactions R4 and R5 have not been documented in the literature. The effect that R4 and R5 have on the production of RGM is discussed in Section 3 of this report.

### 3 Results of ventilated box model calculations

Due to the high concentrations of Mercury and Chlorine found inside the MCCA plants themselves it is expected that a significant part of the chemistry will occur before emission. Measurements of RGM and GEM inside and close to the plant give the relative proportions of these two forms of Mercury and can indicate the chemical path most likely for the formation of RGM.

Table 2 lists the measured or estimated concentrations of GEM, RGM and Cl<sub>2</sub> in the 3 plants under study, along with estimated volume and ventilation rates. The Plant in Rosignano Solvay is slightly different to the two other plants in that it is an open plant with no walls so ventilation and emission is dependent on wind speed.

Table 2. Concentration and emission data from the 3 plants. For the Rosignano plant  $U$  is wind speed in (m/s).

	Bohus	Rosignano	Tarnow
GEM concentration ( $\mu\text{g}/\text{m}^3$ )	11.2		35, 125 <sup>(1)</sup>
RGM concentration ( $\mu\text{g}/\text{m}^3$ )	0.086		10
$\text{Cl}_2$ concentrations ( $\mu\text{g}/\text{m}^3$ )	800		392 <sup>(1)</sup>
Volume ( $\text{m}^3$ )	27 900	30 000	73 440
Ventilation ( $\text{m}^3/\text{hr}$ )	620 000		220 000
GEM emission (kg/yr)	62 <sup>(2)</sup> , 50 <sup>(3)</sup>	72.1 x $U$ <sup>(3)</sup>	68 <sup>(2)</sup> , 243 <sup>(3)</sup>
RGM emission (kg/yr)	0.5 <sup>(2)</sup>		19 <sup>(2)</sup>
$\text{Cl}_2$ emission (kg/yr)	4300	5000 x $U$ <sup>(4)</sup>	738, 1100 <sup>(4)</sup>

<sup>(1)</sup> Concentrations calculated from emission and ventilation data

<sup>(2)</sup> Emissions calculated from concentration and ventilation data

<sup>(3)</sup> Emissions calculated from Lidar measurements

<sup>(4)</sup> Chlorine emissions calculated from Chlorine production relative to Bohus plant.

The values listed in Table 2 are based on direct and indirect measurements. Results are not always compatible with each other in this regard.

### 3.1 Simple ventilated box model calculations for Hg and $\text{Cl}_2$

If we assume that only the gas phase reaction  $\text{Hg} + \text{Cl}_2$  (R1) occurs within the MCCA plant then it is possible to calculate a steady state RGM ( $\text{HgCl}_2$ ) concentration assuming a continuous emission of Hg and  $\text{Cl}_2$  within the plant. This is based on the following formula

$$\frac{d\text{RGM}}{dt} = k_1 [\text{Cl}_2] [\text{Hg}^0] - \text{RGM} \frac{\text{Ventilation}}{\text{Volume}} = 0 \quad (1)$$

which can be solved for RGM.

Using the values given in Table 2 and the reaction rate listed in Table 1 this gives calculated RGM concentrations of  $0.070 \mu\text{g}/\text{m}^3$  for the Bohus plant and  $0.79 \mu\text{g}/\text{m}^3$  for the Tarnow plant. No calculation could be made for the Rosignano plant due to the uncertainty in the ventilation.

The above derived steady state value of RGM at the Bohus plant is close to the measured value of  $0.086 \mu\text{g}/\text{m}^3$  which indicates that if this reaction rate is correct then it is sufficient to explain the measured concentrations within the plant. The value obtained for the Tarnow plant is a factor 12 to low, when compared to observations.



This basic oxidation reaction of Mercury is just one of a number of mechanisms by which RGM can be produced. In the next section the entire reaction mechanism (R1- R12) is employed and the results discussed.

### **3.2 Ventilated box model calculations using the Chemistry mechanism**

The inclusion of the entire set of chemical reactions (R1- R12) requires a numerical solution to the ventilated box model. The difference between the reactions described in the previous section and here is that photolysis of  $\text{Cl}_2$  can be included to produce Cl ions which react quickly with  $\text{O}_3$  and with Hg to create alternative paths to RGM. In a cell house it is unknown how much UV is available, from external sunlight or internal lighting, for the photolysis of  $\text{Cl}_2$  and so a range of possibilities is investigated to see the influence on RGM production.

Taking as an example the Bohus plant, Table 3 shows the influence of radiation, and other less well defined parameters, on the production of  $\text{HgCl}_2$ ,  $\text{HgCl}$  and Cl.

Table 3. Calculated steady state concentrations of  $\text{HgCl}_2$ ,  $\text{HgCl}$  and  $\text{Cl}$  for various input parameters using the ventilated box model for the Bohus plant.

% of maximum radiation intensity	Hg ( $\mu\text{g}/\text{m}^3$ )	$\text{Cl}_2$ ( $\mu\text{g}/\text{m}^3$ )	$\text{O}_3$ ( $\mu\text{g}/\text{m}^3$ )	Reaction rate $k_5$ ( $\text{s}^{-1}$ ) $k_4$ ( $\text{cm}^{-3}\text{mol}^{-1}\text{s}^{-1}$ )	$\text{HgCl}_2$ (RGM) ( $\text{ng}/\text{m}^3$ )	$\text{HgCl}$ ( $\text{ng}/\text{m}^3$ )	$\text{Cl}$ ( $\text{ng}/\text{m}^3$ )
<i>Radiation (<math>k_4=0</math>)</i>							
0	11.2	800	100	$1.0 \times 10^{-1}$ ( $k_5$ )	70	0	0
1.5	11.2	800	100	$1.0 \times 10^{-1}$ ( $k_5$ )	84	95	3.3
5	11.2	800	100	$1.0 \times 10^{-1}$ ( $k_5$ )	165	259	9.1
10	11.2	800	100	$1.0 \times 10^{-1}$ ( $k_5$ )	525	564	19.1
<i>Ozone (<math>k_4=0</math>)</i>							
5	11.2	800	150	$1.0 \times 10^{-1}$ ( $k_5$ )	110	169	5.8
5	11.2	800	100	$1.0 \times 10^{-1}$ ( $k_5$ )	165	259	9.1
5	11.2	800	50	$1.0 \times 10^{-1}$ ( $k_5$ )	445	520	19.3
<i>Thermal disassociation of <math>\text{HgCl}</math> (<math>k_4=0</math>)</i>							
5	11.2	800	100	$5.0 \times 10^{-1}$ ( $k_5$ )	91.5	52	9.2
5	11.2	800	100	$1.0 \times 10^{-1}$ ( $k_5$ )	165	259	9.1
5	11.2	800	100	$2.0 \times 10^{-2}$ ( $k_5$ )	410	990	8.9
<i>Reaction rate for <math>\text{HgCl} + \text{Cl}_2</math> (<math>k_5=1.0 \times 10^{-1}</math>)</i>							
5	11.2	800	100	$3.0 \times 10^{-17}$ ( $k_4$ )	174	259	9.1
5	11.2	800	100	$3.0 \times 10^{-16}$ ( $k_4$ )	282	258	9.2
5	11.2	800	100	$3.0 \times 10^{-15}$ ( $k_4$ )	1130	221	9.2
5	11.2	800	100	$3.0 \times 10^{-13}$ ( $k_4$ )	5710	11.5	8.2

The first two sets of results show that a small amount of UV radiation can increase the amount of  $\text{HgCl}_2$  in the plant significantly and that Ozone concentration has a strong effect on the amount of available  $\text{Cl}$  and hence on the production of  $\text{HgCl}$ .

