

# report

## Experimental evaluation of the flux chamber technique to determine VOC emissions from a water surface



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# **Experimental evaluation of the flux chamber technique to determine VOC emissions from a water surface**

Prepared by the Concaawe Air Quality Management Group's Special Task Force on Emission Reporting Methodologies (STF-69)

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## ABSTRACT

Tests have been undertaken under controlled conditions in a wind tunnel to compare the emission fluxes from an open tank containing an aqueous toluene solution with those determined using a flux chamber mounted on the water surface. The tests showed that the flux chamber under-estimated the toluene emission fluxes by approximately a factor of two. This result was the same for two concentrations of toluene in the aqueous solution and for the range of flux chamber sweep air flows tested.

## KEYWORDS

Air pollution, VOC emissions, flux chamber.

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## SUMMARY

Few techniques are available to determine diffuse volatile organic compound (VOC) emissions from refinery oil-water separation plant. Experience using a remote sensing technique in an earlier Concaawe study [2] has identified the need for further work in this area. The flux chamber technique is suited to measuring emissions from area sources and is a candidate for evaluation. A major question is whether the presence/operation of the flux chamber influences the results.

This report provides the results from a study in which a flux chamber is used to determine the flux of a single VOC from the surface of a VOC/water solution. The study was carried out under the controlled conditions of a wind tunnel which allowed the emissions of the VOC to be measured in the absence of the flux chamber.

The tests were undertaken in a wind tunnel at the Ecole des Mines d'Alès (EMA), Alès, France. This tunnel has an exit duct at which point the tunnel air is well mixed. The emission flux from a water tank mounted in the tunnel can therefore be determined from the known air flow rate and the hydrocarbon concentration measured in the exit duct. The tests were undertaken with two concentrations of a toluene/water solution in the tank; close to saturation (~500 mg/l) and approximately half of that concentration. The air velocity in the tunnel was set to 2 m/s for all the tests.

The flux chamber was designed according to the guidance published by the US EPA [6]. The chamber was of a domed shape with a water interface surface area of approximately 0.2 m<sup>2</sup>. Air was pumped at a controlled rate through the chamber to collect the toluene emissions from the water surface and the concentration measured in the exhaust. The flow rates used for this "sweep air" in the tests were 3, 5 and 10 l/min.

The tests showed that the flux chamber measurements under-estimated the toluene emission flux by approximately a factor of two. This was the same for both concentrations of toluene in the aqueous solution tested and for the range of flux chamber sweep air flows tested.

In these experiments there was no free toluene on the water surface.

To try to obtain a better understanding of why the flux determined using the flux chamber was so much smaller than that from the open tank, modelling of the emissions was undertaken using mass transfer theory.

For the open tank the flux estimates provided by the model were in good agreement with the values measured in the test programme, being virtually independent of the wind speed. The model indicated that for low tunnel wind speeds (equivalent to less than 3.25 m/s at 10 m height in the atmosphere) the evaporation rate was mass limited by the liquid phase mass transfer coefficient. This has important implications for mass transfer at full scale because it suggests evaporation rates under these conditions may be less dependent on meteorological conditions and more dependent on the water channel flow.

The flux chamber uses a very low air flow rate to purge the chamber. The detailed flow inside the hemispherical chamber is complicated and modelling of this was beyond the scope of the project. Instead, it was assumed that the mass transfer coefficient was similar to that for a flat plate with laminar flow, the characteristic length

scale being the chamber diameter and time scale given by the ratio of chamber volume to purge (sweep air) flow rate.

The flow chamber model showed that the overall mass transfer was determined by the combined mass transfer coefficient, i.e. both the chamber characteristics and the liquid phase mass transfer. This suggests that by changing the former, in particular increasing the sweep air flow rate, a flux chamber approach could be used to derive or validate correlations for the liquid phase mass transfer coefficient. These could then be used with some confidence to calculate emission fluxes where mass transfer was fully limited on the water side.

These tests were undertaken on an aqueous solution containing a single component. By contrast, an oil-water separator at a refinery will contain many different hydrocarbon compounds with possibly a sheen or thin layer of free oil on the water surface.

Further work is needed to:

- Test/develop chambers of other designs.
- Use other compounds/mixtures in solution.
- Investigate the effect of a free oil layer being present.

## 1. INTRODUCTION

In 2011 Concaawe undertook a study to assess the adequacy of the emission factors used to estimate volatile organic compound (VOC) emissions from gravity type oil-water separator systems [2]. That study was designed to compare the emission fluxes from a separator determined using measurement techniques against those estimated using industry standard emission factors and algorithms. Field tests were conducted on separators at two refineries. Amongst the measurement techniques assessed during the planning process for that project were remote VOC monitoring systems and flux chambers.

A flux chamber can be used to determine emissions from area sources by sampling. The chamber is rested on the surface of a section of an emission source. Air is drawn into the chamber at a known rate and the emission concentration is measured in the vent flow. The emission flux from the area under the chamber is calculated from the product of the concentration and the sweep air flow rate through the chamber – see **Section 2**.

During the preparation for the Concaawe project it was learned that an unpublished comprehensive flux chamber study had found considerable variations in flux estimates between flux chambers of the same make and also between different types. It was, therefore, decided not to use a flux chamber in the project. On completion of the project, as described in [2], determination of the mass emission flux from oil-water separation using the remote sensing technique proved particularly problematic at one of the sites. A further means of determining such emissions is therefore needed.

Concaawe decided to look afresh at the potential use of flux chambers on oil-water separators. A review was carried out. Potential problems identified were that both the presence of the flux chamber on the surface of the separator and the induced air flow may influence the rate of VOC emission from the water surface. The review identified a lack of data and a need for a programme of testing

This report provides the results from experiments carried out to investigate whether a flux chamber is able to reproduce the flux of VOC from a water surface. A simple one component solution was chosen. The experiments were carried out using a water tank mounted inside a wind tunnel to provide a control for the evaporative flux. A flux chamber was mounted on the surface of the liquid within the tank. The tests were undertaken for Concaawe by EMA using the wind tunnel facilities at the Ecole des Mines d'Alès (EMA), Alès, France. This report provides a summary of the results. More details are contained in the *EMA Study Test Report* reproduced in **Appendix 2**.



## 2. FLUX CHAMBER

An emission isolation flux chamber comprises an enclosure which is mounted on the surface from which emissions are emanating. There are a number of different types of flux chambers. The US EPA has published guidance on the design, specification and use of one particular domed shaped chamber [6]. The flux chamber used in the Concaawe tests was an Odoflux® chamber designed in compliance with the EPA specifications. Although the original guidance was for the use of this type of chamber on soil (e.g. land fill sites), they have been used for a number of applications including liquid surfaces [3][5]. The latter normally requires the fitting of floats or suspending the chamber on/over the surface. In the Concaawe tests the chamber was mounted on supports within the tank so that the skirt of the chamber extended 20 mm into the water, as per the EPA guidance.

Clean, dry air is pumped into a chamber at a controlled, measured rate. Within the chamber the air inlet distributor is designed to ensure that this sweep air mixes efficiently with the emitted vapours. The concentration of the VOCs in the exhaust gas is measured in the vent flow.

The mass flux rate is calculated from:

$$M = FC/A$$

where:

M = mass flux rate (g/h/m<sup>2</sup>)

F = sweep air flow rate (m<sup>3</sup>/h)

C = VOC concentration (g/m<sup>3</sup>)

A = area of liquid enclosed by the flux chamber = 0.1964 m<sup>2</sup> for the Odoflux® type chamber used.

In the EPA design the excess pressure in the chamber is limited using a relief valve. For these tests the pressure was measured; it increased from 45 Pa at a sweep air flow rate of 1 l/min to 250 Pa at 10 l/min. This increase in pressure has an insignificant impact on the emission flux rate.

The Reynolds number calculated for the air flow within the flux chamber used was very low (i.e. Re = 28 at the maximum sweep air flow rate of 10 l/min used in these tests) indicating laminar flow.

A photograph and schematic diagram of the Odoflux® chamber used are provided in **Appendix 2**.

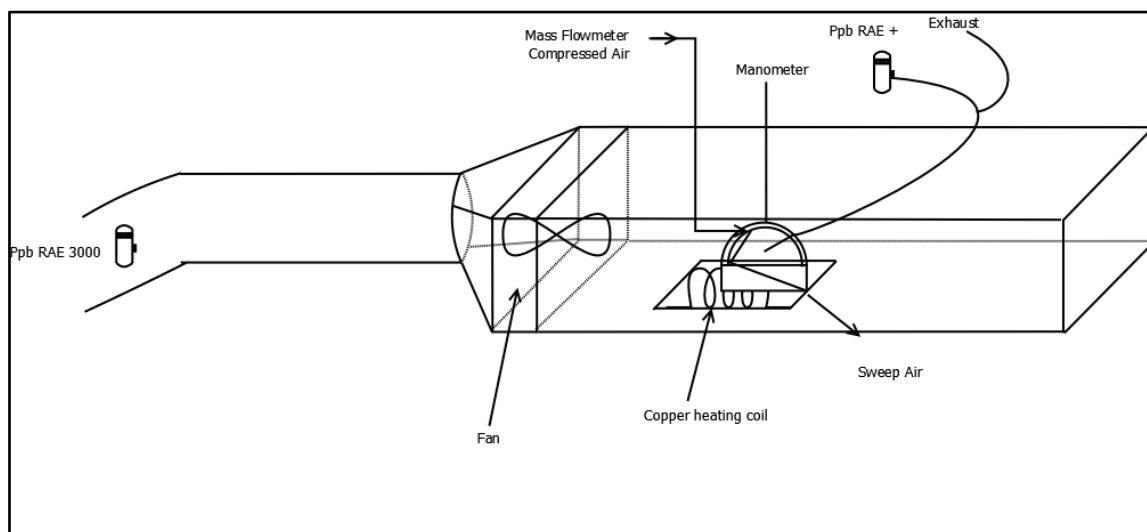
### 3. TEST EQUIPMENT, PROGRAMME AND PRE-TESTING

#### 3.1. EQUIPMENT

The wind tunnel at EMA comprises a 9m long rectangular chamber, 1m wide and 0.5m high. Air is drawn through the tunnel by a fan at the exit, with all of the exhaust air passing through a duct in which the VOC monitor was located.

The water tank was located 7m from the inlet to the tunnel with the top of the tank level with the tunnel floor. The tank was 1.25m long by 0.6m wide with a depth of 0.2m, thus holding 150 litres of water and having a surface area of 0.75 m<sup>2</sup>. The tank could be heated to about 25°C using a heating coil through which hot water was circulated. An array of sampling tubes fitted into the tank permitted water samples to be drawn for analysis. The flux chamber, when mounted on the tank, covered 26.2% of the water surface. A schematic of the wind tunnel, tank and the flux chamber with test equipment is shown in Figure 1 (from EMA Study Test Report, **Appendix 2**).

**Figure 1** Schematic of test flux chamber mounted on surface of water tank in wind tunnel



The mass emission flux from the water surface was obtained from measurements of both the VOC concentration in the vent of the tunnel and the air flow. The concentration was measured using a portable VOC monitor incorporating a photo-ionisation detector (Ppb RAE 3000). A similar detector was used to measure the flux chamber vent concentration. The velocity of the air in the tunnel was measured using a hot wire anemometer. The flux chamber sweep air was supplied from a compressor and regulated by a mass flow controller.

Tests were undertaken with aqueous solutions of toluene at two concentrations; at approximately the saturated concentration (~500 mg/l) and at about 250 mg/l. Pre-testing was also undertaken with a free

### 3.2. OVERVIEW OF TEST PROGRAMME

The primary objective of the test programme was to compare emissions from the aqueous solution within the test tank without the flux chamber in place with those determined from flux chamber measurements.

Testing was planned using toluene as this VOC is found in refinery effluent streams, is readily obtainable and can be safely stored/handled within the laboratory environment. A model was used to estimate emissions (see **Appendix 1**) and the results indicated that toluene had the appropriate physical properties to provide emission fluxes within the measurement capability of the test equipment.

A series of pre-tests were undertaken to test the equipment, determine the rate at which the toluene concentration decreases within the aqueous solution, establish the key parameters to be used (e.g. air velocity in the tunnel), etc.

The pre-tests also explored whether the thin layer of free oil that may be found on the water surface in gravity type separators could be simulated. The results were not positive and this approach was not carried forward.

### 3.3. PRE-TESTING

The airflow profile in the tunnel was established by measuring at eight heights above nine points distributed across the tank. Profiles were obtained for five velocities (1 to 5 m/s). These showed similar profiles for all velocities at all nine points. Calculation of the Reynolds number confirmed the presence of turbulent flow at all of the wind speeds considered for the tests.

For the pre-tests a near-saturated solution of toluene was used. This was pre-prepared using 400 ml of toluene mixed in 260 l of water contained in a 300 l tank, which was then used to fill the test tank. A fresh batch was prepared for each day of the tests.

To determine the air velocity to be used in the main programme, the emission fluxes from the water tank (without the flux chamber) were determined for a range of tunnel wind speeds. The results are shown in **Table 1**.

**Table 1** Toluene emission flux for different air velocities

Air velocity m/s	Toluene emission flux g/h/m <sup>2</sup>
0.6	6.0±1.5
1.0	4.8±1.1
1.5	5.2±1.1
2.0	5.1±1.0
2.5	5.1±1.0
3.0	5.5±1.0

**Table 1** shows that the emission flux was similar for the range of wind speeds tested. This was in good agreement with the results from the emissions modelling (see **Appendix 1**). The model predicted that the theoretical overall mass transfer coefficient was dominated by the liquid phase mass transfer coefficient which is dependent solely on the relative diffusivity of toluene in water.

From these test results an air velocity of 2.0 m/s was chosen for the main programme of comparative tests with the flux chamber.

## 4. SUMMARY OF THE RESULTS

### 4.1. TEST SCHEDULE

The pre-tests indicated the limitations of only testing with one toluene concentration. For the test programme a concentration of about half of the saturated solution (i.e. about 250 mg/l) was also used, being made up from 70 ml of toluene mixed into 200 l of water.

For all the tests the air velocity in the wind tunnel was fixed at 2 m/s. In all the tests the water was heated to approximately 20°C.

The planned test programme is shown in **Table 2**.

**Table 2** Planned test programme

Test	Toluene concentration mg/l	With flux chamber	Flux chamber sweep air flow l/m
1	500	No	-
2	500	No	-
3	500	Yes	3
4	500	Yes	3
5	500	Yes	5
6	500	Yes	5
7	500	Yes	5
8	500	Yes	10
9	500	Yes	10
10	250	No	-
11	250	No	-
12	250	Yes	3
13	250	Yes	5
14	250	Yes	10

### 4.2. SUMMARY OF RESULTS

#### 4.2.1. Emissions from aqueous solution – determined from tunnel vent concentration measurements

**Table 3** provides the average results from tests number 1 and 2, and from tests number 10 and 11. In these tests the toluene concentration was measured in the vent from the tunnel.

**Table 3** Emission flux rates from aqueous toluene solution in tank without flux chamber

Test numbers	Average toluene concentration in water mg/l	Average toluene concentration in tunnel vent ppb	Average normalised emission flux g/h/m <sup>2</sup>
1 and 2	470	261	5.0 <sup>1</sup>
10 and 11	261	134	2.3 <sup>2</sup>

Table notes:

1. Normalised for a toluene concentration in water of 500 mg/l
2. Normalised for a toluene concentration in water of 250 mg/l

These data are, within the uncertainties of the test, consistent with the toluene emission flux being proportional to the concentration of toluene in the aqueous solution i.e. in accordance with Henry's law.

#### 4.2.2. Emissions from aqueous solution – determined with a flux chamber

**Table 4** shows the average results from the tests with the flux chamber in place on the water tank containing a near saturated toluene solution.

**Table 4** Emission fluxes calculated from flux chamber measurements – toluene concentration approximately 500 mg/l

Test numbers	Average toluene concentration in water mg/l	Sweep air flow rate l/min	Average toluene concentration in flux chamber vent ppm	Average normalised emission flux g/h/m <sup>2</sup> Note 1
3 and 4	508	3.0	580	2.0
5, 6 and 7	492	5.0	448	2.7
8 and 9	461	10.0	171	2.1
AVERAGE				2.4

Table notes:

1. Normalised for a toluene concentration in water of 500 mg/l

**Table 5** shows the average results from the tests with the flux chamber in place on the water tank containing approximately 50% saturated toluene solution.

The data from both of these tables show that the emission flux, for a given toluene concentration, is relatively independent of the sweep air flow rate within the range used (3 – 10 l/min) and is proportional to the toluene concentration in the water.

**Table 5** Emission fluxes calculated from flux chamber measurements – toluene concentration approximately 250 mg/l

Test numbers	Average toluene concentration in water mg/l	Sweep air flow rate l/min	Average toluene concentration in flux chamber vent ppm	Average normalised emission flux g/h/m <sup>2</sup> Note 1
12	249	3.0	295	1.0
13	259	5.0	229	1.2
14	186	10.0	80.3	1.2
AVERAGE				1.1

Table notes:

1. Normalised for a toluene concentration in water of 250 mg/l

#### 4.2.3. Comparison of determined emission flux values

**Table 6** shows the ratio of the emission fluxes from the water tank without the flux chamber in place with those determined using the flux chamber.

**Table 6** Comparison of emission fluxes from the water tank with those determined using the flux chamber

Toluene concentration mg/l	Average normalised emission flux g/h/m <sup>2</sup>		Ratio of flux values determined from tunnel and flux chamber measurements
	From tunnel vent measurements	From flux chamber measurements	
500	5.0	2.4	2.1
250	2.3	1.1	2.1

The fluxes calculated using the flux chamber were about 50% of those calculated from the tunnel vent concentration measurements for both values of toluene concentration in the test tank.

## 5. DISCUSSION

In both flux chamber and control experiments the emission rate was proportional to the concentration of toluene in water in accordance with Henry's law.

The emission flux of toluene measured with the flux chamber, under the conditions of the tests undertaken, was approximately half the emission flux of toluene measured during the control experiment from the surface of the open tank. This factor was similar for both concentrations of toluene in the aqueous solution tested and for the range of flux chamber sweep air flow rates tested.

To try to obtain a better understanding of why the flux was reduced to such an extent by the presence of the flux chamber, modelling of the emissions from the water surface was undertaken. For the control tests, without the flux chamber in place, the theoretical rate of volatilisation of toluene from the aqueous solution was determined using the equations based on mass transfer theory provided in Section 4.3.2 of the US EPA Publication AP-42 [7] (see **Appendix 1**).

For the open tank the flux estimates provided by the model were in good agreement with the measurement values in both the pre-test and main control test programmes, being virtually independent of the wind speed. The model indicated that this was due to the dominance of the liquid phase mass transfer coefficient which is dependent only on the relative diffusivity of toluene in water.

The accuracy of the measurements of +/- 1 mg/m<sup>2</sup>/hr at a concentration of 500 g/m<sup>3</sup> aqueous solution is a spread equivalent to +/- 20% in the liquid phase mass transfer coefficient about its base value.

The main difference between the open tank and the flux chamber is the significant reduction in the air flow rate across the water surface. The flux chamber used in the tests was hemispherical and detailed modelling of the flow within this was beyond the scope of the project. As an approximation, the flux chamber was modelled as laminar flow over a flat plate. A typical velocity was defined as  $D/\tau$  where the time-scale  $\tau$  is the mean residence time (chamber volume  $\div$  flow rate). It was assumed that the liquid phase mass transfer coefficient was not affected by the presence of the chamber, which covered only a portion of the tank area.

The predicted flux chamber emission fluxes were larger than the measured fluxes but less than those from the open tank. The ratio was 3.8/5 rather than 2.7/5 observed in the experiments for the 5 l/min purge rate and 500 g/m<sup>3</sup> [aq] solution. Altering environmental factors such as chamber volume, characteristic length scale and water temperature does not significantly affect this ratio. To reconcile model predictions for the two cases it is necessary in the model to change the liquid phase mass transfer coefficient so that it is smaller when the flux chamber is in-situ. It is credible that the water surface under the flux chamber is less disturbed than that in the open tank. This could result in less mixing of the liquid below the flux chamber, particularly within the skirt of the chamber that extends 20 mm into the water. The liquid phase mass transfer coefficient does not have to change very substantially to account for the observed differences; a 20% reduction would make error ranges overlap and 40% would align mean values.

The study therefore suggests that careful use of a flux chamber, particularly one designed with a higher sweep air flow rate, in experiments to determine liquid phase mass transfer rates rather than emission fluxes explicitly may be a good tool to inform the use of modelled emissions from oil-water separators.

These tests were undertaken on an aqueous solution containing a single component. An oil-water separator at a refinery will treat streams from a number of sources and thus will contain many



different hydrocarbon compounds and possibly have a thin layer of free oil on the water surface. Some preliminary experiments using a free oil layer were conducted, see Appendix 2, but the results were not subjected to the same scrutiny as for the single component solution case and are not reported in this summary report. Further work is needed to address the use of a flux chamber to measure vapour losses from water having a free oil layer.

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## APPENDIX 1 RESULTS FROM EMISSIONS MODELLING

The theoretical rate of volatilisation of toluene from the aqueous solution in the open tank, as predicted by mass transfer theory, was determined using the equations provided in Section 4.3.2 of the US EPA Publication AP-42 [7].

The gas phase and liquid phase mass transfer coefficients ( $k_g$  and  $k_L$  respectively (m/s)) are used in the model to calculate the overall mass transfer coefficient,  $K$ , and thence the emissions. The algorithms in **Section A1.1** to estimate the emissions from the toluene/water solution in the open tank are from [7], assuming that the wastewater treatment is not aerated, has no free oil layer and is not biologically active.

For the flux chamber the correlation for laminar flow over a flat plate was used [1] – see **Section A1.2**.

The model is straightforward. Mass transfer toward the surface is assumed according to:

$$\frac{\dot{M}}{A} = k_g(C_s^g - C_\infty^g) = -k_L(C_s^L - C_\infty^L)$$

where  $k_g$ ,  $k_L$  denote the gas and liquid mass transfer coefficients (m/s), the subscript  $s$  denotes the surface concentration, the subscript  $\infty$  denotes free stream conditions,  $A$  is the surface area exposed and  $\dot{M}$  is the mass transfer rate.

For convenience the concentration units are  $g/m^3$ . At the surface the conversion from liquid ( $g/m^3$  aqueous solution) to gas phase concentration ( $g/m^3$ ) is given by:

$$C_s^g = \lambda C_s^L$$

where  $\lambda$  is a Henry law constant [4] incorporating the appropriate unit conversions. The value of  $\lambda$  depends on temperature, having a value for toluene of 0.605 at 15°C and 0.932 at 25°C using typical parameters from [4].

For the conditions of these tests  $C_\infty^g$  can be set to zero as the free stream gas concentration is too low to impact the mass transfer (this was tested) and, for the flux chamber, the effect of total pressure variation with flow rate on gas phase concentrations is also negligible.

Eliminating the surface concentrations gives the effective diffusion coefficient  $K$ , m/s

$$\frac{1}{K} = \frac{1}{k_L} + \frac{1}{\lambda k_g}$$

### A1.1 ESTIMATION OF EMISSION FLUX FROM OPEN TEST TANK

Test tank dimensions:

Length = 1.2 m

Width = 0.6 m

Depth = 0.2 m

Wind speeds used in wind tunnel: 0.6, 1.0, 1.5, 2.0, 2.5 and 3.0 m/s

### **Gas phase mass transfer coefficient ( $k_g$ )**

The mass transfer coefficient is semi-empirical and derived from field experiments for evaporating liquid pools. The reference velocity in the correlation below was measured at 10 m height. To apply to the wind tunnel it was assumed that the wind speed should be scaled according to the friction velocity so that  $U_{10} = \frac{u_*}{\kappa} \log\left(\frac{10}{z_r}\right)$  where the roughness length ( $z_r$ ) can be taken as 0.03 m. The friction velocity  $u_*$  was derived from the wind tunnel experiments, by fitting a rough wall profile to the wind tunnel data.

The mass transfer co-efficient,  $k_g$ , (in m/s) is given by:

$$k_g = 4.82E-03 U^{0.78} Sc_G^{-0.67} d_e^{-0.11}$$

Where:

$U_{10}$  = wind speed (m/s) = 0.326  $U_{ref}$  where  $U_{ref}$  is the tunnel speed measured at 0.2 m height. This low value reflects that the tunnel walls are low roughness and generate less turbulence, and hence mass transfer, than in the atmospheric boundary layer.

$Sc_G$  = Schmidt number on gas side =  $\mu_{air} / (\rho_{air} \times D_{air}) = 1.73$

$\mu_{air}$  = viscosity of air = 1.81E-04 g/cm/s

$\rho_{air}$  = density of air = 1.2E-03 g/cm<sup>3</sup>

$D_{air}$  = diffusivity of toluene in air = 8.7E-02 cm<sup>2</sup>/s

$d_e$  = effective diameter =  $2 \times (A/\pi)^{0.5} = 0.977$  m

A = surface area of water in test tank = 0.75 m<sup>2</sup>

### **Liquid phase mass transfer coefficient ( $k_L$ )**

The following algorithm applies for a wind speed < 3.25 m/s:

$$k_L = 2.78E-06 (D_w / D_{ether})^{0.667}$$

Where:

$D_w$  = diffusivity of toluene in water = 8.6E-06 cm<sup>2</sup>/s

$D_{ether}$  = diffusivity of ether in water = 8.5E-06 cm<sup>2</sup>/s

Hence:

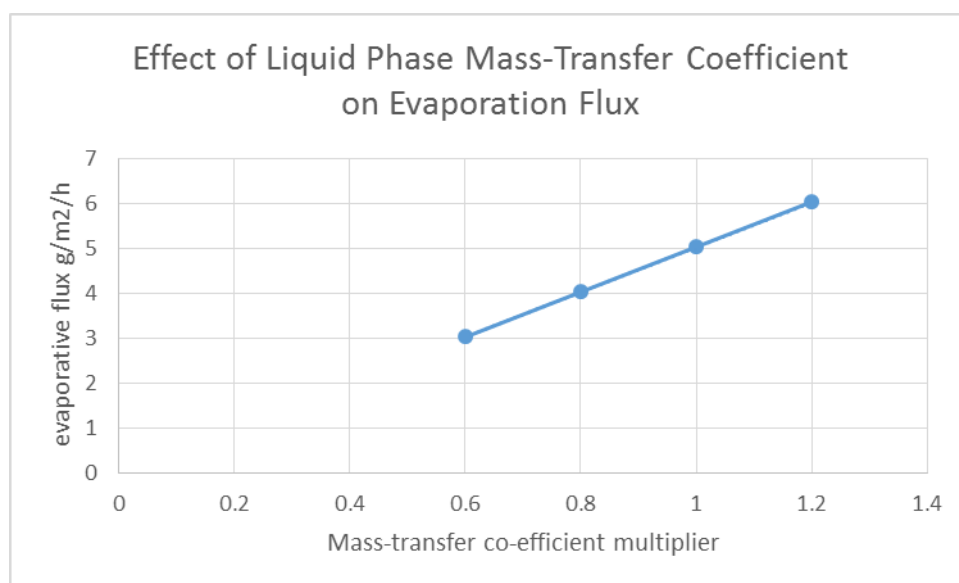
$$k_L = 2.80E-06 \text{ m/s}$$

Flux calculations are shown in **Table 7** for a temperature of 293 K, as used in the final trials. It can be seen that the gas phase mass transfer coefficient is much larger than the liquid phase coefficient which is controlling. The surface concentration in the liquid is very small compared to the tank concentration and the surface flux is 5 g/m<sup>2</sup>/h for a toluene concentration of 500 g/m<sup>3</sup> and half that for 250 g/m<sup>3</sup>. These values are in line with the experimental results which placed emission flux in the range 4.8 - 5.2 g/m<sup>2</sup>/h with an average value 5.0 +/-1 g/m<sup>2</sup>/h. This is quite a surprising agreement given the use of a liquid phase mass transfer coefficient derived from full scale measurements. The correlation for gas phase mass transfer essentially has no effect on the flux results. **Figure 2** shows that the flux is virtually linear with changes in the liquid phase mass transfer coefficient. During tests to see if the presence of the flux chamber influenced the emission from the remaining free area it was observed that the emission flux from the free area behind the chamber increased to an average 6 g/m<sup>2</sup>/h. The surface of this free area was visibly more disturbed during these tests. It was hypothesised that the increased flux was due to enhanced mixing in the tank. In the model the higher flux is accounted for by a 20% increase in the liquid phase mass transfer coefficient.

**Table 7** Calculations of flux from open tank

Reference Tunnel Wind Speed	Gas Phase mass-transfer coefficient	Liquid phase mass transfer coefficient	Overall mass transfer coefficient	Liquid conc. at surface	Gas conc. at surface	Liquid phase conc.	Emission Flux
U, m/s	$k_g$ , m/s	$k_L$ , m/s	K, m/s	$C_s^L$ g/m <sup>3</sup> [aq]	$C_s^g$ g/m <sup>3</sup>	$C_\infty^L$ g/m <sup>3</sup> [aq]	g/h/m <sup>2</sup>
0.6	9.361E-04	2.802E-06	2.791E-06	1.330	1.002	5.0E+02	5.023
1.0	1.394E-03	2.802E-06	2.794E-06	1.330	1.002	5.0E+02	5.030
1.5	1.913E-03	2.802E-06	2.796E-06	1.330	1.002	5.0E+02	5.033
2.0	2.394E-03	2.802E-06	2.797E-06	1.330	1.002	5.0E+02	5.035
2.5	2.849E-03	2.802E-06	2.798E-06	1.330	1.002	5.0E+02	5.037
3.0	3.285E-03	2.802E-06	2.799E-06	1.330	1.002	5.0E+02	5.037
0.6	9.361E-04	2.802E-06	2.791E-06	0.665	0.501	2.5E+02	2.512
1.0	1.394E-03	2.802E-06	2.794E-06	0.665	0.501	2.5E+02	2.515
1.5	1.913E-03	2.802E-06	2.796E-06	0.665	0.501	2.5E+02	2.517
2.0	2.394E-03	2.802E-06	2.797E-06	0.665	0.501	2.5E+02	2.518
2.5	2.849E-03	2.802E-06	2.798E-06	0.665	0.501	2.5E+02	2.518
3.0	3.285E-03	2.802E-06	2.799E-06	0.665	0.501	2.5E+02	2.519

**Figure 2** Effect of liquid phase mass transfer coefficient on evaporation flux from open tank



## A1.2 ESTIMATION OF EMISSION FLUX FROM BELOW FLUX CHAMBER

Dimensions of Odoflux® type flux chamber used in tests:

Diameter = 0.5 m

Water surface area enclosed = 0.196 m<sup>2</sup>

Assumed cross-sectional area of dome (A) = 0.098 m<sup>2</sup>

Volume = 47 l (estimate)

Sweep air flow rates (S) used: 3.0, 5.0 and 10.0 l/min.

Flat plate of length D.

### **Gas phase mass transfer coefficient ( $k_{gas}$ )**

$k_g = 0.664Re^{0.5}Sc^{0.33} \frac{D_{air}}{D}$  (m/s) where  $D_{air}$  is the molecular diffusivity of toluene in air and D the diameter of the flux chamber

$Sc = \text{Schmidt number on gas side} = \mu_{air} / (\rho_{air} \times D_{air}) = 1.73$

The results of the flux chamber modelling, using nominal values of concentration, are shown in **Table 8**, **Table 9** and **Figure 3**. It is assumed that the action of the wind on the tank induces the same degree of water mixing under the flux chamber as seen for the open tank, so the same liquid phase mass transfer coefficient value has been used.

The model showed that flux would be expected to increase with wind speed whereas the test data showed the highest fluxes at a sweep air flow of 5 l/min. The results are more sensitive to temperature (Henry coefficient) than those for the open tank varying from 3.58 to 3.98 g/m<sup>2</sup>/h as temperature varies between 15°C and 25°C for a concentration of 500 g/m<sup>3</sup> [aq] and a sweep air flow of 5 l/min. The model is not sensitive to the chamber volume.

The model predicts greater values than measured. The sensitivity to the liquid phase mass transfer coefficient is less than for the open tank.

If we assume there is no uncertainty coming from the model and measurement, to account for the data the liquid phase mass transfer coefficient would have to be smaller under the flux chamber than for the open tank by about 40%. This is not unreasonable to suppose. The screening trials showed some enhancement of emission from the open surface in the presence of the flux chamber and attributed this to surface disturbance. The flux chamber could well have the opposite effect. Circulation in the tank at level below the surface could be expected to maintain consistent water concentrations.