The third set of results indicate the sensitivity of the model to the thermal decomposition rate of  $\text{HgCl}$ , which is not defined in the literature. This too can make a significant difference in the amount of RGM produced.

Finally the reaction rate for reaction R5 has been varied as this is unknown. It can also lead to significant changes in the steady state RGM concentration. It is quite possible that this is an important path to RGM production due to the high levels of  $\text{Cl}_2$  available within the plant. However, until more research is carried out on this reaction, this will not be included in the further model calculations.

## 4 Results of dispersion calculations with TAPM for Rosignano Solvay

Model calculations were carried out using data from the second EMECAP measurement campaign in the summer of 2002 at Rosignano Solvay. A 12 day period was modelled using both TAPM and EPISODE models as previously described.

### 4.1 Meteorological conditions at Rosignano Solvay

During the campaign period meteorological conditions were dominated by the land/sea breeze. During the day warm air rising from the land surface leads to a temperature gradient between land and sea resulting in the sea breeze circulation, circulating air at the surface from sea to land. During the night, cooling of the land surface leads to the reverse circulation where air circulates from land to sea. As a result, the wind direction oscillates from east to west during day and night respectively. During the day wind speeds are high and the boundary layer is convective (well mixed) and during the night the wind speeds are low and stable (poorly mixed). The observed wind speed and direction are shown in Figure 1.

No precipitation was observed, or modelled, during this period and so wet deposition of Mercury could not occur.

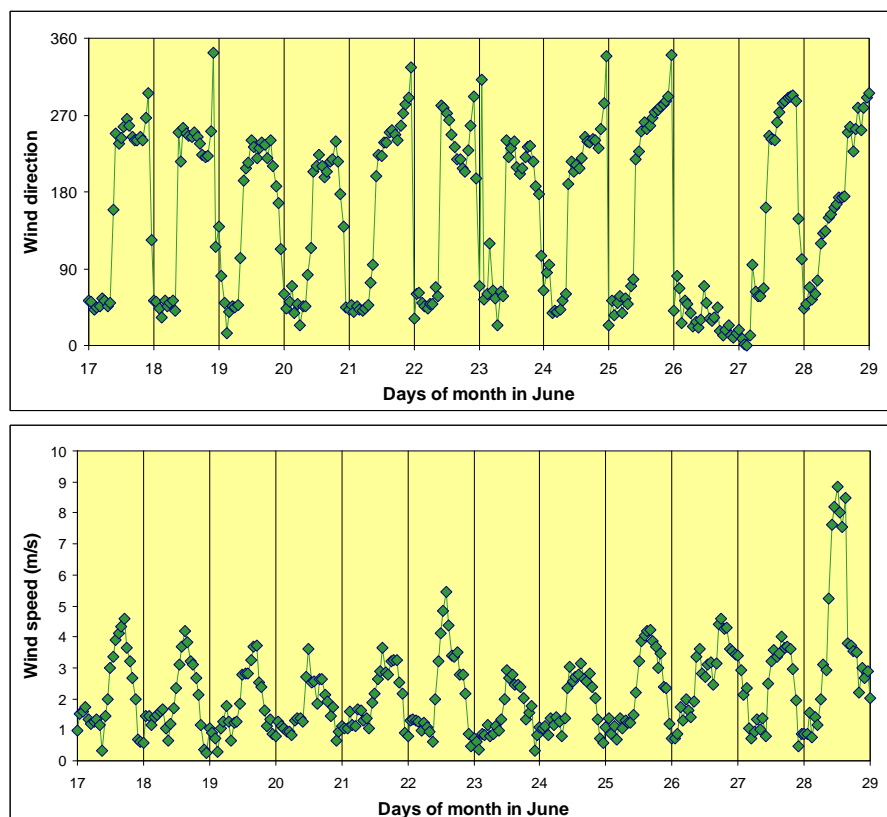


Figure 1. Observed wind speed and direction at the MCCA plant during the second EMECAP campaign.

## 4.2 Model set up

TAPM was set up using 4 nested meteorological grids, Figure 2.

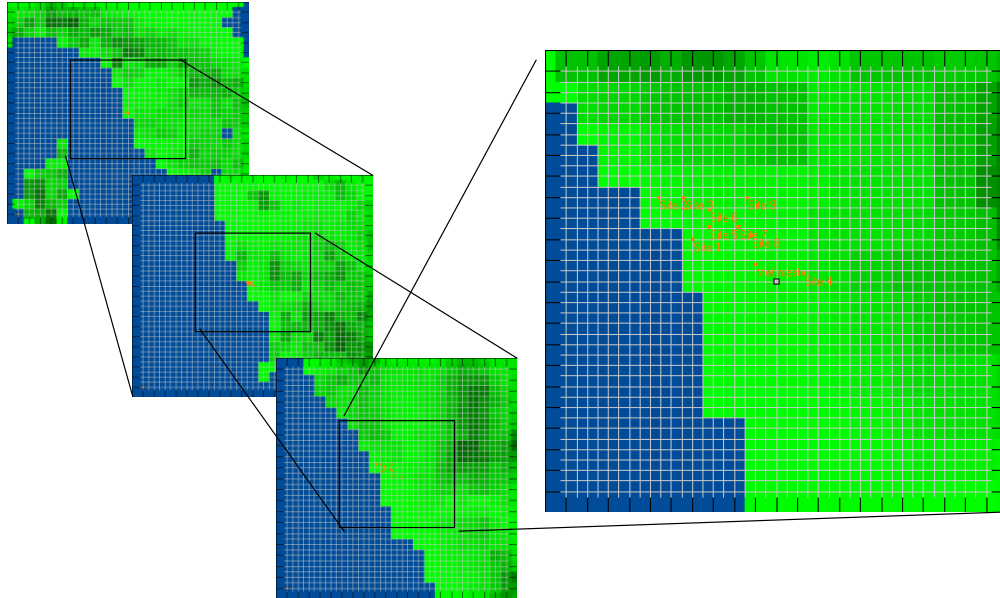


Figure 2. Showing the 4 nested meteorological grids used in the model simulations.

Table 4 gives details of the grid structure. The pollution grid was set to half the meteorology grid, which allows an increased resolution in the dispersion calculations.

Table 4. Model parameters used in the TAPM simulation

Horizontal grid dimensions	25 x 25
Horizontal grid size	From 15 km to 500 m
Horizontal pollution grid size	From 7.5 km to 250 m
Vertical grid dimensions	30
Vertical grid size	Lowest level 10 m, up to 8000 m
TGM emissions	5.5 mg/s
TGM background concentration	1.5 ng/m <sup>3</sup>

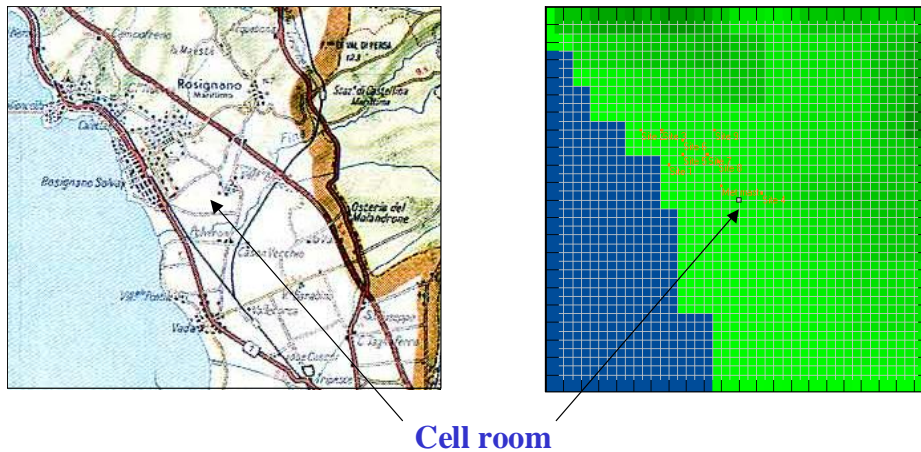


Figure 3. Position of the cell room in Rosignano Solvay and topography in TAPM. Also shown are the measurement sites placed in the model.