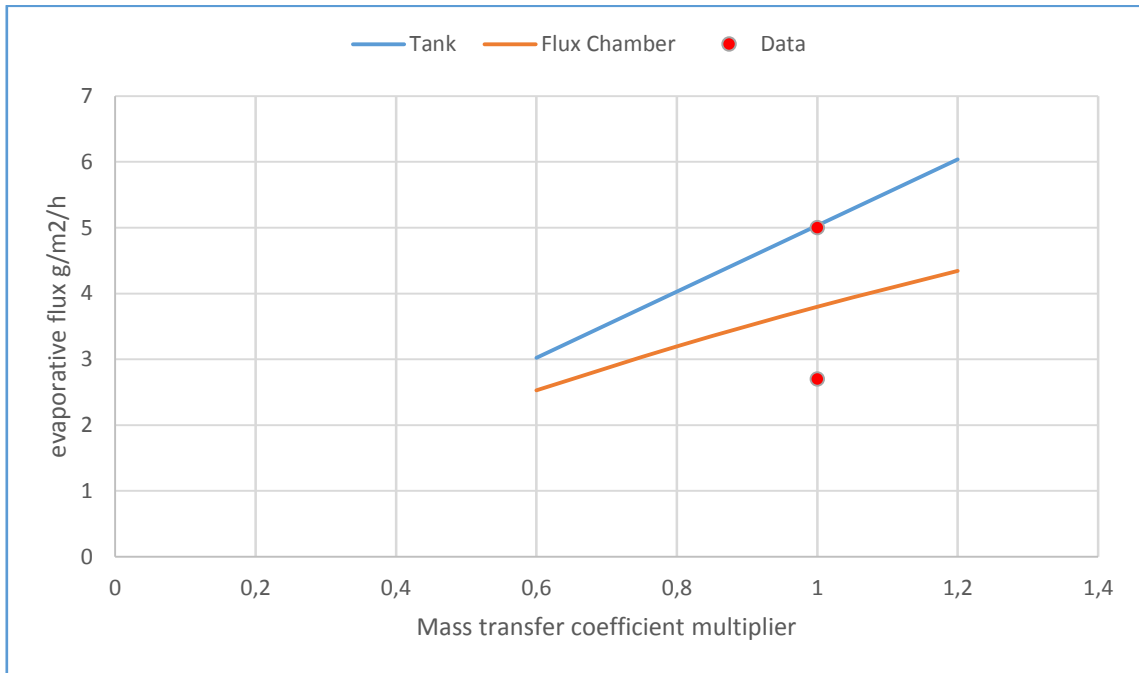
**Table 8** Calculation of flux from surface enclosed by flux chamber; water temperature of 25°C

Sweep air flow rate	Gas phase mass transfer coefficient $t$	Liquid phase mass transfer coefficient $t$	Overall mass transfer coefficient $t$	Liquid conc. at surface	Gas conc. at surface	Liquid phase conc.	Derived Emission Flux	Test data
l/min	$k_g, m/s$	$k_L, m/s$	$k$	$C_s^L$ g/m <sup>3</sup> [aq]	$C_s^g$ g/m <sup>3</sup>	$C_\infty^L$ g/m <sup>3</sup> [aq]	g/m <sup>2</sup> /h	g/m <sup>2</sup> /h
3	8.789E-06	2.802E-06	2.088E-06	127.450	118.758	5.0E+02	3.757	2.0 +/- 0.3
5	1.135E-05	2.802E-06	2.215E-06	127.450	118.758	5.0E+02	3.986	2.7 +/- 0.4
10	1.605E-05	2.802E-06	2.360E-06	127.450	118.758	5.0E+02	4.247	2.1 +/- 0.3
3	8.789E-06	2.802E-06	2.088E-06	63.725	59.379	2.5E+02	1.877	0.8 +/- 0.1
5	1.135E-05	2.802E-06	2.215E-06	63.725	59.379	2.5E+02	1.992	1.1 +/- 0.2
10	1.605E-05	2.802E-06	2.360E-06	63.725	59.379	2.5E+02	2.123	1.2 +/- 0.2

**Table 9** Calculation of flux from surface enclosed by flux chamber; water temperature of 15°C

Sweep air flow rate	Gas phase mass transfer coefficient $t$	Liquid phase mass transfer coefficient $t$	Overall mass transfer coefficient $t$	Liquid conc. at surface	Gas conc. at surface	Liquid phase conc.	Derived Emission Flux	Test data
l/min	$k_g, m/s$	$k_L, m/s$	$k$	$C_s^L$ g/m <sup>3</sup> [aq]	$C_s^g$ g/m <sup>3</sup>	$C_\infty^L$ g/m <sup>3</sup> [aq]	g/m <sup>2</sup> /h	g/m <sup>2</sup> /h
3	8.789E-06	2.802E-06	1.835E-06	172.543	104.384	5.0E+02	3.302	2.0 +/- 0.3
5	1.135E-05	2.802E-06	1.990E-06	172.543	104.384	5.0E+02	3.580	2.7 +/- 0.4
10	1.605E-05	2.802E-06	2.174E-06	172.543	104.384	5.0E+02	3.913	2.1 +/- 0.3
3	8.789E-06	2.802E-06	1.835E-06	86.271	52.192	2.5E+02	1.649	0.8 +/- 0.1
5	1.135E-05	2.802E-06	1.990E-06	86.271	52.192	2.5E+02	1.789	1.1 +/- 0.2
10	1.605E-05	2.802E-06	2.174E-06	86.271	52.192	2.5E+02	1.956	1.2 +/- 0.2

**Figure 3** Effect of liquid phase mass transfer coefficient on evaporation flux within flux chamber





## **APPENDIX 2                      EMA STUDY TESTS REPORT**

This Appendix contains the main body of the report of tests (without Annexes) provided by EMA



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6, avenue de Clavières  
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75272 PARIS Cedex 06

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## STUDY TESTS REPORT

**« STUDY OF THE PERFORMANCE OF FLUX CHAMBER AS METHOD TO ESTIMATE DIFFUSIVE VOCs EMISSIONS FROM WASTEWATER AREAS »**

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*Proposed to*

**Concawe**

**(Research Agreement n° 201407060)**

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Pour Vérification
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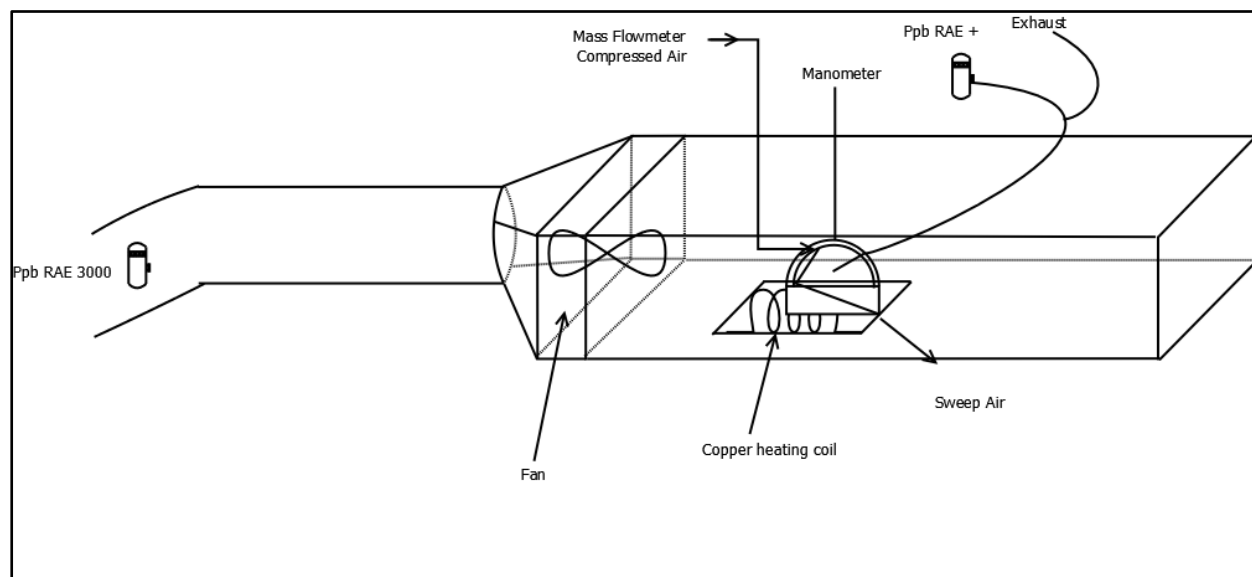
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## SUMMARY

The purpose of this study is to evaluate the performance of a flux chamber to estimate diffuse volatile organic compound (VOC) emissions from waste water areas. The purpose of the measurements is to compare the VOC emissions estimated by applying the flux chamber method and the actual emissions generated in a controlled environment.

To obtain these results, the flux chamber is set on a test tank filled with a toluene solution at two different concentrations ( $250 \text{ mg L}^{-1}$  and  $500 \text{ mg L}^{-1}$ ).



Pre-tests were conducted in the first part of the study to validate the use of PID device and UV to measure emission in air and water, to validate the toluene mass balance evaluation between air and water and to determine the wind speed to apply in the wind tunnel and the range of sweep air to evaluate the use of flux chamber in the measurement of VOC emissions.

The conclusions of these pre-tests are:

- Possibility to use PID to measure toluene emission in air,
- UV analysis not enough accurate to measure toluene loss from water
- Wind speed in the tunnel to apply for the test :  $2 \text{ m s}^{-1}$
- Sweep air flow range:  $3$  to  $10 \text{ L min}^{-1}$

In the second part of the study, it was concluded that

- Toluene emission is stable in the flux chamber regardless the sweep air flow between  $3$  and  $10 \text{ L min}^{-1}$ ,
- Toluene emission measurement in the flux chamber is half the emission in the wind tunnel due to the difference in the friction velocity between the wind tunnel and the flux chamber,
- The area emission measured with a  $250 \text{ mg L}^{-1}$ -toluene solution is half the area emission of a saturated solution (at  $500 \text{ mg L}^{-1}$ ). This result is consistent with the Henry's law.

## 1. CONTEXT AND AIM OF THE STUDY

The purpose of this study is to evaluate the performance of a flux chamber to estimate diffuse volatile organic compound (VOC) emissions from waste water areas. The purpose of the measurements is to compare VOC emissions estimated with the flux chamber method and the actual emissions generated in a controlled environment.

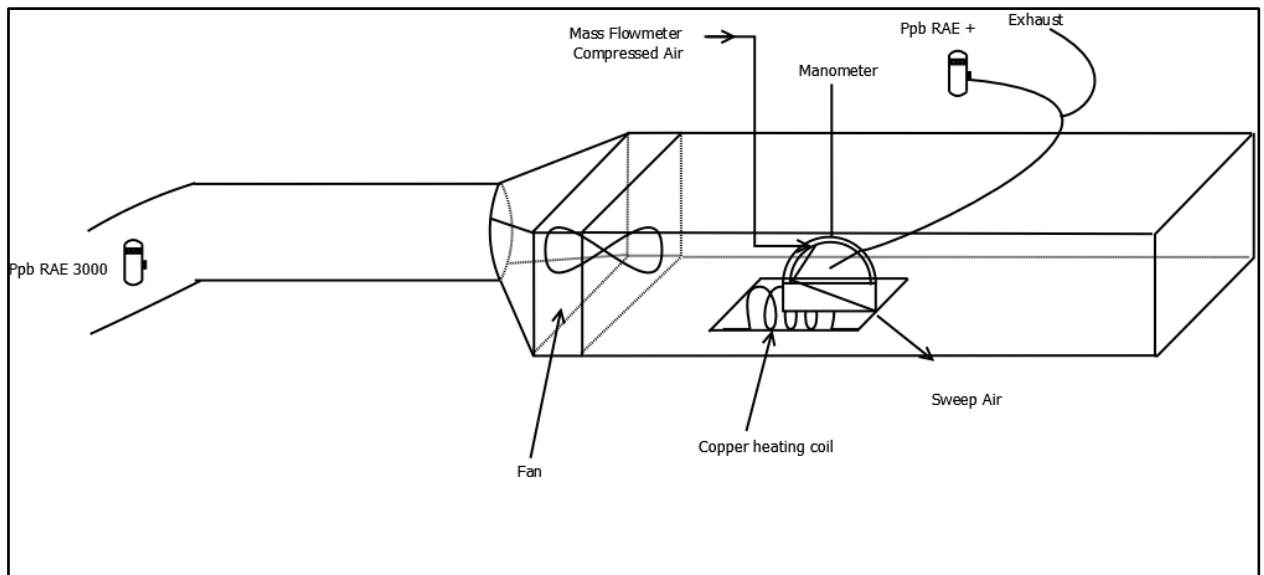
The study was divided into 2 phases. The first one was a pre-testing. Once the results from the pre-testing were considered satisfactory it was followed by a second phase (study-test).

The results of the second phase are presented below. The measurements were carried out in the Ecole des mines d'Alès according to the protocol prepared by ARMINES on 16/07/2014 ("ARMINES Protocol") and updated by Concawe after pre-testing 09/10/2014.

## 2. MATERIALS AND METHODS

The conception of the wind tunnel used in this study is similar to that of other existing tunnels, with a tank representing the surface area positioned in the air flow generated by a horizontal fan. The role of the wind tunnel is to simulate the action of the wind in the environment, and to duct the emission (Figure 1).

This device allows evaluating the emission of the source on the basis of the air flow rate in the wind tunnel by measuring the amount of pollutants transferred from liquid to gaseous phase.



**Figure 1: Scheme of the experimental set up**

## 2.1 THE WIND TUNNEL

The wind tunnel (Figure 2) is a 9 m-long parallelepiped 1 m wide and 0.5 m high with a rectangular cross-section built with « U » shaped transparent plastic pieces ( $e=5\text{mm}$ ) lying on wood boards.

The air flow (maximum value:  $10000\text{ m}^3\cdot\text{h}^{-1}$ ) is generated by a fan in aspiration mode. A frequency converter (Leroy Somer FMV 2107) allows the accurate control of wind speed between 1 and 5 m/s.

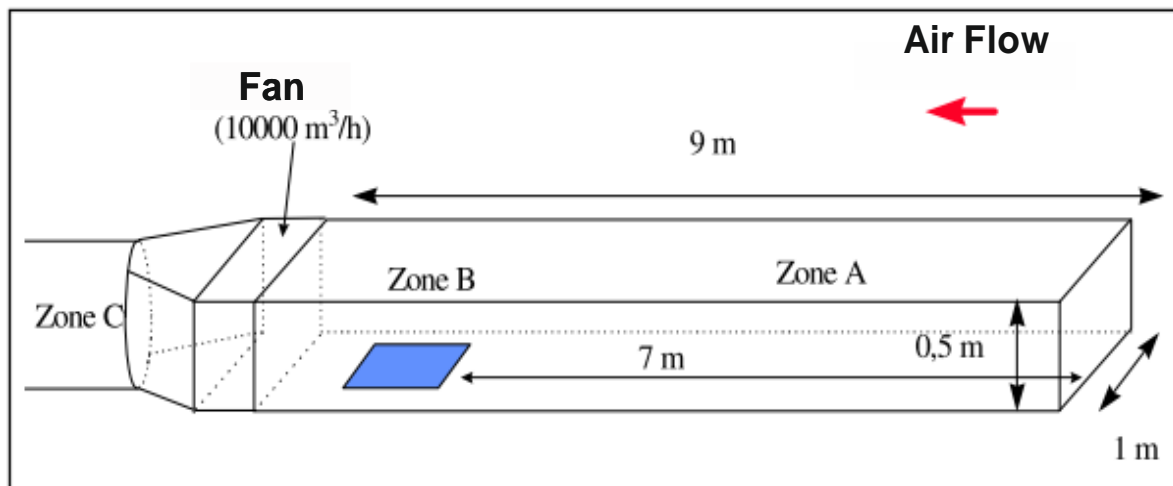


Figure 2: Wind tunnel schema.

Three zones are considered:

- Zone A, located upstream of the tank, is dedicated to the air flow stabilization;
- Zone B is the zone where the tank simulating the area source is located;
- Zone C, downstream of the fan, allows the homogenization of the air flow and its venting outside.

On the basis of mass conservation, it can therefore be said that all the compounds transferred from the liquid to the gaseous phase pass through zone C.

Some more details and illustrations of these three zones are given below.

### 2.1.1 Zone A: Wind tunnel inlet

The wind tunnel inlet is illustrated by figure 3.