Local meteorological data was also available for the simulation period and this was used in the model, using the nudging technique, to help improve wind speeds near the plant site.

Simulations were carried out using Total Gaseous Mercury (TGM) only as no Mercury chemistry is available in TAPM. Emissions of TGM were placed in the grid model as a volume source. Emissions were held fixed during this period at 5.5 mg/s (175 kg/yr) as this is the average emission value determined from LIDAR measurements during the measurement campaign.

### 4.3 Concentrations at the observational sites

Concentrations of TGM were measured at 9 sites during the measurement campaign. At 1 of these sites continuous half hourly measurements are available. The other sites measured half daily average values only.

Results of the comparison between calculated and measured concentrations at site 1 are shown in Figure 4. In this figure the ‘observed’, ‘simulated’ (without wind field nudging) and ‘assimilated’ (with wind field nudging) results from TAPM are shown.

Wind field nudging tends to improve results, as would be expected. In general the simulated concentrations reflect those observed. The most significant variation occurs during early morning when simulated concentrations can peak to quite high values. This is due to the lack of mixing in the boundary layer under stable conditions and, as we will see in the following section, that emission rates are actually dependent on wind speed for the Rosignano Solvay plant.

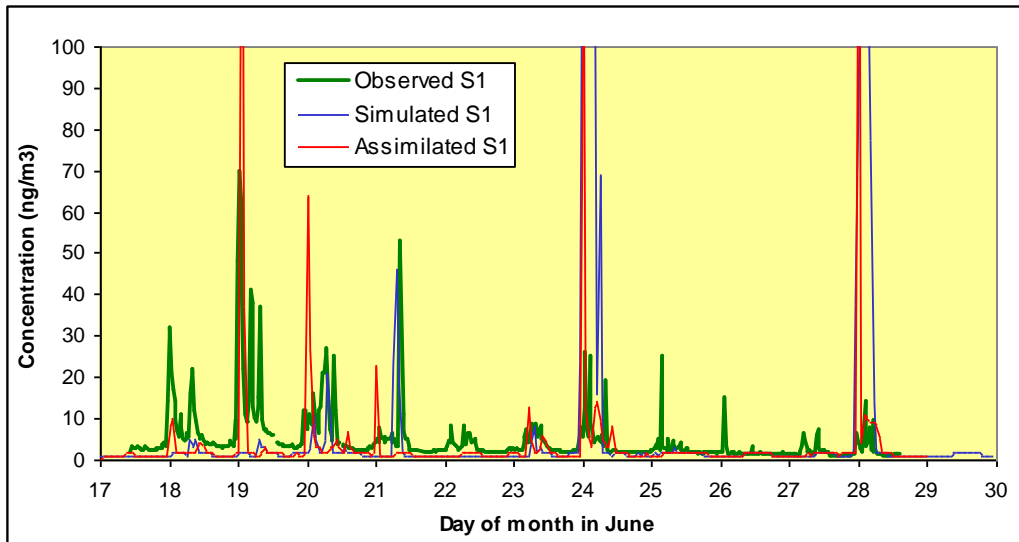
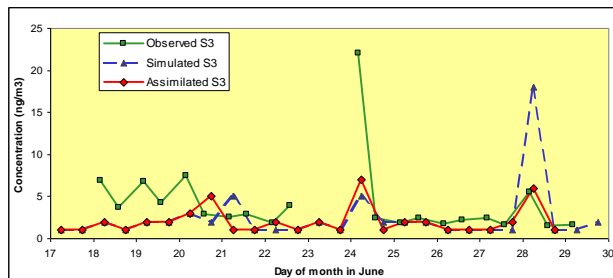
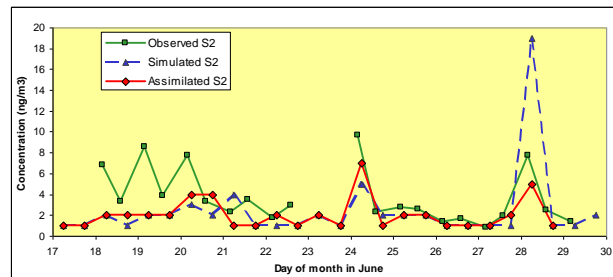


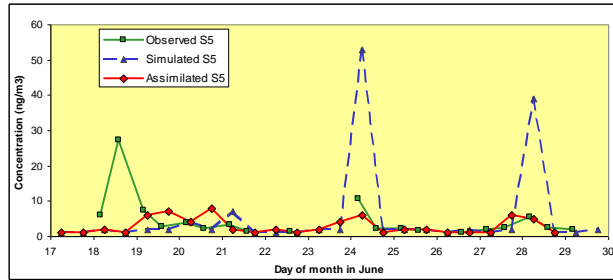
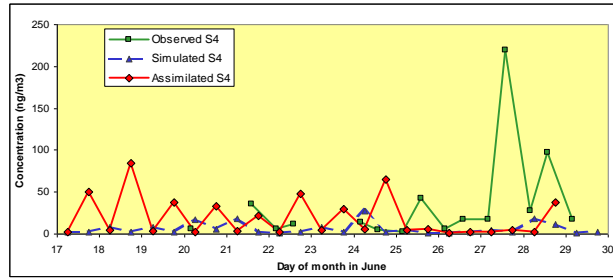
Figure 4. Hourly average concentrations of TGM at site 1 showing observed, simulated and assimilated values. See text for details.

In Figure 5 the 12 hourly average concentrations from observations and TAPM simulations are shown. Model results are improved by the use of nudging. Most sites, with the exception of S4 and S6 give quite reasonable results. Site S4 is very close to the plant itself, within 2 grid squares, and so concentrations at this site are also dependent on grid resolution. It is not known why observed values at S6 are significantly higher than at other sites in the village. This is not reflected in the model results.



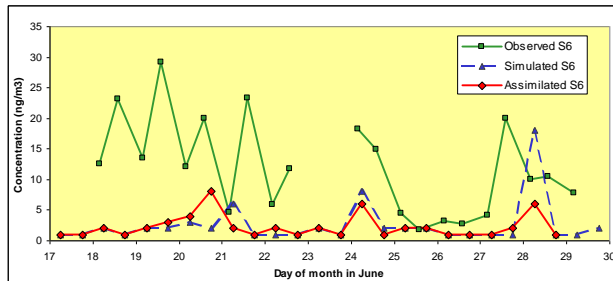
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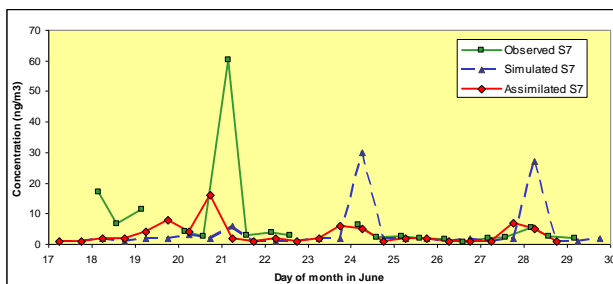
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S6

S7



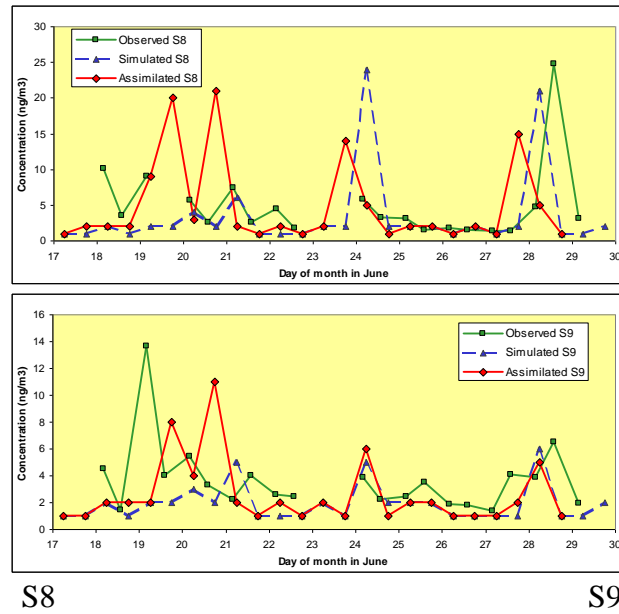


Figure 5. 12 hourly average concentrations of TGM at sites 2 to 9 showing observed, simulated and assimilated values. See Text for details.

The results for the TAPM runs are summarized in the Figure 6, which shows the average concentrations of TGM during the observational period

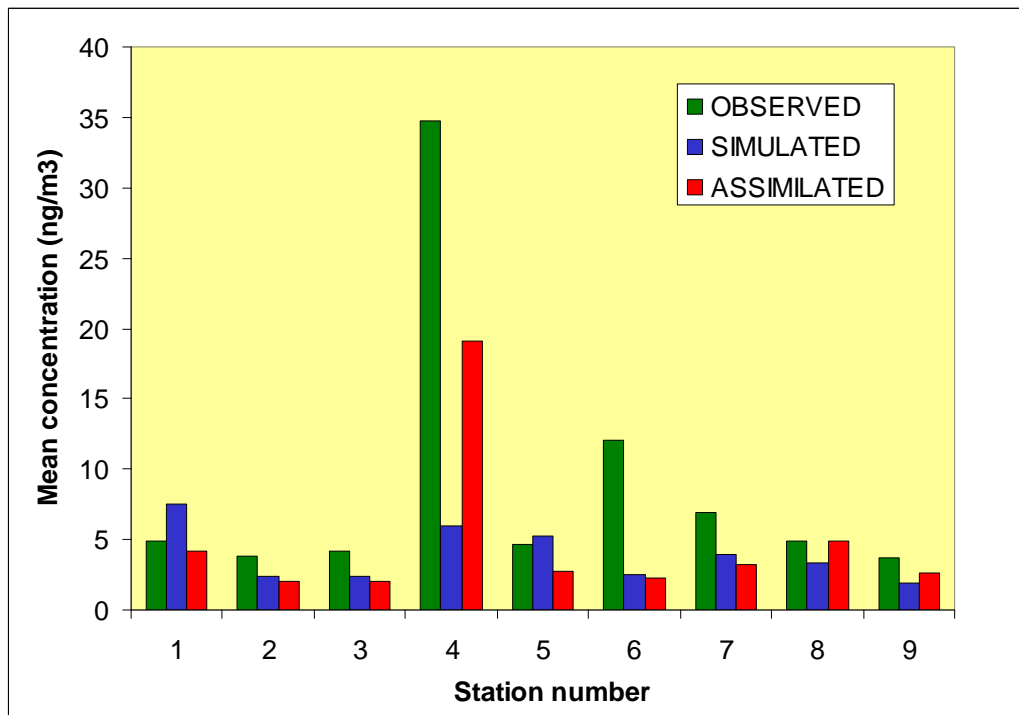


Figure 6. Average concentrations of TGM at sites 1 to 9 for the duration of the second EMECAP campaign. Showing observed, simulated and assimilated values. See Text for details.

The results using TAPM indicate that many, but not all, of the plume impact events are represented by the model. On several occasions, particularly in the first few days of the simulation, plumes are being simulated but their duration is much shorter than in reality.



This is likely to be the result of a deficiency in the simulated meteorological fields associated with the complex land/sea breeze situation that sweeps simulated plumes past the measurement sites faster than it occurs in reality.

## **5 Results of dispersion calculations with EPISODE**

The EPISODE model has been used to simulate the chemistry and transport of Mercury using hourly average meteorological fields taken from TAPM. Results of these simulations are described in the following section. The main aim is to include the effects of chemical reactions, differing deposition rates and wind dependent emissions on the concentration and deposition of Mercury in the region surrounding the Rosignano Solvay MCCA plant.

### **5.1 Comparison of TAPM and EPISODE calculations**

The EPISODE CTM uses hourly average wind fields taken from TAPM, including turbulence fields, and calculates the transport, chemical reactions and deposition of the various Mercury species. It uses the same grid spacing and number as defined in the TAPM meteorological grid.

Results from the EPISODE model are not expected to be exactly the same as those from TAPM, even when they are run with exactly the same emissions, as EPISODE uses the meteorological grid of TAPM (500 m) and also uses hourly average meteorological values, whereas TAPM uses values at every meteorological time step (~ 2 minutes). This will lead to some differences between the two models. Results from the comparison are shown in Figures 7 where the average results over the simulation period are shown.

With the exception of Site 4, which is the closest station to the plant and where interpolation between grids can strongly affect the result, the average values are very similar for all sites. From this point on reference will only be made to the results from the EPIODE model.

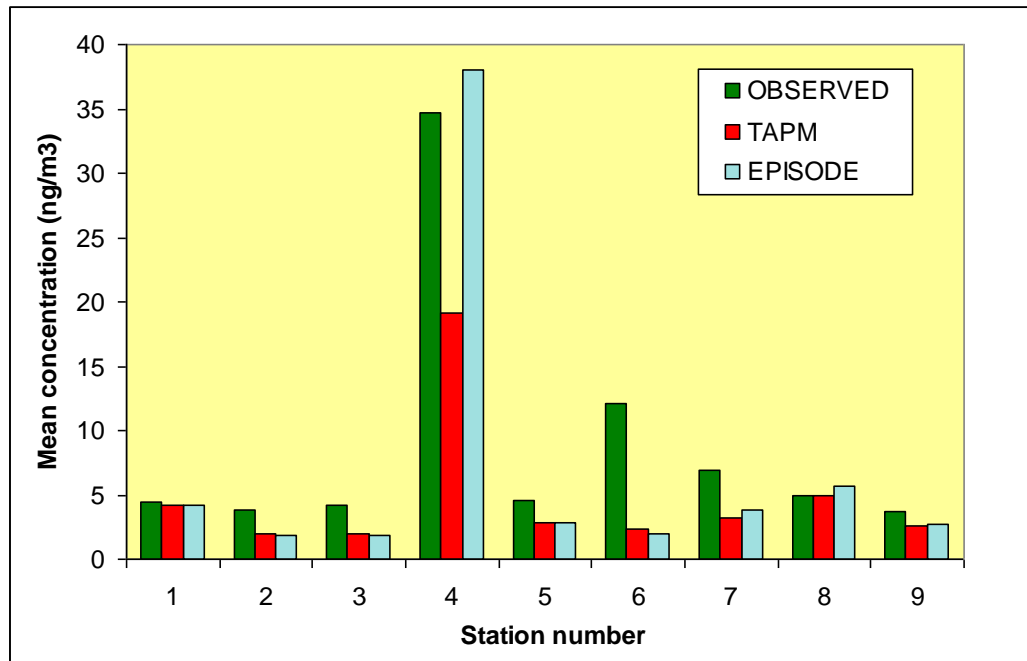


Figure 7. Comparison of observed, TAPM simulated and EPISODE simulated average concentrations at the 9 measurement sites. Input parameters, Table 4, are the same for both models.