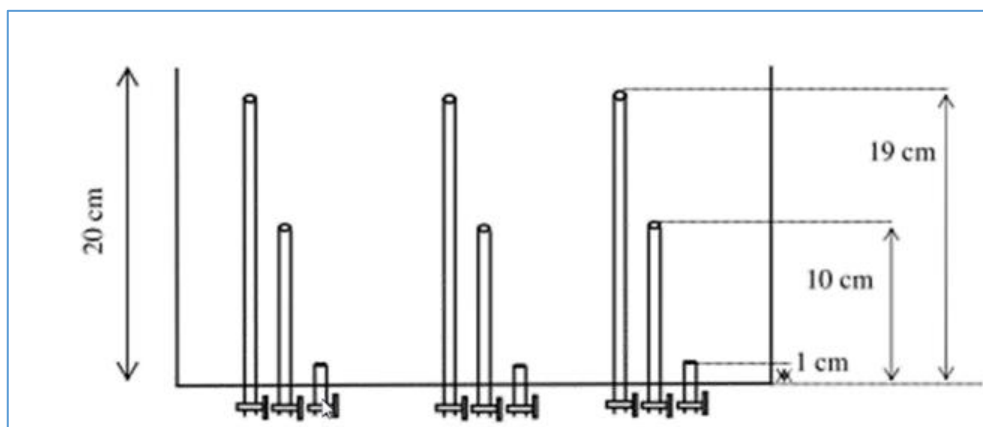
**Figure 3: Wind tunnel inlet.**

- The PVC cover of the wind tunnel is pierced above the tank to allow the setup of measurement instruments.
- The air intake to the wind tunnel comes from indoors and the exhaust is vented outside of the installation. The background concentration in the test hall is checked at least hourly.

### 2.1.2 Zone B: Test tank

The test tank is of stainless steel made. Its size is 125cm (length) \*60cm (width) \*20cm (depth) and its volume is 150 litres. It is located below the wind tunnel floor level.

The test tank is equipped with nine tubes for water sampling in three different heights of the pool (1, 10 and 19 cm) (figure 4).



**Figure 4: EMA's test tank and sampling tubes.**

In the measurement protocol it was required to work with a water temperature of 25°C to match with typical waste water temperature at a refinery. With the EMA system, it was not possible to heat the preparation tank water and the heating in the test tank was not high enough to raise the required temperature that is why



during the pre-test experiments, the temperatures of water were around 25°C, while in the study test experiments, there were close to 20°C.

Heating of test tank water is performed using a copper heating coil in which hot water flows. The test tank water temperature is measured and recorded continuously.



**Figure 5: Water heating system.**

### **2.1.3 Zone C: Wind tunnel exhaust**

During the pre-test, the wind tunnel exhaust was modified in order to allow a good homogenization of the airflow. A 4m-straight pipe was directly connected to the exhaust of the fan, followed by a flexible pipe (Figure 6).



**Figure 6: Wind tunnel exhaust.**

As seen on figure 6, the test hall door had to be opened during the measurement in order to allow the exit of the flexible pipe from the test hall.

## 2.2 FLUX AND CONCENTRATION MEASUREMENTS

### 2.2.1 Air flow measurements

Air velocity in the wind tunnel is measured with a hot wire anemometer (KIMO VT 300) (calibration certificate in annex). The anemometer is sat in position 8 (see figure 16) at 20 cm height to measure the wind speed in the wind tunnel before each experiment.

The air flow in the flux chamber is controlled continuously with a mass flowmeter (BROOKS 5850 TR) calibrated by Serv'Instrumentation in the 0-20 L min<sup>-1</sup> range (calibration certificate in annex 5).

### 2.2.2 Toluene concentration measurements

Two PID portable VOCs analyzers (ppbRAE plus and ppbRAE 3000, RAE Systems) were used for VOCs measurements. The ppbRAE plus was always used at the flux chamber outlet and the ppbRAE 3000 at the wind tunnel exhaust.

The analyzer is equipped with a 10.6 eV UV-lamp and a built-in sample diaphragm pump that provides a minimum flow of 400 ml/min.

When measuring toluene concentration in the wind tunnel, the detector is positioned in the flexible pipe to pump in the middle of the exhaust flow (figure 7). This positioning was chosen after verifying the homogeneity of toluene concentrations throughout the pipe section.

The PID portable VOCs analyzer has an auto-logging that allows recording measurements.



**Figure 7: Positioning of PID analyzer in the wind tunnel exhaust.**

When measuring toluene concentration in the flux chamber, the PID analyzer is positioned at the exit of the flux chamber to continuously record the concentration.

For all experiments it was considered that steady state was reached if the relative standard deviation was less than 10% for 30 min (detected by periodic readings of the PID values).

### 2.2.3 PID calibration

The instrument was calibrated once a day to measure real-time VOCs levels in the ppb and ppm range. The calibration was done with isobutylene at 10 ppm for the ppbRAE 3000 and with isobutylene at 100 ppm for the ppb RAE Plus, (certificates of the bottles in Annex 3). A calibration curve is done with toluene to obtain the real correction factor for each PID analyzer (Annex 1).

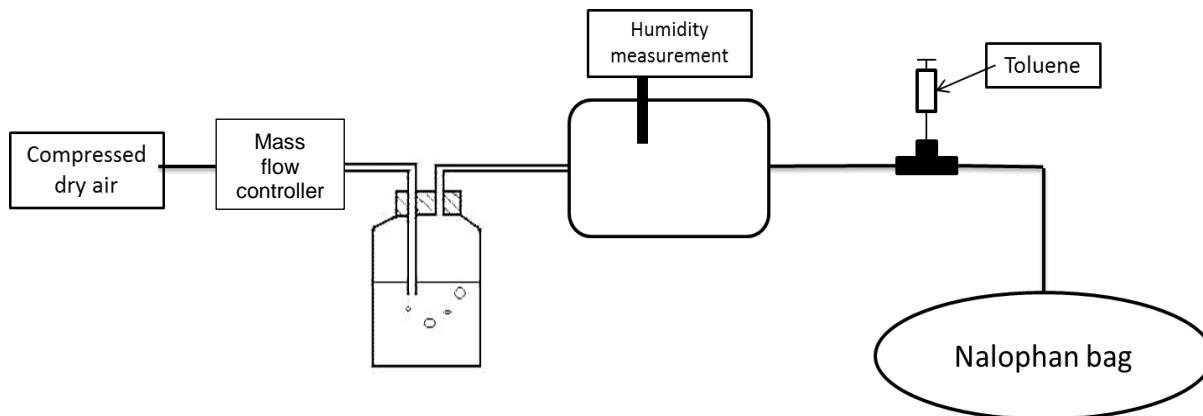
While analyzing the pre-test results, some remarkable deviations between the wind tunnel emissions with and without the flux chamber were noticed. Therefore an additional parallel test was performed to investigate the reasons for the deviations. In the additional test the two PIDs were exposed to the same moist gas in the wind tunnel after calibration with certified bottles. The toluene concentrations (corrected with the calibration curve) showed an important difference between the two PIDs (more than 100 ppb eq. toluene) meaning that both PIDs are sensitive to the humidity therefore moist calibration was needed to obtain reliable results.

So, calibrations curves were done in dry and moist air to obtain response factors for toluene.

The moist air is generated as described in figure 8.

A dry air flow goes through a vial with water. The humidity level is measured by a Hannah thermo-hygrometer (HI 9564) (Accuracy +/- 3%).

Injections of known amounts of toluene are realized with a Hamilton glass syringe in the moist air flow to fill a Nalophan® bag. The complete volatilization of liquid is obtained if the air speed is sufficient. A high-concentration gas is obtained. To reach low concentrations, a dilution of this air is performed with a gas-tight syringe.



**Figure 8: System for the generation of toluene moist gas**

The response factors were obtained for high concentrations (0-400 ppm) on the PID plus to correspond to the concentrations measured in the flux chamber and low concentrations (0-1 ppm) for the PID 3000 to follow toluene concentrations at the exhaust of the wind tunnel (Table 1).

**Table 1: Response factor and standard deviation obtained for the calibration of the two PIDs**

<b>PID detector</b>	<b>Concentration (ppm)</b>	<b>Relative humidity (%)</b>	<b>Response factor</b>	<b>Standard deviation</b>
ppbRAE Plus	0-1	0	1.02	0.02
	0-1	65	1.33	0.11
	0-400	0	0.97	0.04
	0-400	70	1.07	0.02
ppb RAE 3000	0-1	0	0.63	0.05
	0-1	65	0.48	0.02
	0-400	0	1.03	0.04
	0-400	70	0.69	0.02

The internal humidity correction of the ppb RAE 3000 leads to a better stability of the response factor for low concentration and moist air (standard deviation with internal humidity correction is 0.02 for the ppb RAE 3000 compared with 0.11 with the ppb RAE Plus having no internal humidity correction). That's why ppb RAE 3000 was used at the exhaust of the wind tunnel. The complete report of the calibration is in Annex 6.

In pre- and study tests, and of course in all this report, the response factor used for the ppb RAE plus is  $1.07 \pm 0.02$  (for the measurement of high concentration and moist air) and  $0.48 \pm 0.02$  for the ppb RAE 3000 (low concentration and moist air).

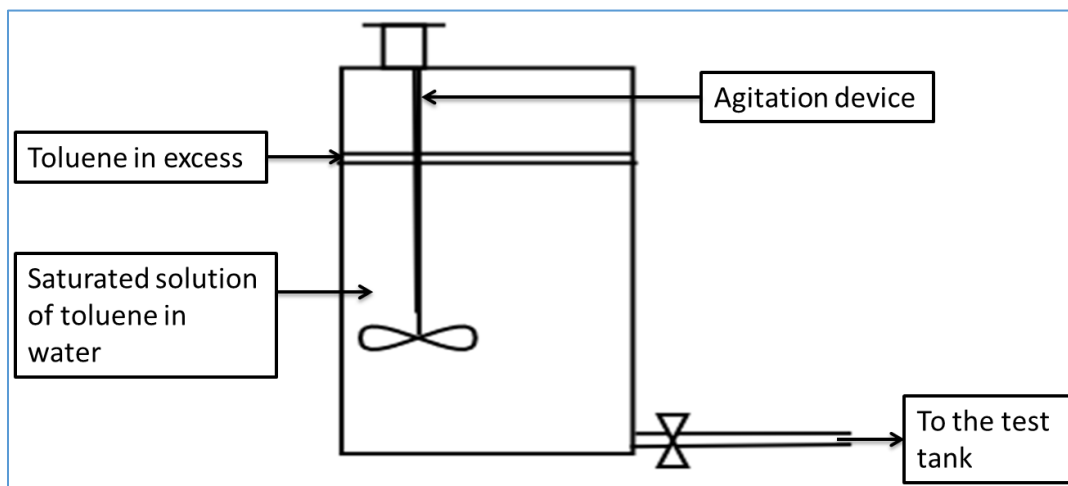
## **2.3 TEST SOLUTION PREPARATION**

### **2.3.1 Aqueous solution of Toluene**

A solution of toluene is prepared for each experiment, according to the procedure described hereafter. Two different toluene solutions, prepared in a 300 L-tank (figure 9), were used during the study tests: a saturated and a low concentration solution.

For the saturated solution the tank is filled with 400 mL (346.8 g) toluene and 260 L water. This solution is agitated during 3h. Then, the mixing device is stopped and the solution rests for 12h. This leads to an over-saturated solution.

For the lower concentration solution, 70 mL of toluene are added to 200 L of water in the preparation tank (in order to achieve a test tank toluene solution around 250 mg/L). Then, this solution is agitated during 3h. The mixing device is stopped and the solution left still for 12h.



**Figure 9: Saturated toluene solution preparation.**

A new batch is prepared every day for each experiment. The concentration in the preparation tank is reported in the following tables.

**Table 2: Initial toluene concentration in the preparation tank and test tank for each experiment**

Saturated solution		Toluene concentration in the preparation tank (mg L <sup>-1</sup> )	Toluene concentration in the test tank (mg L <sup>-1</sup> )
without FC, wind 2 m/s	01.12.2014	500	436
without FC, wind 2 m/s	08.01.2015	606	521
with FC, sweep air 3 l/min, wind 2 m/s	14.01.2015	620	508
with FC, sweep air 3 l/min, wind 2 m/s	15.01.2015	669	533
with FC, sweep air 5 l/min, wind 2 m/s	09.01.2015	618	482
with FC, sweep air 5 l/min, wind 2 m/s	12.01.2015	648	509
with FC, sweep air 5 l/min, wind 2 m/s	13.01.2015	638	519
with FC, sweep air 10 l/min, wind 2 m/s	15.12.2014	544	452
with FC, sweep air 10 l/min, wind 2 m/s	22.01.2015	611	502

Low concentration solution		Toluene concentration in the preparation tank (mg L <sup>-1</sup> )	Toluene concentration in the test tank (mg L <sup>-1</sup> )
without FC, wind 2 m/s	9.12.2014	295	284
without FC, wind 2 m/s	19.01.2016	380	257
with FC, sweep air 3 l/min, wind 2 m/s	20.01.2015	275	259
with FC, sweep air 5 l/min, wind 2 m/s	11.12.2014	312	264
with FC, sweep air 10 l/min, wind 2 m/s	12.12.2014	220	193

The toluene concentration in the preparation tank is around 100 mg L<sup>-1</sup> higher than the toluene concentration in the test tank. This loss of toluene is due to the agitation of the solution when the test tank is filled.

In two batches (saturated solution 01.12.2015 and low solution 12.12.2014) the concentrations in the preparation tank were relatively lower comparing to the other batches. Same amounts of toluene and water were used for the solution preparation of each batch as described above. A possible reason for these lower initial

concentrations might be that test hall heating is shut down at 5 PM and turned on at 6 AM. So the water in the preparation tank was more impacted by the outside temperature.

## 2.4 FLUX CHAMBER

The flux chamber used in this part of the study is an Odoflux® flux chamber. The flux chamber is set on supports for all the experiments. The sweep air is injected in the chamber with a 1/4" connection located on the side of the chamber. Sweep air is delivered tangentially 10 cm above the surface of the liquid, after a spiral path. During the pre-testing (while the flux chamber was still leaking, see description below the figure 11), the exit (1/4" hole) was located on the top of the chamber. That was enough to prevent the flux chamber from floating

Figure 10 and 11 show the flux chamber and all its connections with PID and manometer. Sweep air is compressed air produced by a compressor (Compare Luchar®) (RH=0%, Hydrocarbon concentration : <10 ppb eq. Toluene, T=20°C). It is regulated by a mass flow controller (Brooks 5850 TR) and injected near the surface (10 cm) of the toluene solution. These connections are in compliance with EPA guidance [US Environmental Protection Agency: Measurement of gaseous emission rates from land surfaces using an emission isolation flux chamber, 1986].

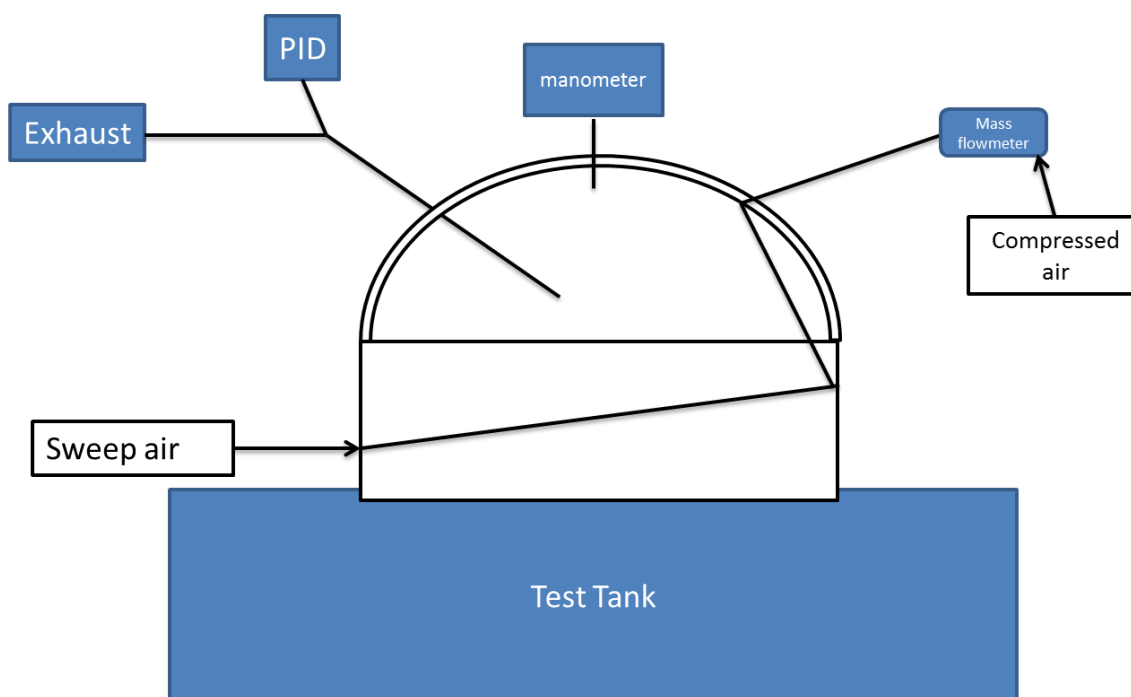
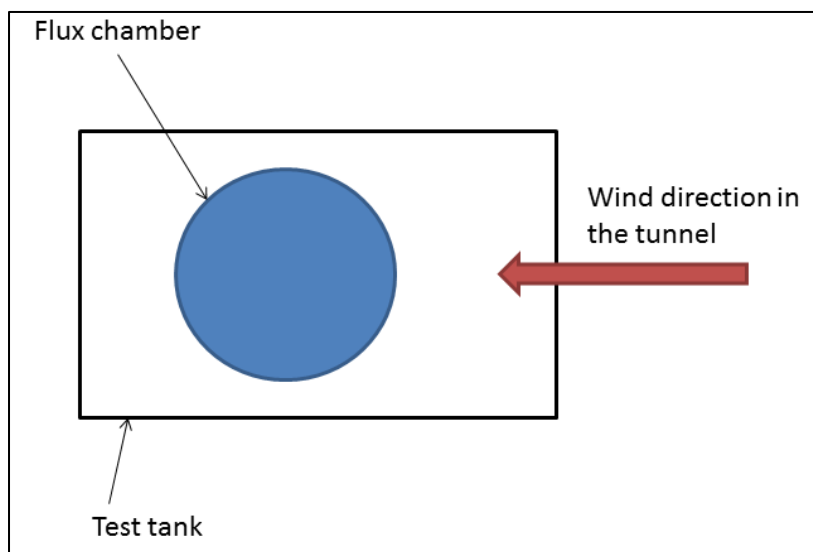


Figure 10: Flux chamber and its connections – Schema.