## 5.2 Effect of wind dependent emission on the calculations

Due to the open structure of the Rosignano Solvay plant, emission from the plant has been found using LIDAR observations to be wind dependent. The relationship is assumed to be linear and a best fit to the available data from the various campaigns gives the relationship as shown in table 2.

The average wind speed of 2.4 m/s during the second EMECAP campaign, which is being modelled here, gives an average emission of 172 kg/year. This is the value used in the previous calculations.

The wind dependence of emission is important in the Rosignano region because of the strong daily cycle in wind speed, see Figure 2. Wind speeds, as well as vertical dispersion, are low during night, which is the period when Mercury concentrations near the ground should be highest. However, because emissions are wind speed dependent, mercury concentrations will not be as high as would normally be expected during the night and early morning period.

In Figure 8 observed and modelled results, with and without wind speed dependent emissions, is shown for site S1. There is a distinct reduction in the early morning peaks associated with the stable meteorological conditions when the wind dependent emissions are included. This is more realistic when compared to observations.

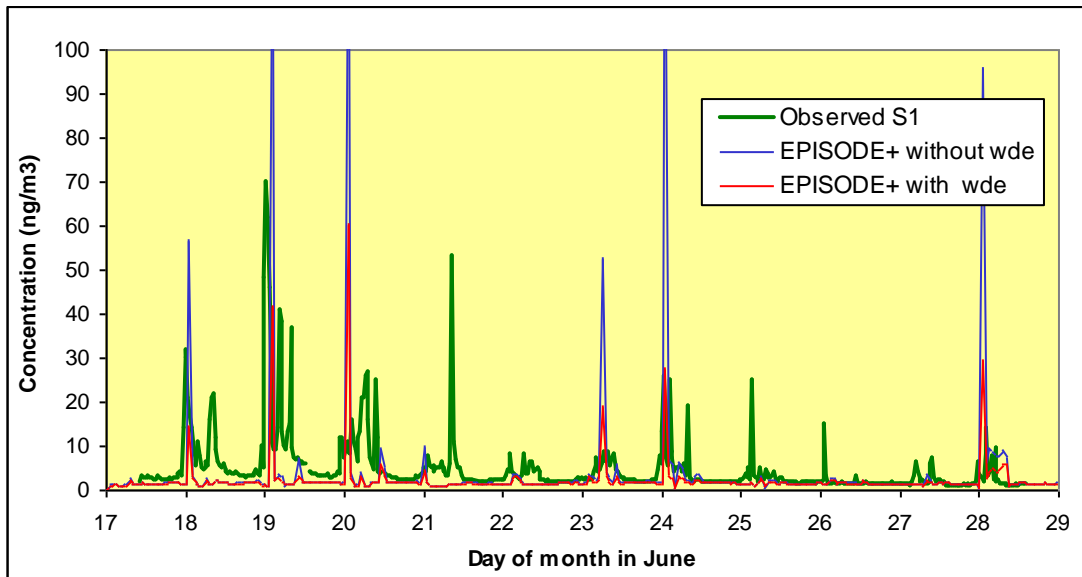


Figure 8. Comparison of observed and simulated hourly average concentrations of GEM. Shown are observations and EPISODE simulations with and without wind speed dependent emissions (wde).

### 5.3 Effect of chemistry and deposition on GEM and RGM concentrations

The model was run, using wind dependent emissions, both with and without chemistry as well as with and without deposition for the 12 day June period. Emissions and background values used in the model are listed in Table 5. Emission rates for GEM are based on LIDAR observations carried out during the campaign period. The background concentration for GEM is taken from the minimum measured values at the stations in Rosignano Solvay, whilst the background concentration for RGM is based on measurements from the background station at Donoratico, 20 km from the plant.

No measurements of emissions or internal concentrations for RGM are available for the Rosignano Solvay plant and estimates of RGM concentrations from box model calculations cannot be made due to the open nature of the plant. Two RGM emission scenarios were thus made, setting RGM emission to 2% and 20% of the GEM emissions. These must be considered as rough estimates that cover the range of values measured at the other two MCCA plants, see Table 2.

Table 5. Parameters used in the EPISODE calculations. The percentage in brackets indicates the two different RGM emission scenarios.

Compound	Emission (mg/s)	Background concentration (ng/m <sup>3</sup> )	Dry deposition velocity (cm/s)	Wet scavenging ratio
GEM (Hg <sup>0</sup> )	2.28 x U	1.5	0.05	1 x 10 <sup>6</sup>
RGM (HgCl <sub>2</sub> ) (2%)	0.045 x U	.10	2.0	1 x 10 <sup>6</sup>
RGM (HgCl <sub>2</sub> ) (20%)	0.45 x U	.10	2.0	1 x 10 <sup>6</sup>

	Background concentration (ug/m3)
O3	100
NO	1.5
NO2	15

The results for these runs are summarized in Figures 9 and 10.

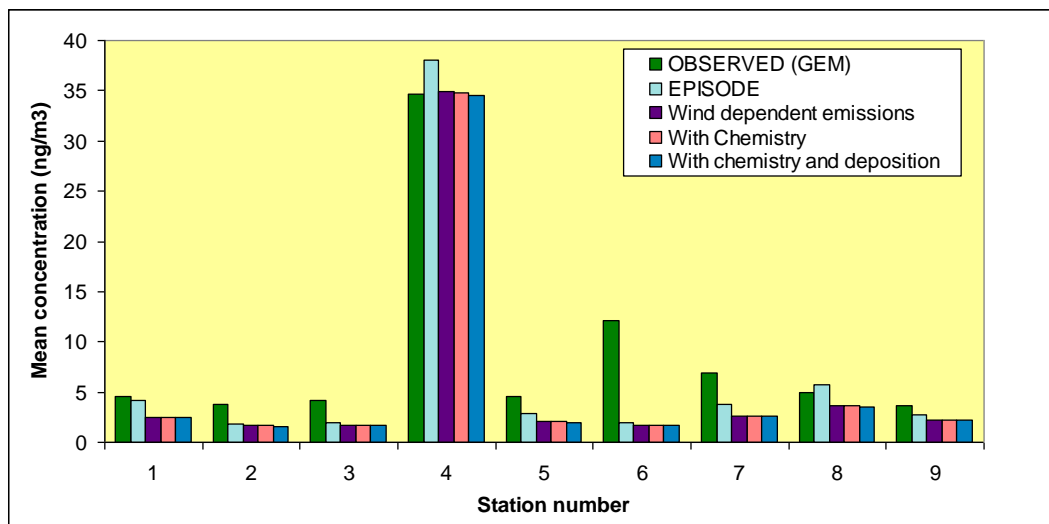


Figure 9. Observed and simulated mean concentrations of GEM for the simulation period. The simulation labelled EPISODE is the one described in Section 5.2 without chemistry, deposition or wind dependent emissions.

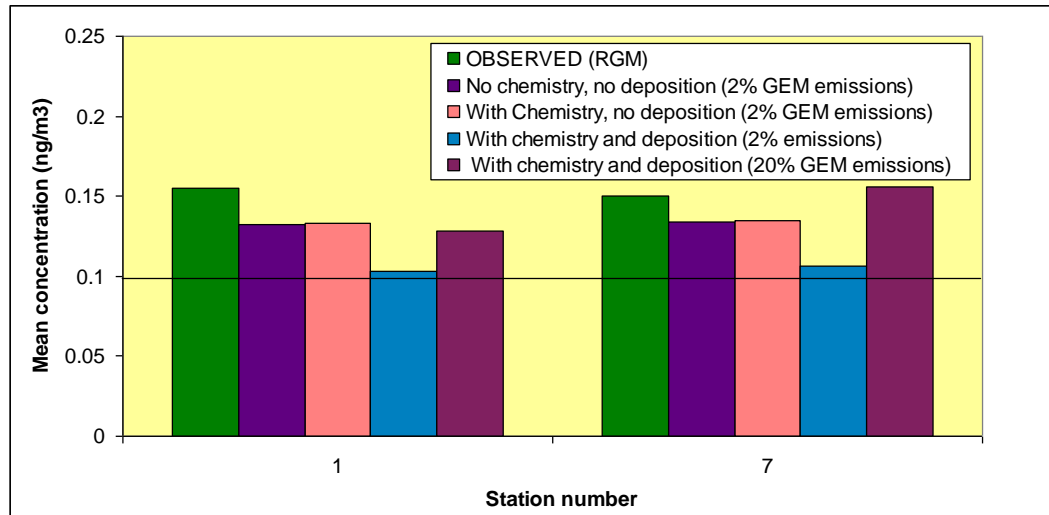


Figure 10. Observed and simulated mean concentrations of RGM for the simulation period. Observations of RGM are only available from sites 1 and 7. The black line indicates the background level.

The results show that the concentration of GEM is barely affected by either deposition or chemistry. Once the plume is dispersed in the atmosphere, reaction rates reduce dramatically due to the reduction in concentrations. The conversion of GEM to RGM becomes severely limited under normal atmospheric conditions. Deposition rates for GEM are low and so, within the local region, dry deposition does not affect the concentration of GEM.

A slight increase in the RGM concentration can be seen when chemistry is included in the model. This increase in RGM is, however, no greater than 4% on average. This indicates that atmospheric chemistry is not an important factor in determining the concentration of RGM in the region close to the emissions.

The deposition velocity for RGM is quite high, 40 times that of GEM, and results in a significant reduction in RGM when dry deposition is included in the model calculations. The results presented in Figure 10 indicate that measurements are best reproduced when either

- 1) emissions are low (2% of GEM) and the deposition is small or
- 2) emissions are high (20% of GEM) and the deposition is large.

It is not possible to distinguish between these two scenarios without further information concerning concentrations close to or inside the plant. However measurements made at the Bohus plant at 50 and 500 m from the plant do not indicate a strong reduction in RGM relative to GEM. Unfortunately the distances involved are not large enough for dry deposition processes to have a significant effect. Deposition will be discussed further in the following section.

## 6 Concentration and deposition fields

Model calculations of the average concentration and deposition fields during the simulation period have been made with the EPISODE model including chemistry and deposition. The results are shown in Figures 11 - 14 and summarized in Tables 6 and 7.

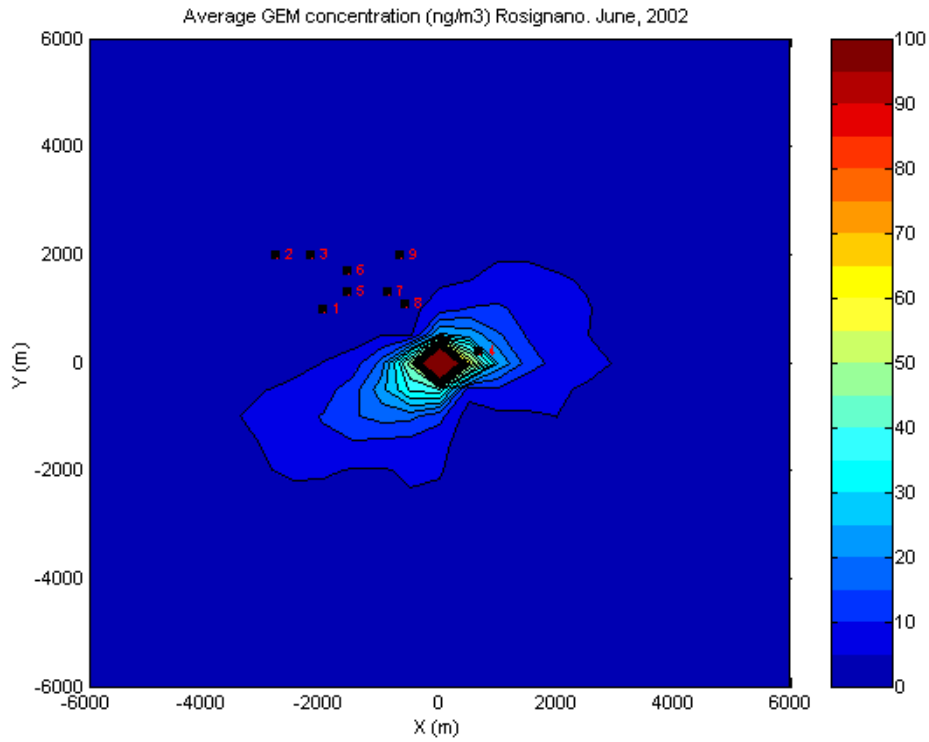


Figure 11. Mean concentration field for GEM calculated for the campaign period 17 – 28 June, 2002 at Rosignano Solvay. Scale is in ng/m<sup>3</sup>.