**Figure 11: Flux chamber and its connections – Photography**



**Figure 12: Position of the flux chamber on the test tank**

During the study tests an unexpected pressure drop of the internal pressure of the flux chamber was detected and the air sweep flow was checked. A leak was found with soap on the sweep airline inlet. After correction, the air flow at the exit of the flux chamber was close to 0 even with an inlet flow of  $4 \text{ L min}^{-1}$ . To locate leaks, the flux chamber was placed under helium pressure and a Restek leak detector (figure 13) based on the measurement of the thermal conductivity of gas was used.



**Figure 13: Restek leak detector (picture from Restek©)**

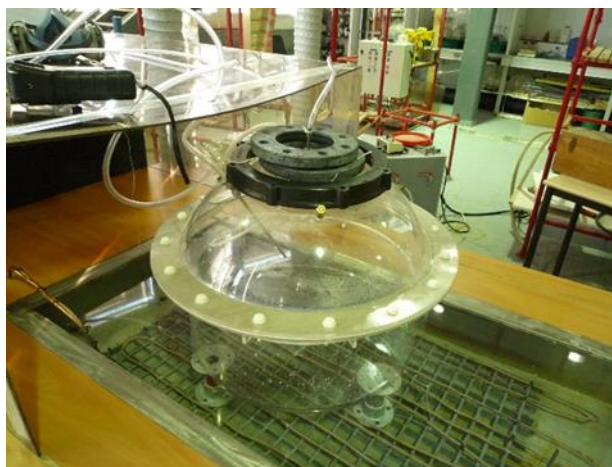
It shows that leaks occurred all around the flux chamber, at the junction between the lower and the upper part of the flux chamber. The chamber was sealed with a low emission Soudal<sup>®</sup>-adhesive sealant for swimming pool.

The chamber stands on supports in the tank in order to extend 2 cm into the water (or water/oil layer). The Odoflux® chamber is 0.5 m in diameter ( $A = 0.1964 \text{ m}^2$ ), and thus covers 26.19% of the test tank surface ( $0.75 \text{ m}^2$ ). As mentioned above, the flux chamber was sealed to avoid any leaks; after sealing the outlet flow equals the inlet flow. To decrease the pressure in the flux chamber and prevent floating, the exit is modified to use a 8mm tube. In this condition, the pressure in the flux chamber increases when the inlet flow rate increases (Table 3). These pressure values are obtained without PID connection. The increased pressure influence is very limited compared to the atmospheric pressure.

**Table 3: Evolution of the pressure in the flux chamber in function of the inlet sweep air flow**

Inlet Sweep air flow ( $\text{L min}^{-1}$ )	Pressure (Pa)
1	45
2	70
3	95
4	125
5	165
10	250

With a pressure of 250 Pa at  $10 \text{ L min}^{-1}$ , the flux chamber floats therefore weights were set on the top of the flux chamber to prevent floating (Figure 14).



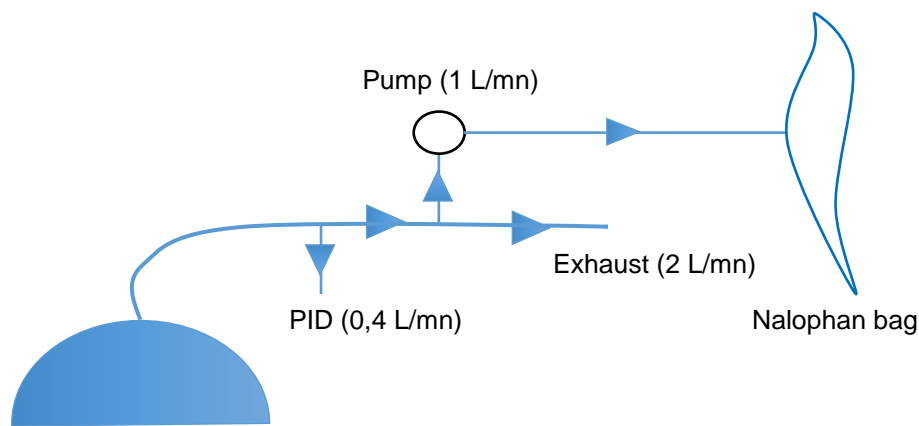
**Figure 14: Flux chamber with 10 l/min sweep air requires weights to prevent it floating**

## 2.5 NALOPHAN® BAG ANALYSIS

A diaphragm pump (KNF pump) and a 5 L-home made Nalophan® bag are connected in by-pass on the exhaust of the flux chamber (figure 15).

Once the toluene concentration is constant at the exhaust of the chamber, the sampling is realized. After sampling, the bag is connected to the VOCs analyzer and the toluene concentration is measured. During the pre-testing 2 samples per pre-test were collected. No sampling was done during the study tests.





**Figure 15: Nalophan bag sampling device.**

## 2.6 WATER ANALYSIS

The analysis of toluene concentrations in the aqueous phase was performed by a double beam high performance UV spectrophotometer, UVIKON XL. The toluene stock solution is made by weighing, using toluene of analytical grade and acetonitrile as solvent. Acetonitrile does not absorb in UV. The test solutions are obtained by dilution of the stock solution in MilliQ water.

UV spectra were acquired from 200 to 400 nm using Suprasil quartz cuvette (1 cm optical path). A high absorption at the beginning of the spectrum (200 - 230 nm) and a specific absorption between 230 and 280 nm are noted. The latter is characterized by the presence of a shoulder followed by two structured peaks. The absorption maximum is located at 261 nm (annex 2).

Toluene has a low molar absorptivity ( $\epsilon$ ) at its maximum absorption wavelength:

$$\epsilon_{261} = 237 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$$

This analysis shows a good repeatability with a relative standard deviation less than 1% and a detection limit estimated to  $10 \text{ mg L}^{-1}$  with standard.

Water sample were collected from the nine tubes of the test tank (Figure 3). Before filling nine glass tubes for the analysis with 10 mL, at least 5 mL of solution is purged before taking sample (Figure 3). Then each sample is analyzed and an average is made with all the values.

With this protocol including the sampling stage, during the pre-testing it was noticed that the combined real accuracy of UV analysis and the water sampling was close to 25%.

## 2.7 DATA RECORDING SYSTEM

Temperature of water in the test tank, of ambient air and of tunnel air is measured and recorded continuously with several thermocouples type K. The data recording system is a National Instrument NI cDAQ-9172 (an eight-slot USB chassis) equipped with a NI USB-9211/9211A data acquisition device that provides an USB interface for four channels of 24-bit thermocouple inputs with integrated signal conditioning. Data are recorded on a laptop.

As previously mentioned, the VOCs concentrations are directly recorded using the auto-logging system of the PID VOCs analyzer.

## 2.8 CALCULATION METHODS USED

In this paragraph, the calculation methods of mass flow in the wind tunnel and in the flux chamber are described. The calculation of the mass of toluene in water is also included.

### 2.8.1 Wind tunnel:

The toluene concentrations measured with the PID are recorded in ppb. For the mass flow calculation, toluene concentrations in ( $\text{g}/\text{m}^3$ ) are required.

$$[\text{Toluene}] (\text{g m}^{-3}) = [\text{Toluene}] (\text{ppb}) \times M_{\text{Toluene}} / Vm_{\text{air}} \times 10^{-6}$$

With  $Vm_{\text{air}}$ : molar volume of air (L)  
 $M_{\text{toluene}}$ : molecular mass of toluene (g/mol)

The wind tunnel temperatures were in the 18-22°C range so we decided not to correct the molar volume of air for temperature.

Then, the toluene mass flow emitted from the test tank can be calculated as described in the following equation.

$$\begin{aligned} \text{Mass flow } (\text{g m}^{-2} \text{ h}^{-1}) \\ = [\text{toluene}] (\text{g m}^{-3}) \times \text{Air flow } (\text{m}^3 \text{ h}^{-1}) / \text{test tank area } (\text{m}^2) \end{aligned}$$

### 2.8.2 Flux chamber:

In the flux chamber, the toluene mass flow rate is calculated with

$$\begin{aligned} \text{Mass flow } (\text{g m}^{-2} \text{ h}) \\ = [\text{toluene}] (\text{g m}^{-3}) \times \text{Sweep Air } (\text{m}^3 \text{ h}^{-1}) / \text{Flux chamber area } (\text{m}^2) \end{aligned}$$

### 2.8.3 Test tank water:

The mass of toluene in the test tank is calculated with the following equation

$$\begin{aligned} \text{Mass of toluene } (\text{g}) \\ = \text{toluene concentration in water } (\text{mg L}^{-1}) \times V_{\text{tank}} (\text{L}) \times 10^{-3} \end{aligned}$$

### 3. SUMMARY OF PRE-TEST RESULTS

#### 3.1 AIRFLOW CHARACTERIZATION OF THE TUNNEL

Before considering mass transfer, it is important to realize an air flow study of the tunnel. Nine points of characterization were used to establish the airflow profiles in the tunnel above the water tank (figure 16).

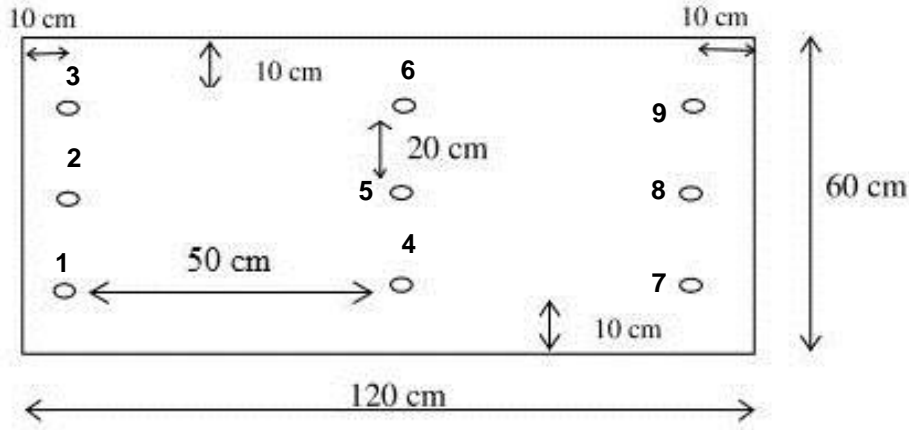
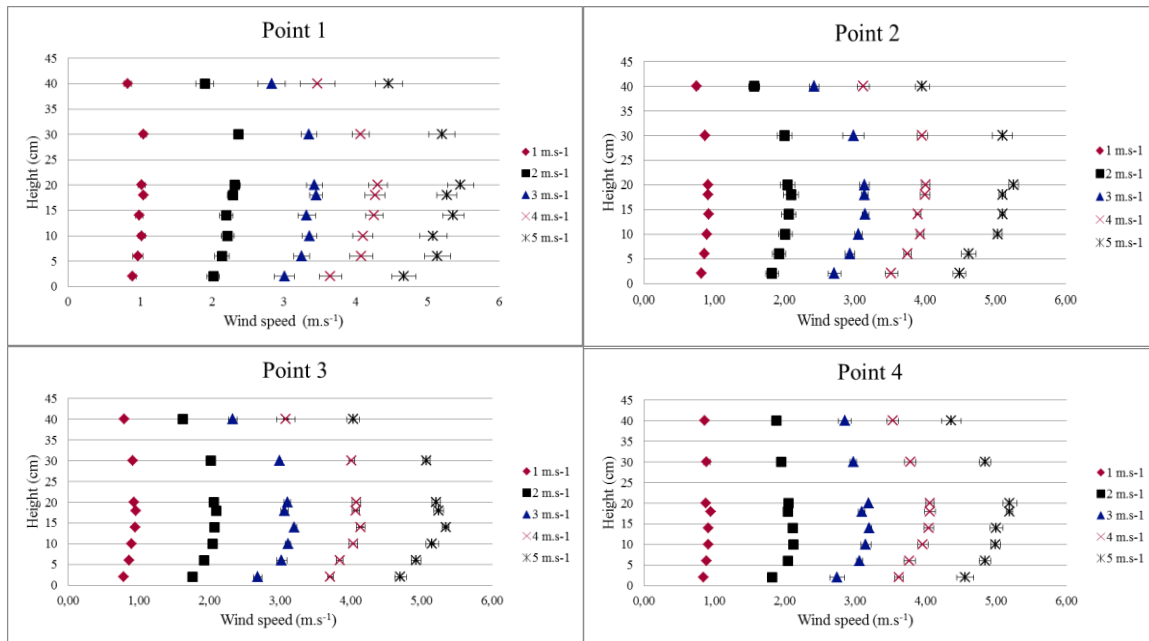
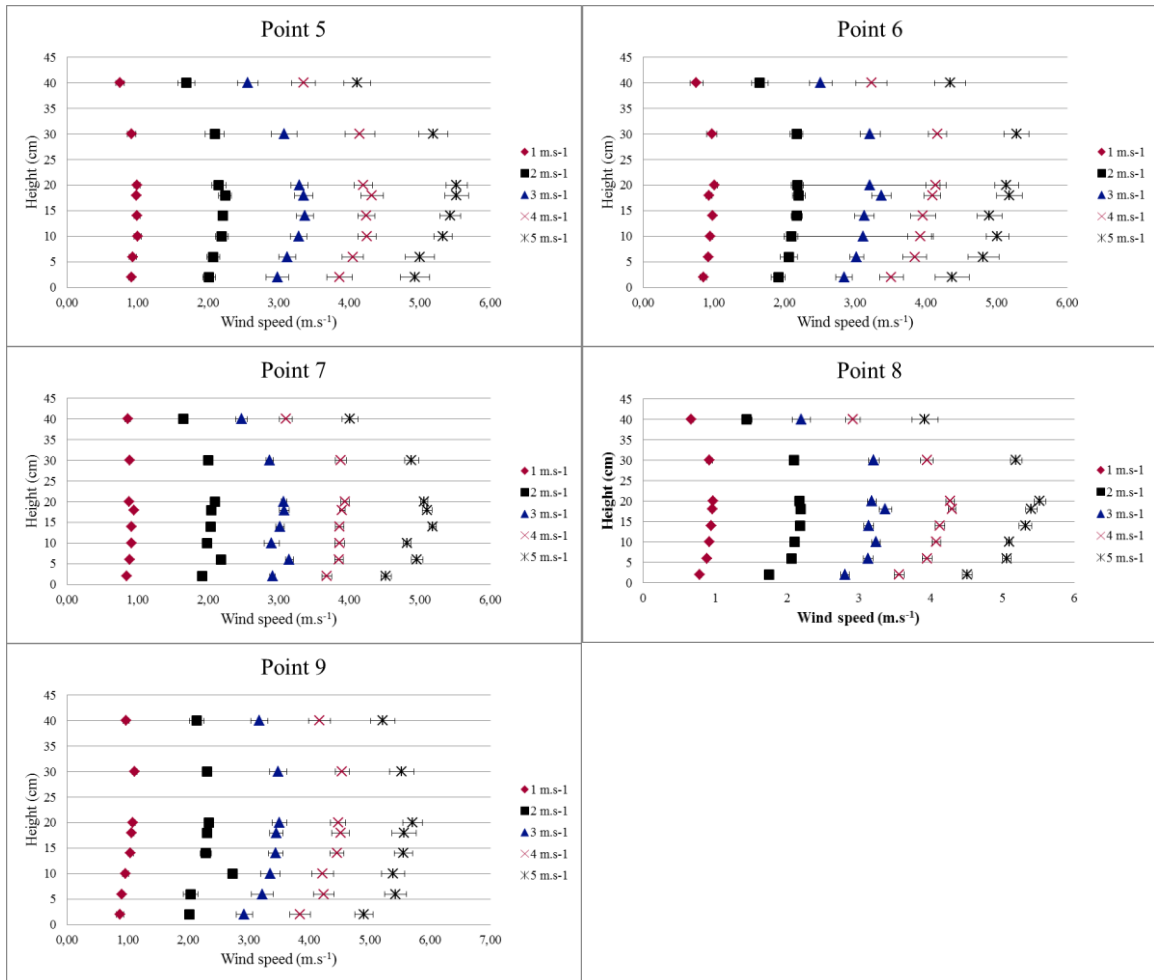


Figure 16: Spatial distribution of the nine points of wind speed measurement.