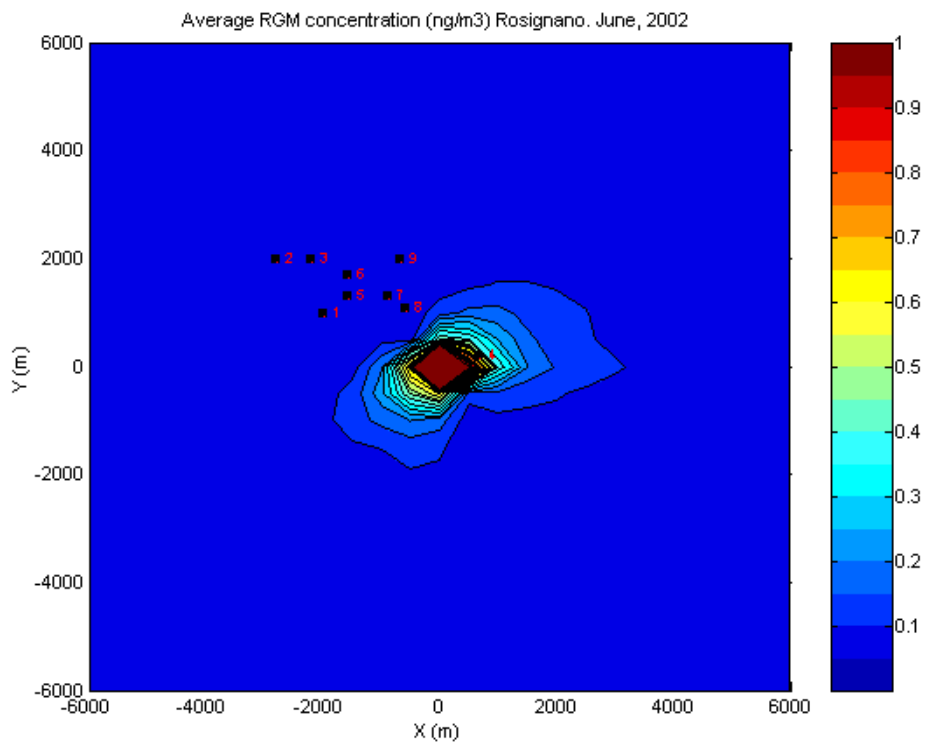


Figure 12. Mean concentration field for RGM calculated for the campaign period 17 – 28 June, 2002 at Rosignano Solvay using RGM emissions at 2% that of GEM. Scale is in ng/m<sup>3</sup>.

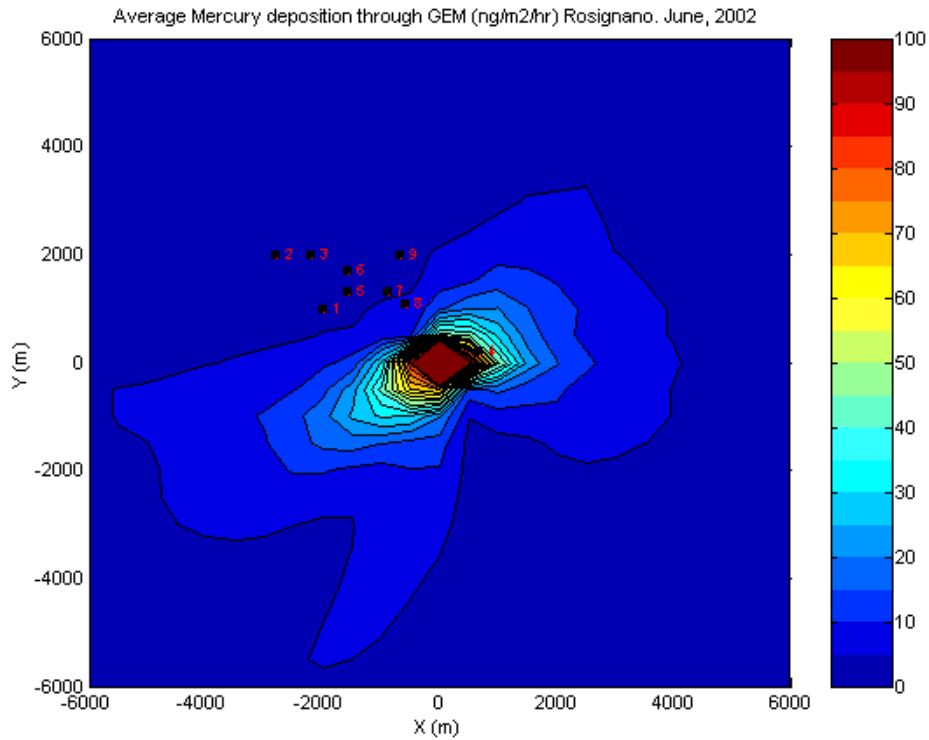


Figure 13. Mean deposition field for Mercury through GEM calculated for the campaign period 17 – 28 June, 2002 at Rosignano Solvay. Scale is in ng/m<sup>2</sup>/hour.

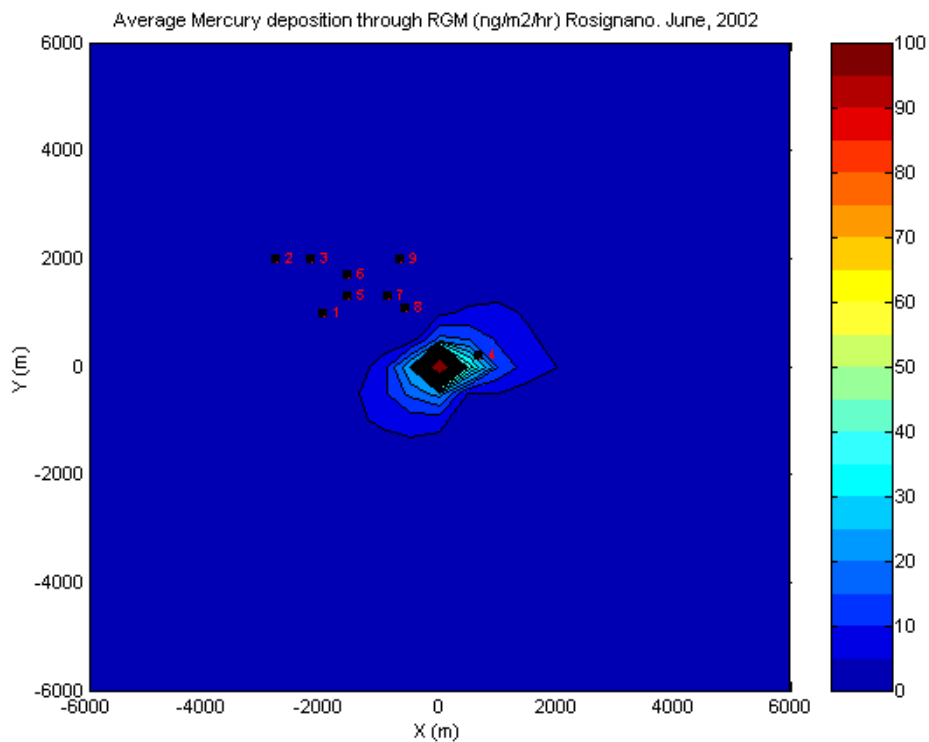


Figure 14. Mean deposition field for Mercury through RGM calculated for the campaign period 17 – 28 June, 2002 at Rosignano Solvay using RGM emissions at 2% that of GEM. Scale is in ng/m<sup>2</sup>/hour.

Table 6. Summary of maximum, minimum and mean concentrations of GEM and RGM in the model domain (12.5 x 12.5 km). The percentage in brackets indicates the % of RGM emitted in relation to GEM

Compound	Maximum concentration (ng/m <sup>3</sup> )	Background concentration (ng/m <sup>3</sup> )	Mean concentration (ng/m <sup>3</sup> )
GEM (Hg <sup>0</sup> )	189	1.5	3.29
RGM (HgCl <sub>2</sub> ) (2%)	3.45	.10	.119
RGM (HgCl <sub>2</sub> ) (20%)	32.8	.10	.283

Table 7. Summary of maximum, minimum, mean and total deposition of Mercury from GEM and RGM in the model domain (12.5 x 12.5 km). The percentage in brackets indicates the % of RGM emitted in relation to GEM

Compound	Maximum deposition (ng/m <sup>2</sup> /hr)	Background deposition (ng/m <sup>2</sup> /hr)	Mean total deposition (ng/m <sup>2</sup> /hr)	Mean deposition from emissions (ng/m <sup>2</sup> /hr)	Total deposition from emissions (g/hr)
GEM (Hg <sup>0</sup> )	341	2.6	5.9	3.28	0.51
RGM (HgCl <sub>2</sub> ) (2%)	241	2.4	3.8	1.37	0.21
RGM (HgCl <sub>2</sub> ) (20%)	2370	2.4	15.6	13.2	2.06