Figure 17 shows the wind speed profile established for each point at eight different heights (2, 6, 10, 14, 18, 20, 30, 40 cm) above the water tank and at five velocities (1, 2, 3, 4 and 5 m.s<sup>-1</sup>).





**Figure 17: Wind speed at different heights in the tunnel.**

These graphs show that the airflow profiles are similar in every point. Moreover, these profiles are characteristic of a turbulent airflow. This result is verified calculating the Reynolds number (Table 4). For rectangular pipes, the Reynolds number is calculated using the hydraulic diameter of the pipe ( $D_H$ ):

$$D_H = \frac{4 * S}{P}$$

$S$ : area of the pipe ( $m^2$ )

$P$ : perimeter of the pipe ( $m$ )

$$Re = \frac{D_H * U * \rho}{\mu}$$

$U$ : wind speed ( $m/s$ )

$\rho$ : specific gravity of the air ( $kg/m^3$ )

$\mu$ : kinematic viscosity of the air ( $kg/m^2.h$ )

**Table 4: Re number in the wind tunnel vs wind speed.**

wind speed (m/s)	Re
1	44444
2	88889
3	133333
5	222222

Re appears to be more than 2100 for any wind speed considered, confirming a turbulent flow.

Wind speeds follow a logarithmic law in the turbulent boundary layer over the interface. This corresponds to a turbulent boundary layer over a rigid plate, what allowed us to calculate the friction velocity (see section 3.4).

### 3.2 SATURATED TOLUENE SOLUTION

Short summary of the pre-tests results with the saturated toluene solution is presented below including:

- Wind tunnel + toluene
- Wind tunnel + flux chamber + toluene

The whole pre-test report is provided in annex 8.

In the pre-tests, several wind speeds in the wind tunnel were studied (0.6, 1, 1.5, 2, 2.5 and 3 m s<sup>-1</sup>). The same toluene solution was used for all the wind speeds. The toluene area emission is calculated for all these speeds. The results are summarized in table 5.

**Table 5: Toluene area emission for different wind speed in the tunnel**

Wind speed	Wind tunnel toluene mass emissions
m/s	g/m <sup>2</sup> .h
0.6±0.07	6.0±1.5
1±0.08	4.8±1.1
1.5±0.1	5.2±1.1
2±0.11	5.1±1.0
2.5±0.13	5.1±1.0
3±0.14	5.5±1.0

Overall, the toluene area emission is close to (5.5±1.0) g m<sup>-2</sup> h<sup>-1</sup> when considering a wind speed from 0.6 to 3 m s<sup>-1</sup>.

The toluene mass balance between air and water for the pre-test without the flux chamber is presented in table 6. At the beginning of the experiment the mass of toluene in water was 78.8 g based on UV analysis.

**Table 6: Mass balance for the experiment without the flux chamber**

Wind speed (m/s)	duration of the test (s)	Mass of Toluene emitted (air) (g)	Loss of toluene (water) (g)
0.6±0.07	1800	2.2±0.6	1.5±0.4
1±0.08	1680	1.7±0.4	2.1±0.5
1.5±0.1	1980	2.1±0.4	0.8±0.2
2±0.11	1800	1.9±0.4	2±0.5
2.5±0.13	1800	1.9±0.4	2.3±0.6
3±0.14	1920	2.2±0.4	0.8±0.2

Due to the lack of accuracies of the water analyses, the loss of toluene between two wind speeds was in the same order of magnitude as the standard deviation. So drawing conclusion based on these values is not realistic.

For tests with the flux chamber a wind speed of  $2 \text{ m s}^{-1}$  was set in the tunnel. Area emissions for all used sweep air flows are summarized in table 7.

**Table 7: Toluene area emission for different sweep air flow rates**

Sweep air flow rate ( $\text{L min}^{-1}$ )	Wind tunnel toluene mass emissions at $2 \text{ m s}^{-1}$ ( $\text{g m}^{-2} \text{ h}^{-1}$ )	Flux chamber toluene area emission ( $\text{g m}^{-2} \text{ h}^{-1}$ )
$3 \pm 0.03$	$5.1 \pm 1.0$	$0.6 \pm 0.1$
$5 \pm 0.05$	$5.1 \pm 1.0$	$1.0 \pm 0.2$
$6 \pm 0.06$	$5.1 \pm 1.0$	$0.9 \pm 0.1$
$8 \pm 0.08$	$5.1 \pm 1.0$	$0.8 \pm 0.1$
$10 \pm 0.1$	$5.1 \pm 1.0$	$0.8 \pm 0.1$
$12 \pm 0.12$	$5.1 \pm 1.0$	$0.9 \pm 0.1$
$20 \pm 0.2$	$5.1 \pm 1.0$	$1.2 \pm 0.2$

Pre-test results show that the toluene emission in the flux chamber is independent of the sweep air flow rate in the range explored in this study. It is close to  $1 \text{ g m}^{-2} \text{ h}^{-1}$ .

Table 8 shows the mass balance between air and water for pre-tests with the flux chamber.

**Table 8: Mass balance between air and water for pre-tests with FC**

Sweep air flow ( $\text{L min}^{-1}$ )	duration (s)	Toluene emission in the wind tunnel (g)	Toluene emission in the flux chamber (g)	Loss of toluene in water (g)
3	7180	$6.8 \pm 1.3$	$0.2 \pm 0.03$	$2.9 \pm 0.7$
5	2070	$2.2 \pm 0.4$	$0.1 \pm 0.02$	$3.1 \pm 0.8$
6	2595	$2.8 \pm 0.5$	$0.1 \pm 0.02$	$2.9 \pm 0.7$
8	5325	$5.3 \pm 1.0$	$0.2 \pm 0.03$	$6.2 \pm 1.6$
10	2160	$2.0 \pm 0.4$	$0.1 \pm 0.02$	$1.9 \pm 0.5$
12	2160	$2.0 \pm 0.4$	$0.1 \pm 0.02$	$2.2 \pm 0.6$
20	2705	$2.6 \pm 0.5$	$0.2 \pm 0.03$	NA*

\*The lack of accuracy of the UV analysis leads to outliers (negative value for the loss of toluene with a sweep air velocity of  $20 \text{ L min}^{-1}$ ).

It can be concluded that toluene emissions obtained during the pre-testing in the wind tunnel without the flux chamber are five times higher than emissions in the flux chamber regardless the sweep air flow (table 7). It should be noticed that all the pre-tests were realized with a leaking flux chamber and it could have had an effect on the results.

### 3.3 OIL LAYER TEST

Short summary of the pre-tests results with the oil layer is presented below including:

- Dodecane vrs. silicon oil test
- Wind tunnel + oil layer
- Wind tunnel + flux chamber + toluene + oil layer

The whole pre-test report is provided in annex 8.

The aim of this part of the pre-test was to evaluate the emission of toluene from the tank using an oil layer as a “protective film” on the surface of the solution.

The first step was to determine whether dodecane or silicone oil is suitable to prevent incorrect measurement of toluene concentrations in the air using the PID VOCs analyzer. It appears that the analyzer is relatively sensitive to dodecane (between 100 and 200 ppb eq toluene) whereas it is hardly sensitive to silicone oil (< 10 ppb). So, it was decided to use silicone oil to simulate an oil layer on the surface of the toluene solution. In the following tests with oil, one liter of silicone oil was spread on the surface of the test tank that corresponds to a 1.3 mm-film thickness.

Table 9 shows the area emission measured in the wind tunnel. In this test, only one solution was used to evaluate the impact of several wind speed on toluene emission.

**Table 9: Toluene area emission from the oil layer for different wind speed in the tunnel**

<b>Wind speed</b>	<b>Wind tunnel toluene mass flow</b>
<b>m s<sup>-1</sup></b>	<b>g m<sup>-2</sup> h<sup>-1</sup></b>
0.6±0.07	3.7±0.9
1±0.08	2.5±0.6
1.5±0.1	2.0±0.4
2±0.11	0.7±0.1
2.5±0.13	0.3±0.1

Table 10 presents the toluene mass balance between air, water and silicone oil for the pre-test without the flux chamber at the end of the test with each wind speed in the tunnel.

**Table 10: Mass balance between water, silicone oil and air**

MASS BALANCE					
Wind speed	duration	Water	Air	Silicone Oil (SO) (calculated)	Silicone Oil (calculated)
		loss of toluene	Toluene emitted	Toluene absorbed in SO	[toluene] in SO
m/s	s	(g)	(g)	(g)	(g/L)
0.6	7120	6.1±1.5	4.7±0.9	1.4	1.4
1	7130	4.2±1.1	3.7±0.7	0.5	1.9
1.5	3625	3.4±0.9	1.5±0.3	1.9	3.8
2	1850	2.1±0.5	0.2±0.04	1.9	5.7
2.5	2520	2.1±0.5	0.1±0.02	2.0	7.7
<b>Sum</b>		17.9	10.2	7.7	

The mass of toluene in the silicon oil has been determined by calculating the difference between toluene in water and in air for each wind speed. Then, the concentration of toluene in silicone oil is calculated considering the silicone oil volume (1L); it is the sum of the toluene still in the silicone oil from the previous analysis and the toluene added at the considered wind speed.

The last pre-test was lead to determine the toluene area emission in the flux chamber on a liquid surface covered by an oil layer. As in the study without the oil layer, the wind speed in the tunnel is fixed at 2 m s<sup>-1</sup> for all tests. Table 11 shows the results of this pre-test.

**Table 11: Area emission in the wind tunnel and in the flux chamber when an oil layer is set on the toluene solution**

Sweep air flow (L min <sup>-1</sup> )	Area emission in the flux chamber (g m <sup>-2</sup> h <sup>-1</sup> )
3±0.03	2.7±0.4
5±0.05	3.0±0.5
6±0.06	3.2±0.5

The toluene emission in the flux chamber is approximately (3.0±0.5) g m<sup>-2</sup> h<sup>-1</sup> regardless of the sweep air flow.

The toluene mass balance between air, water and silicone oil is presented in table 12.



**Table 12: Mass balance for experiment with silicone oil and flux chamber (wind speed 2m s<sup>-1</sup>).**

Mass Balance					
Sweep Air Flow	Water	Air	Silicone Oil		Silicone Oil
L/mn	loss of toluene	Tol emitted (WT+FC)	Initial mass of toluene in silicone oil *	Mass of Tol in SO at the end of the test (calculated)	[tol] in SO (calculated)
	(g)	(g)	(g)	(g)	(g/L)
3	7.5±1.9	12.5±2.4	21.2	16.2	16.2
5	2.7±0.7	5.7±1.1	16.2	13.2	13.2
6	2.0±0.5	2.6±0.5	13.2	12.6	12.6
<b>Sum</b>	12.2	20.8			

\* Mass of toluene in silicone oil at the beginning of each sweep air flow test.

As seen in table 10 and 12, the calculated toluene concentrations in the silicone oil were significantly different for the pre-test with and without the flux chamber. In these conditions, the comparison between area emission in the wind tunnel and in the flux chamber is not possible.

### **3.4 WIND TUNNEL EXHAUST EMISSIONS WITH AND WITHOUT THE FLUX CHAMBER**

Based on the results described above, the wind tunnel results with and without the flux chamber are difficult to compare, because the flux chamber on the test tank increases the level of turbulences on the test tank surface (Table 13).

Considering that the flux chamber was leaking for the pre-test, the toluene mass flow at the exit of the wind tunnel cumulate emission from the free surface of the test tank and emission from the surface of the flux chamber. With the free surface toluene mass flow, it is possible to calculate the toluene area emission of the free surface of the test tank (Table 12). For example with a 3L min<sup>-1</sup>-sweep air flow, the toluene mass flow are respectively 947 µg s<sup>-1</sup> at the exhaust of the wind tunnel and 30 µg s<sup>-1</sup> in the flux chamber. So, the mass flow for the free surface is 916 µg s<sup>-1</sup> and the toluene area emission is (6.0±1.2) g m<sup>-2</sup>h<sup>-1</sup>.

**Table 13: Determination of the toluene emission of the free surface of the test tank considering the leaks**

WT	FC		Toluene mass flow			Toluene area emission	
Wind speed	Sweep Air Flow Rate		Total WT	FC	WT Free surface	Free surface area emission	
m/s	L/min	m <sup>3</sup> /s	µg/s	µg/s	µg/s	g/m <sup>2</sup> .h	accuracy
2	3	0.00005	947	30	916	<b>6.0</b>	1.2
2	5	0.00008	1043	52	990	<b>6.4</b>	1.3
2	6	0.00010	1066	47	1018	<b>6.6</b>	1.3
2	8	0.00013	1004	43	961	<b>6.2</b>	1.2
2	10	0.00017	924	43	881	<b>5.7</b>	1.1
2	12	0.00020	916	47	869	<b>5.7</b>	1.1
2	20	0.00033	966	65	901	<b>5.9</b>	1.1

Table 14 shows the impact of the flux chamber leaks on the emission of toluene in the wind tunnel when the flux chamber is set on the test tank.

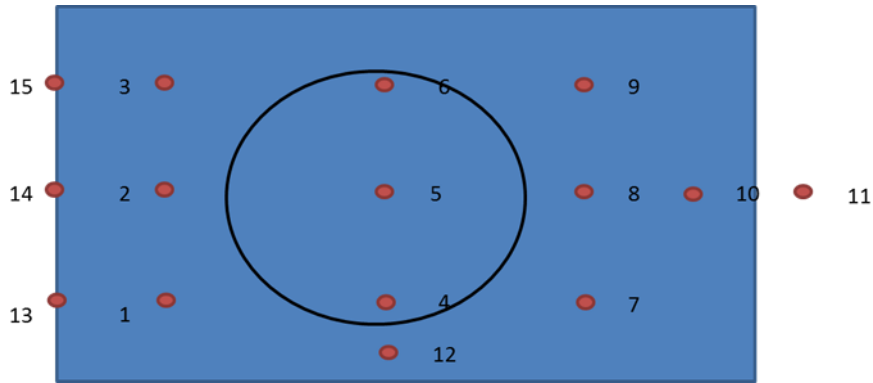
**Table 14: Comparison of the toluene emission of the free surface considering FC leaks or not**

Wind speed	without considering FC leaks	considering FC leaks	without FC
m/s	g/m <sup>2</sup> .h	g/m <sup>2</sup> .h	g/m <sup>2</sup> .h
2	6.2±1.2	6.0±1.2	
2	6.8±1.3	6.4±1.3	
2	6.9±1.4	6.6±1.3	
2	6.5±1.3	6.2±1.2	5.5±1.0
2	6.0±1.2	5.7±1.1	
2	6.0±1.2	5.7±1.1	
2	6.3±1.2	5.9±1.1	

Despite uncertainties, it appears that flux chamber leaks have a small impact (less than 8%) on the increase of toluene emission in the wind tunnel when the flux chamber is set on the test tank.

To confirm this phenomenon, the wind speed is measured in several points in the wind tunnel when the flux chamber is on the test tank surface (figure 16).

As seen in figure 17, ten centimeters above the liquid surface, the wind speed is 2 m s<sup>-1</sup> in every measurement location without the flux chamber. A 2 m s<sup>-1</sup> wind speed is set in the wind tunnel (point 11) (figure 18).



**Figure 18: Spatial distribution of the 15 points of wind speed measurement**

The results of these measurements are shown in table 15.

**Table 15: Wind speed around the flux chamber.**

Point	Wind speed (m/s)	Standard deviation (m/s)	Comments
1			Impossible to do measurement
2			
3			
4	3.00	0.04	on the top of the flux chamber
5	2.92	0.05	
6	3.14	0.08	
7	1.66	0.07	Roughly at 10 cm-high from the test tank surface
8	0.81	0.12	
9	1.81	0.06	
10	1.57	0.07	
11	1.92	0.05	
12	2.53	0.04	
13	1.65	0.21	
14	0.29	0.05	
15	0.48	0.18	

Measurements at the top of the flux chamber (approximately 3 cm above the flux chamber surface) show an increase of the wind speed from 2 to 3 m s<sup>-1</sup>. The same phenomenon is observed on the side of the flux chamber (point 12). A decrease of wind speed is observed on other points before (7, 8) and after (13, 14, 15) the flux chamber. Furthermore, small waves appear on the surface when the flux chamber is set on the test tank. In these conditions, the emission area increases (from 0.75 m<sup>2</sup> to an unknown surface). This test confirms a modification of the air flow in the wind tunnel and the impact of the flux chamber on the turbulences at the test tank surface comparatively to paragraph 3.1.

### 3.5 PRE-TEST CONCLUSIONS

It has to be noticed that all pre-tests were done with a leaking flux chamber.

From the pre-test, it can be concluded that whatever the sweep air flow rate in the flux chamber, the toluene flux is underestimated when compared to the values obtained for the uncovered surface.

Mass balance is difficult to establish for “short duration” tests, as the method used for evaluating toluene concentration in the water is not sufficiently sensitive (see conclusions of the pre-test report).

## 4. STUDY TEST RESULTS

For all the study tests, with saturated and low toluene concentration and with or without the flux chamber the wind speed in the wind tunnel is fixed at 2 m/s.

The raw data are available in annex (see Table 16).

All Excel files for experiment with the flux chamber have four sheets. The “Data” sheet gives the raw PID values. The “graph” sheet shows a graph with the evolution of toluene concentration in the wind tunnel and in the flux chamber. In the “T, P, RH” sheet, the values and graph for the temperature of ambient air, wind tunnel air and water, the relative humidity and the pressure in the flux chamber are figured. For the experiment without the flux chamber, the excel files have only three sheets because the graph is on the “Data” one.

The last sheet “Mass balance” presents the evolution of toluene concentration in water, the calculation of the toluene area emission and the mass balance between water and air.

Table 16 gives the localization of the raw data.

**Table 16: Classification of the raw data in Excel files.**

Saturated solution		
Experiment	File	Annex Number
without FC, wind 2 m/s	WT + Toluene 2014-12-01	9
without FC, wind 2 m/s	WT + Toluene 2015-01-08	10
with FC, sweep air 3 l/min, wind 2 m/s	WT + FC + Toluene 2015-01-14	11
with FC, sweep air 3 l/min, wind 2 m/s	WT + FC + Toluene 2015-01-15	12
with FC, sweep air 5 l/min, wind 2 m/s	WT + FC + Toluene 2015-01-09	13
with FC, sweep air 5 l/min, wind 2 m/s	WT + FC + Toluene 2015-01-12	14
with FC, sweep air 5 l/min, wind 2 m/s	WT + FC + Toluene 2015-01-13	15
with FC, sweep air 10 l/min, wind 2 m/s	WT + FC + Toluene 2014-12-15	16
with FC, sweep air 10 l/min, wind 2 m/s	WT + FC + Toluene 2015-01-22	17

Low concentration solution		
Experiment	File	Annex Number
without FC, wind 2 m/s	WT + Toluene 2014-12-09	18
without FC, wind 2 m/s	WT + Toluene 2015-01-19	19
with FC, sweep air 3 l/min, wind 2 m/s	WT + FC + Toluene 2015-01-20	20
with FC, sweep air 5 l/min, wind 2 m/s	WT + FC + Toluene 2014-12-11	21
with FC, sweep air 10 l/min, wind 2 m/s	WT + FC + Toluene 2014-12-12	22

### 4.1 SATURATED TOLUENE SOLUTION

The first part of the tests is realized with saturated solution like in the pre-tests.

### 4.1.1 Temperature, humidity

Table 17 gives the initial, end and average temperature and relative humidity for all the tests with saturated solution. The evolution of temperature and relative humidity for all study tests are shown in annex 7.

**Table 17: Relative humidity and temperature of water and tunnel for each experiment**

Saturated solution		Temperature (°C) Water			Temperature (°C) Tunnel			Relative Humidity (%)		
		Start	End	Average	Start	End	Average	Start	End	Average
without FC, wind 2 m/s	01.12.2014	20.0	21.2	20.4	17.8	16.3	16.7	48.8	51.9	51.1
without FC, wind 2 m/s	08.01.2015	19.2	21.4	20.0	18.8	20.0	19.2	34.7	32.7	33.7
with FC, sweep air 3 l/min, wind 2 m/s	14.01.2015	19.0	20.4	19.7	19.4	19.6	19.8	51.0	44.1	43.5
with FC, sweep air 3 l/min, wind 2 m/s	15.01.2015	18.9	20.3	19.5	18.7	19.0	18.8	41.9	44.3	43.1
with FC, sweep air 5 l/min, wind 2 m/s	09.01.2015	20.7	23.0	22.0	19.2	21.9	20.6	36.8	33.1	35.3
with FC, sweep air 5 l/min, wind 2 m/s	12.01.2015	20.0	21.6	20.7	18.8	19.0	18.3	26.6	26.6	27.3
with FC, sweep air 5 l/min, wind 2 m/s	13.01.2015	14.8	21.6	19.7	19.3	18.5	18.5	29.1	30.6	30.0
with FC, sweep air 10 l/min, wind 2 m/s	15.12.2014	20.1	23.5	22.0	18.9	21.0	20.0	57.3	53.0	53.9
with FC, sweep air 10 l/min, wind 2 m/s	22.01.2015	19.6	20.1	19.6	19.7	17.1	17.4	37.5	45.2	42.3

The temperatures for the tests are lower comparing to the pre-testing because the experiments are done in December and January when the the pre-tests were performed in August. Furthermore, the heating system in the test hall cannot heat all the volume and reach the temperatures measured in August.

The average temperature of water is close to 20°C instead of 25°C in the pre-tests.

### 4.1.2 Area emission in the wind tunnel exhaust

The emission of toluene in the wind tunnel is summarized in table 18.

**Table 18: Toluene concentration in water and air, area emission for the experiment without the flux chamber**

Concentration ppb eq toluene			Area emission (g m <sup>-2</sup> h <sup>-1</sup> )	Water mg L <sup>-1</sup>		Area emission (Normalized value*) (g m <sup>-2</sup> h <sup>-1</sup> )
background	WT outlet	Outlet - background		initial	end	
34	262	228	4.2±0.8	436	415	4.8±0.9
116	410	294	5.4±1.1	521	507	5.2±1.0

\* Normalization is done for a toluene concentration in water of 500 mg L<sup>-1</sup>

An important difference exists between the two experiments in table 18; in the first one the initial toluene concentration in the water is lower (436 mg L<sup>-1</sup>) and leads to an area emission at 4.2 g m<sup>-2</sup> h<sup>-1</sup>. In the second one, the initial concentration in the water is close to the theoretical saturation point and the area emission is 5.4 g m<sup>-2</sup> h<sup>-1</sup>.

If normalization is done for a concentration of toluene of 500 mg L<sup>-1</sup>, the emissions are similar and the area emission average in the wind tunnel is (5±1) g m<sup>-2</sup> h<sup>-1</sup>. The aim of the normalization is to overcome the variations of toluene concentration in water.

### 4.1.3 Area emission in the flux chamber

Table 19 shows the toluene concentration measured at the exit of the wind tunnel, in the flux chamber for different sweep air flow (3, 5 and 10 L min<sup>-1</sup>). The toluene area emission is also figured in this table.

**Table 19: Toluene concentration, area emission and pressure in the flux chamber for each test with saturated solution**

Concentration ppb toluene				Sweep air l/min	area emission g/m <sup>2</sup> .h	Water mg/l		Pressure Pa	Area emission (Normalized value*) (g m <sup>-2</sup> h <sup>-1</sup> )
background	WT outlet	Outlet - background	FC	FC	FC	initial	end	Inside FC	
110	372	262±37	586 35 2 ±82 089	3	2.1±0.3	508	491	95	2.1±0.3
115	359	244±34	572 86 0 ±80 200	3	2.0±0.3	533	499	97	1.9±0.3
72	317	245±34	473 94 8 ±66 353	5	2.8±0.4	482	462	160	2.9±0.4
150	368	218±31	443 56 3 ±62 099	5	2.8±0.4	509	482	160	2.8±0.4
115	349	234±33	425 51 3 ±59 572	5	2.5±0.4	519	496	163	2.4±0.4
110	492	382±53	152152 ±21 301	10	1.8±0.3	452	427	70	2.0±0.3
72	368	296±41	190728 ±26 70 2	10	2.2±0.3	502	460	410	2.2±0.3

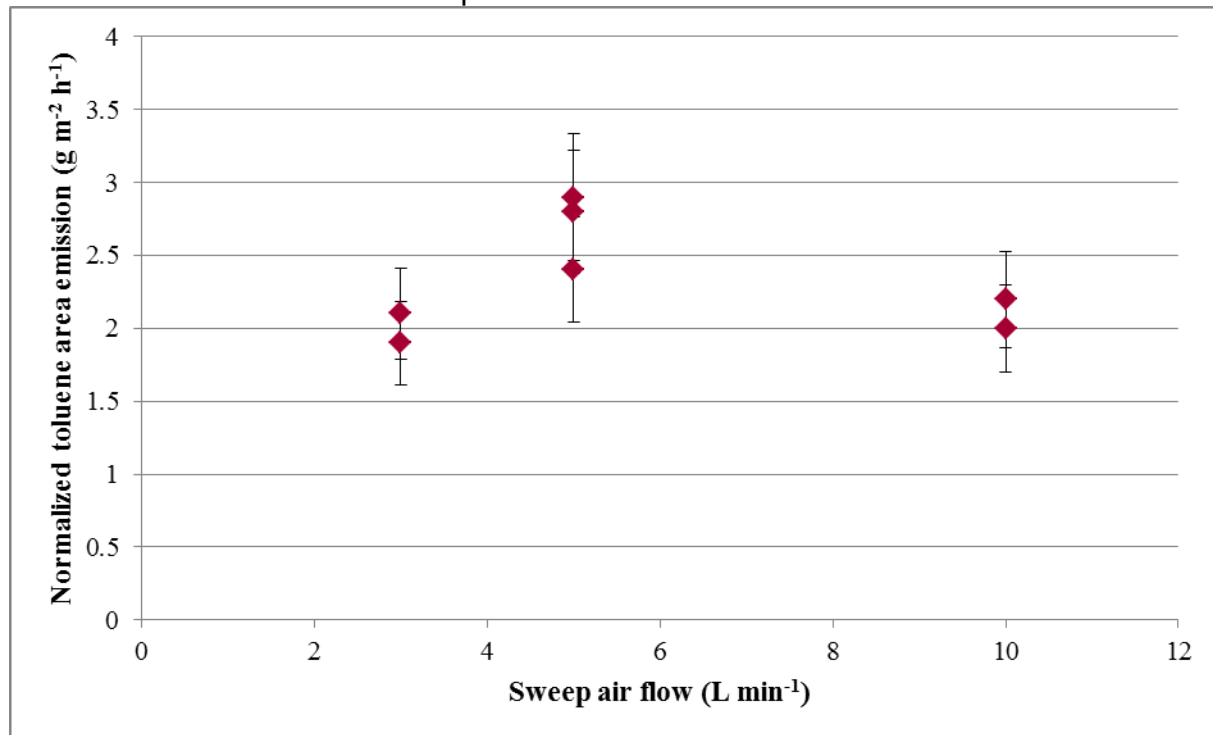
The toluene concentrations in water are similar for all experiments. The pressure in the flux chamber is similar to the values measured in table 3 except for experiments at 10 L min<sup>-1</sup>.

The toluene concentration in the wind tunnel exhaust is stable at 250 ppb eq toluene except with the first experiment at 10L min<sup>-1</sup>.

The average toluene concentration in the flux chamber outlet with 3 L min<sup>-1</sup> sweep air flow is 580 ppm, 450 ppm with 5 L min<sup>-1</sup> sweep air flow and 175 ppm with 10 L min<sup>-1</sup> sweep air flow. For each toluene concentration, the deviation is under 6% except for a sweep air flow of 10 L min<sup>-1</sup> (13%). In this case, the deviation could be explained by the difference in the toluene concentration in water.

In the first experiment with the 10 l/min sweep air, the pressure is 70 Pa because the flux chamber was still leaking. In the second test with the 10 l/min sweep air, with the sealed flux chamber, the pressure drop, increased to 410 Pa (160 Pa due to connection of the analytical device (PID) to the exhaust flux).

The figure 19 presents the evolution of the toluene area emission in the flux chamber in function of the sweep air flow.



**Figure 19: Evolution of the toluene area emission in function of the sweep air flow in the flux chamber**

Considering the inaccuracy of the results, the normalized toluene area emission is similar whatever the sweep air flow in the range from 3 to 10 L min<sup>-1</sup>. Overall, the area emission is  $(2.4 \pm 0.4) \text{ g m}^{-2} \text{ h}^{-1}$ .

Moreover, it has to be noticed that experiments realized with a flux chamber with and without leaks and a 10 L min<sup>-1</sup> sweep air flow leads to similar area emission  $((2.1 \pm 0.3) \text{ g m}^{-2} \text{ h}^{-1})$  and therefore it can be concluded that the leaks were not influencing the operation of the flux chamber: the location of the outlet flow was from all over (from all the leaks) the flux chamber instead of from the one point (outlet line)

A factor 2 exists between area emission in the wind tunnel and in the flux chamber. The difference between the wind tunnel and flux chamber is explained by the difference in emission conditions between the tunnel and the chamber. Indeed, the sweep area velocity, defined as the ratio between the air flow and the surface, is 3200 times higher in the tunnel than in the flux chamber.

The Reynolds numbers in the flux chamber are figured in the table 20.

**Table 20: Reynolds numbers in the flux chamber vs sweep air flow**

Sweep air flow (L min <sup>-1</sup> )	Re
3	8
5	14
10	28

Re are very low whatever the sweep air flow applied in the flux chamber, confirming a laminar flow.

To conclude, the friction velocity is greater in the tunnel and therefore the renewal of the boundary layer is faster.

Table 21 presents the toluene mass balance between water solution and air. A gap exists between the loss of toluene in water and the mass of toluene recovered in the air phase.

**Table 21: Mass balance between water and air for the tests with saturated solution**

Saturated solution		Loss of toluene in water (g)	Toluene emitted in the wind tunnel (g)	Toluene emitted in the flux chamber (g)
without FC, wind 2 m/s	01.12.2014	3.3±0.8	6.5±1.3	
without FC, wind 2 m/s	08.01.2015	2.1±0.5	8.0±1.6	
with FC, sweep air 3 l/min, wind 2 m/s	14.01.2015	2.6±0.7	7.6±1.5	0.8±0.1
with FC, sweep air 3 l/min, wind 2 m/s	15.01.2015	5.2±1.3	7.1±1.4	0.8±0.1
with FC, sweep air 5 l/min, wind 2 m/s	09.01.2015	2.9±0.7	6.6±1.3	1.1±0.2
with FC, sweep air 5 l/min, wind 2 m/s	12.01.2015	4.0±1.0	6.2±1.2	1.1±0.2
with FC, sweep air 5 l/min, wind 2 m/s	13.01.2015	3.5±0.9	6.7±1.3	1.0±0.2
with FC, sweep air 10 l/min, wind 2 m/s	15.12.2014	3.9±1.0	15.5±3.0	1.0±0.2
with FC, sweep air 10 l/min, wind 2 m/s	22.01.2015	6.3±1.6	11.8±2.3	1.3±0.2

The lack of accuracy of UV-analysis and the short time of the experiment do not favor the calculation of a precise loss of toluene in water. So, the mass balance between loss of toluene in water and toluene recovered in air is not accurate.

#### 4.1.4 Conclusion

At the end of the tests realized with a saturated solution of toluene, it can be concluded that:

- The area emission in the flux chamber is stable at (2.4±0.4) g m<sup>-2</sup> h<sup>-1</sup> regardless the sweep air flow between 3 and 10 L min<sup>-1</sup>.
- A factor 2 exists between the area emission in the flux chamber and the real emission in the wind tunnel for the toluene. This factor is due to the difference in the friction velocity between the wind tunnel and the flux chamber.