Table 8. Summary of total deposition of elemental Mercury from GEM and RGM in the model domain (12.5 x 12.5 km). The percentage in brackets indicates the % of RGM emitted in relation to GEM

Compound	Emissions of Hg (g/hr)	Total deposition of Hg in model domain (g/hr)	Percentage of emissions deposited (%)	Percentage of total deposition (%)
GEM (Hg <sup>0</sup> )	20	0.51	2.5	82 (2% scenario) 32 (20% scenario)
RGM (HgCl <sub>2</sub> ) (2%)	0.21	0.11	53	18
RGM (HgCl <sub>2</sub> ) (20%)	2.1	1.1	53	68
TOTAL Hg (2%)	20.2	0.62	3.1	
TOTAL Hg (20%)	22.1	1.61	7.2	

In Table 6 it can be seen that the mean concentrations of GEM and RGM within the model region are not significantly higher than the background values. This is of course dependent on the domain size but Mercury concentration levels reach background levels at just a couple of kilometres from the plant. In addition it is interesting to note that the dominant sea/land breeze wind direction means that concentrations are lowest in the North-south direction, i.e. in the village area (Figure 11). The maximum concentration is of course found in the region closest to the plant. The grid box into which emissions are made, accounts for around 30% of the total concentration of Mercury in the model domain.



Deposition of Mercury emitted from the MCCA plant, as GEM and RGM, has also been determined within the model domain by running the model with and without background concentrations, Table 7. Deposition from ambient sources has been determined but this is likely to be compensated to a certain degree by reemission from the soil, which is not included in the model. Deposition of GEM is of the same order as the background deposition rates and similar to reemission values determined from observations. Deposition of RGM is also much lower than background deposition values with the 2% emission scenario.

The total deposition of elemental Mercury, found in both GEM and RGM, from plant emissions has also been determined, Table 8. Of all the GEM emitted by the plant only 2.5% of this is dry deposited in the model domain (150 km<sup>2</sup>). This percentage is much larger for RGM, 53%, due to the much higher deposition velocities. Because of this, the total amount of Mercury deposited is strongly dependent on the amount emitted in the form of RGM. When 20% of the emitted Mercury is in the form of RGM then deposition will increase by more than a factor of 2.

## 7 Summary and conclusions

The chemistry, dispersion and deposition of Mercury emitted from the MCCA plant in Rosignano Solvay, Italy, has been simulated and a comparison made with observations. A ventilated box model has also been used to simulate the chemistry within MCCA plants and two chemistry/transport models have been used to carry out the dispersion simulations.

Results from the box model calculations show that the measured concentration of RGM in the Bohus plant can be explained by the single gaseous reaction of Hg with Cl<sub>2</sub>. These simulations also indicate the sensitivity of the production of RGM to the photolysis of Cl<sub>2</sub> and to O<sub>3</sub> concentrations, which can lead to the production of HgCl and further to HgCl<sub>2</sub>. However the values of several reaction rates, as well as the radiation intensity inside the plant, are not well known so it is not possible to come to solid conclusions concerning Mercury reactions with Cl that lead to the production of HgCl<sub>2</sub>.

The first model used in dispersion calculations, TAPM, is a meteorological and dispersion model in one and has been used to carry out tracer experiments and to produce meteorological fields. The second model, EPISODE, which is a chemistry transport model, has used these meteorological fields to model the chemistry and deposition of Mercury.

A comparison of model results and observed concentrations, measured during the second EMECAP campaign in Rosignano, has shown the model to reproduce quite well the hourly variability of concentration as well as the mean daily values for GEM. The model tends to under predict the concentrations measured in the nearby village of Rosignano Solvay. Comparison with observations show that this is likely to be the result of differences in real and simulated meteorology, rather than emissions. The MCCA plant is situated such that only occasional plumes pass by the village during the land/sea breeze cycle. This means that average concentrations are dependent on single events, rather than continuous values, and if these are not properly described in the

meteorological field then significant differences may occur. This deficiency of the model will not affect the total depositional field.

Runs to test the sensitivity of the model to chemical and deposition processes in the atmosphere show that GEM concentrations are virtually unaffected by these processes. RGM, on the other hand, is quickly reduced in the region surrounding the plant through dry deposition processes. Chemical reactions in the atmosphere appear negligible in regard to RGM concentrations. An increase in concentration of just 4% has been simulated.

The simulations of RGM concentrations using RGM emission at 2% of the GEM emission strongly under predicts the measured RGM concentrations. Simulations at 20% of GEM emissions give improved results. Simulated RGM concentrations are also improved when dry deposition rates are reduced. It is not possible from the current data to ascertain which, if either of these scenarios, is the most correct. This is unfortunate as the two different possibilities can lead to widely varying Mercury deposition.

Concentration and deposition fields have been produced for the simulated campaign period. The concentration fields reach almost background values within just a few kilometres from the plant. The deposition fields indicate that 2.5% of all the Mercury emitted from the plant as GEM is deposited in the 150 km<sup>2</sup> surrounding the plant and that 53% of all Mercury emitted in the form of RGM is deposited in the same area. This indicates that if RGM emissions are high, due to reactions within the plant, then deposition in the nearby region can increase significantly.

Several points should be noted in regard to the simulations. Firstly, as previously mentioned, the reaction rates for several important reactions are not well defined. Secondly, it is difficult to estimate the RGM emission from the Rosignano plant due to its open nature and the fact that RGM has not been measured inside the plant. Hence the wide range given to the two RGM emission scenarios. Thirdly, reemission from the soil has not been included in the calculations. Observations indicate this to be of the same order of magnitude as the deposition.

## 8 References

- Ariya, P.A., Khalizov, A. and Gidas, A. (2002) Reactions of gaseous mercury with atomic and molecular halogens. *J. Phys. Chem.*, 106, 7310-7320.
- Atkinson, R., Baulch, D.L., Cox, R.A., Hampson, R.F., Kerr, J.A., Rossi, M.J., Troe, J. (2000) Evaluated kinetic and photochemical data for atmospheric chemistry: Supplement VIII, Halogen species - IUPAC subcommittee on gas kinetic data evaluation for atmospheric chemistry, *J. Phys. Chem. Ref. Data*, Vol.29, 167-266.
- Hurley, P. (2002) The Air Pollution Model (TAPM) Version 2. Part 1: Technical Description. Aspendale (CSIRO Atmospheric Research Technical Paper No. 55).
- Puri, K., Dietachmayer, G.S., Mills, G.A., Davidson, N.E., Bowen, R.A. and Logan, L.W. (1998) The BMRC limited area prediction system, LAPS. *Aust. Meteorol. Mag.*, 47, 203–223.
- Sander, R. and Crutzen, P.J. (1996) Model study indicating halogen activation and ozone destruction in polluted air masses transported to the sea. *J. Geophys. Res. Vol. 101*, 9121-9138.
- Sliker, R. N., Kramlich, J.C. and Marinov, N.M. (2000) Towards the development of a chemical kinetic model for the homogeneous oxidation of mercury by chlorine species. *Fuel Process. Technol.* 65-66, 423-438.
- Slørdal, L.H., Walker, S.E. and Solberg, S. (2003) The urban air dispersion model EPISODE applied in AirQUIS2003. Technical Description. Kjeller (NILU TR 12/2003).