#### 4.2 LOW TOLUENE SOLUTION

After the pre-test phase, it was decided to evaluate the toluene emission with a lower concentration solution of toluene (around 250 mg L<sup>-1</sup>).

This part of the report presents the results of these experiments.



## 4.2.1 Temperature, humidity

Table 22 summarizes all water and tunnel temperatures and relative humidity obtained in the experiments with low toluene solution. The evolution of temperature and relative humidity for all the study tests is shown in annex 7

**Table 22: Relative humidity and temperature of water and tunnel for each experiment**

Low concentration solution		Temperature (°C) Water			Temperature (°C) Tunnel			Relative Humidity (%)		
		Start	End	Average	Start	End	Average	Start	End	Average
without FC, wind 2 m/s	9.12.2014	17.4	20.8	19.3	20.1	19.3	18.9	22.0	21.0	21.8
without FC, wind 2 m/s	19.01.2016	18.9	20.2	19.4	18.0	17.8	17.9	43.8	42.3	42.6
with FC, sweep air 3 l/min, wind 2 m/s	20.01.2015	18.5	19.7	18.7	18.8	18.7	18.1	40.0	40.4	40.5
with FC, sweep air 5 l/min, wind 2 m/s	11.12.2014	18.9	21.9	20.5	19.1	21.5	20.1	36.0	30.6	34.9
with FC, sweep air 10 l/min, wind 2 m/s	12.12.2014	17.4	22.6	19.7	20.2	20.4	19.7	37.1	37.2	37.4

As for experiments with saturated solutions, the temperatures are close to 20°C. Therefore it will be possible to compare the results of tests realized with saturated and low concentration solution.

As mentioned above, the temperatures for the study tests are lower because the experiments are done in December and January instead of August for the pre-tests. The average temperature of water is close to 20°C instead of 25°C in the pre-tests.

## 4.2.2 Area emission in the wind tunnel exhaust

The emission of toluene in the wind tunnel is summarized in the following table. The values are normalized for a toluene solution at 250 mg L<sup>-1</sup>.

**Table 23: Toluene concentration in water and air, area emission for the experiment without the flux chamber**

Concentration ppb eq toluene			Area emissions (g m <sup>-2</sup> h <sup>-1</sup> )	Water mg/l		Area emissions (Normalized values*) (g m <sup>-2</sup> h <sup>-1</sup> )
background	WT outlet	Outlet - background		initial	end	
72	188	116	2.1±0.4	284	260	1.8±0.5
36	188	152	2.8±0.5	257	243	2.8±0.6

\* Normalization for a toluene concentration in water of 250 mg L<sup>-1</sup>.

Toluene concentrations at the exhaust of the wind tunnel are very low (average 125 ppb eq toluene) not so far from the background level (70 ppb).

The average toluene area emission in the wind tunnel with a low normalized concentration (at 250 mg L<sup>-1</sup>) is 2.3 g m<sup>-2</sup> h<sup>-1</sup>.

## 4.2.3 Area emission in the flux chamber

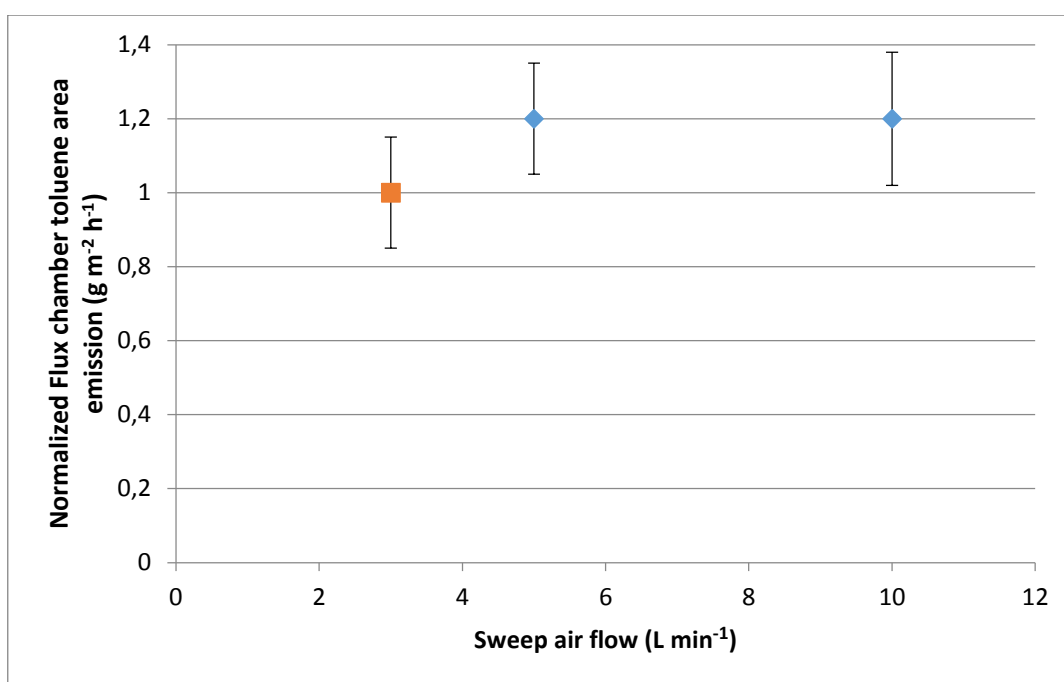
Table 24 shows the toluene concentration measured at the exit of the wind tunnel, in the flux chamber for different sweep air flows (3, 5 and 10 L min<sup>-1</sup>). The toluene area emission is also figured in this table.

**Table 24: Toluene concentration, area emission and pressure in the flux chamber for each test with low toluene solution**

Concentration (ppb toluene)				Sweep air (L min <sup>-1</sup> )	Area emission (g m <sup>-2</sup> h <sup>-1</sup> )	Water (mg L <sup>-1</sup> )		Area emission (Normalized values*) (g m <sup>-2</sup> h <sup>-1</sup> )
background	WT outlet	Outlet - background	FC	FC	FC	initial	end	
73	214	141	295 194	3	1.0±0.2	259	239	1.0±0.2
86	254	168	228721	5	1.3±0.2	264	254	1.2±0.2
86	202	116	80254	10	0.9±0.2	193	179	1.2±0.2

In this table, only the experiment with a 3 L min<sup>-1</sup>-sweep air flow is realized with the sealed flux chamber as shown by the level of pressure in the flux chamber. But as seen with saturated solution (10 L min<sup>-1</sup>-sweep air flow), the results obtained with the flux chamber which was not yet totally sealed can be compared with the ones with a sealed chamber.

Figure 20 presents the evolution of the toluene area emission in function of the sweep air flow in the flux chamber. In black the area emission obtained with a sealed flux chamber and in red with the leaking one.



**Figure 20: Evolution of the toluene area emission in function of the sweep air flow in the flux chamber.**

If we consider the normalized values, toluene emission in the flux chamber is stable whatever the sweep air flow as for saturated solutions. The toluene area emission in this case is half of that with saturated solution. This can be also explained by the Henry's law. The toluene concentration in low concentration solution is half the saturated one. So, the toluene partial pressure in the flux chamber is half the partial pressure obtained with a saturated solution. To conclude, if the toluene concentration in the flux chamber is half the saturated one, the area emission should be half that obtained with saturated solution.

As seen with the saturated solutions, a factor 2 exists between area emission in the wind tunnel and in the flux chamber.

Table 25 presents the toluene mass balance between water solution and air. A gap exists between the loss of toluene in water and the mass of toluene recovered in the air phase.

**Table 25: Toluene mass balance between water and air for low concentration solution**

Low concentration solution		Loss of toluene in water (g)	Toluene emitted in the wind tunnel (g)	Toluene emitted in the flux chamber (g)
without FC, wind 2 m/s	9.12.2014	3.7±0.9	3.0±0.6	
without FC, wind 2 m/s	19.01.2016	2.2±0.6	4.2±0.8	
with FC, sweep air 3 l/min, wind 2 m/s	20.01.2015	3.0±0.8	4.6±0.9	0.5±0.1
with FC, sweep air 5 l/min, wind 2 m/s	11.12.2014	1.5±0.4	5.0±1.0	0.6±0.1
with FC, sweep air 10 l/min, wind 2 m/s	12.12.2014	2.1±0.5	3.4±0.7	0.4±0.1

#### 4.2.4 Conclusion

The main conclusions of the tests with the low concentration are summarized below:

- The area emission in the flux chamber is stable at  $(1.1 \pm 0.2) \text{ g m}^{-2} \text{ h}^{-1}$  for any sweep air flow between 3 and 10  $\text{L min}^{-1}$ .
- The results give a factor 2 for the toluene between the area emission in the flux chamber and the real emission in the wind tunnel. This factor is due to the difference in the friction velocity between the wind tunnel and the flux chamber.
- The area emission measured with a 250  $\text{mg L}^{-1}$ -toluene solution is half that of a saturated solution (at 500  $\text{mg L}^{-1}$ ). This result is following the Henry's law.

### 4.3 ACCURACIES IN THE MEASUREMENTS OF TOLUENE CONCENTRATION

List of accuracies of devices used to measure toluene concentration in air and water:

#### Preparation of the solution

- Volume of toluene: 2%
- Volume of water in the preparation tank: 5%

#### Toluene concentration in water

- UV analysis: 10%, in reality closer to 25% if we consider all the sampling and analysis protocol.

#### Toluene concentration in the wind tunnel

- PIDs (given by the manufacturer): 10% of the response or 20 ppb when the response is less than 200 ppb.
- Response factor: 4%

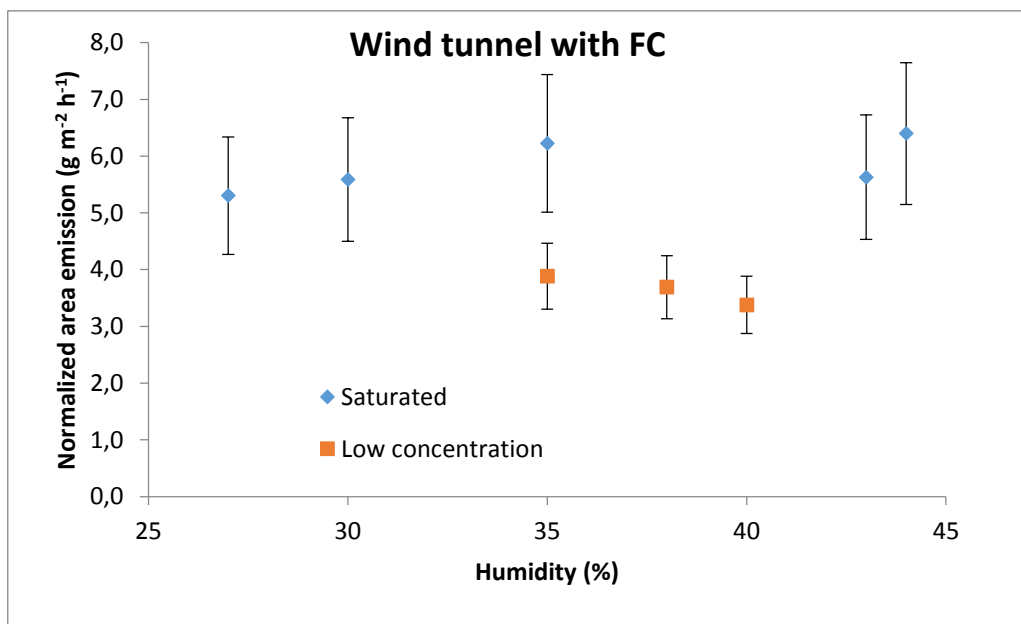
- Wind speed measurement (given by the manufacturer): 3% of the value + 0.05 m s<sup>-1</sup>.

#### Toluene concentration in the flux chamber

- PIDs (given by the manufacturer): 10% of the response or 20 ppb when the response is less than 200 ppb.
- Response factor: 4%
- Mass flow controller (given by the manufacturer): 1%

#### PIDs and humidity

The figure 21 indicates that humidity in the wind tunnel has no impact on the toluene concentration measured and finally on the area emission. For a saturated solution the toluene emission in the wind tunnel is around (6±1) g m<sup>-2</sup> h<sup>-1</sup> and for the low concentration solution the toluene emission is close to (3.7±0.6) g m<sup>-2</sup> h<sup>-1</sup>.



**Figure 21: Impact of humidity on the area emission.**

#### 4.4 CALCULATION OF THE UNCERTAINTY

According Weisstein<sup>1</sup>, the relative error is defined by

$$\partial x = \frac{\Delta x}{x} = \frac{x_0 - x}{x} = \frac{x_0}{x} - 1$$

Where  $x$  is the true value of a quantity,  
 $x_0$  the measured or inferred value,  
 $\Delta x$  is the absolute error.

The relative error of the quotient or product of a number of quantities is less than or equal to the sum of their relative errors

In our case, the uncertainty on toluene flux in the wind tunnel is defined by

$$\frac{\Delta \text{toluene flux}_{WT}}{\text{toluene flux}_{WT}} = \frac{\Delta \text{concentration}_{PID3000}}{\text{concentration}_{PID3000}} + \frac{\Delta \text{Response factor}_{PID3000}}{\text{response factor}_{PID3000}} + \frac{\Delta \text{wind speed}}{\text{wind speed}}$$

In the same way, the uncertainty of toluene flux in the flux chamber is defined by

$$\frac{\Delta \text{toluene flux}_{FC}}{\text{toluene flux}_{FC}} = \frac{\Delta \text{concentration}_{PID+}}{\text{concentration}_{PID+}} + \frac{\Delta \text{Response factor}_{PID+}}{\text{response factor}_{PID+}} + \frac{\Delta \text{Sweep air flow}}{\text{Sweep air flow}}$$

The accuracy of each device is given in paragraph 4.2.

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<sup>1</sup> Weisstein, Eric W. "Relative Error." From MathWorld--A Wolfram Web Resource. (<http://mathworld.wolfram.com/RelativeError.html>)

## 4.5 OVERALL CONCLUSIONS

The main conclusions of the report are summarized below.

To measure concentration in air with a PID, the response-factor of the compound must be evaluate in moist air to be as close as possible to the real concentration.

It appears that the impact of flux chamber leaks is not significant on the measurements.

The area emissions of toluene measured in the wind tunnel with a 2 m s<sup>-1</sup>-wind speed are:

- (5±1) g m<sup>-2</sup> h<sup>-1</sup> for a saturated solution of toluene (around 500 mg L<sup>-1</sup>).
- (2.3±0.6) g m<sup>-2</sup> h<sup>-1</sup> for a solution of toluene at 250 mg L<sup>-1</sup>.

The area emissions in the wind tunnel are correlated with the concentration in the solution for the same wind speed. All exchanges between water and wind tunnel exhaust are subjected to Henry's law ( $H_{tol} = 673 \text{ Pa m}^3 \text{ mol}^{-1}$  at 25°C).

The Henry's law says that if the flux chamber is close to equilibrium:

$$P_{Tol_{air}} = H_{Tol} \times C_{tol_{water}}$$

So a correlation exists between initial water concentration and emissions in the wind tunnel exhaust. In this case, the only parameter that significantly varies is the toluene concentration in the water.

Regardless the sweep air flow in the range from 3 to 10 L min<sup>-1</sup>, the toluene emission rate measured in the flux chamber is half of the area emission rate measured in the wind tunnel for any toluene concentration in water. The difference between the wind tunnel and flux chamber is explained by the difference in emission conditions between the tunnel and the chamber. Indeed, the sweep area velocity, defined as the ratio between the air flow and the surface, is 3200 times higher in the tunnel than in the flux chamber. The flow in the flux chamber is close to a laminar flow while in the wind tunnel it is turbulent.

To conclude, it seems possible to use a flux chamber to determine the emission of pollutant from liquid sources. However, it is likely that the factor of 2 observed with toluene in these tests will be different with others compounds. As the emission depends of the Henry's coefficient and of the friction velocity, the composition of the solution and the geometry of the flux chamber impact on this factor.

In a refinery the mixtures are much more complex than a single compound in water. So, if an "Odoflux<sup>®</sup>" flux chamber is used to estimate the emissions, the factor to apply depends on the volatility of the mixtures. If the mixture volatility is close to that of toluene, the factor 2 can be used for any sweep air flow rates from 3 to 10 L min<sup>-1</sup>. If the mixture volatility is different, the factor is unknown and must be determined again. If the flux chamber is not an "Odoflux<sup>®</sup>", the factor will be different too even for toluene in water.

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