

5 Results and Discussion

5.1 Calibration and reliability

For the calibration line each point was measured between three and eight times. In a linear regression R^2 was determined to be 0,9971 and the variation coefficient was in a range of 1 to 5% for all without one of the measuring points. The values obtained for the different volumes and the variation coefficient can be seen in Appendix 1 figure (7.1).

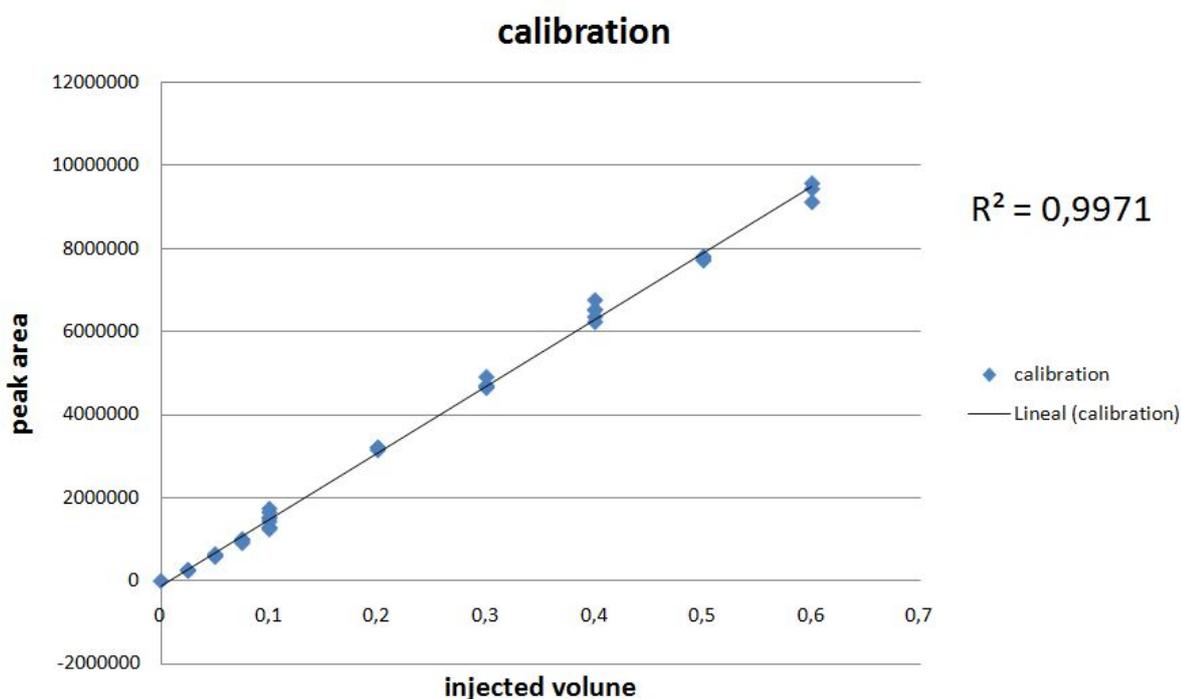


Figure 5.1: Linear regression for the values obtained injecting different volumes of a defined standard to obtain a calibration line

5.2 Masstransfer coefficient

5.2.1 Experimental condition

For the determination of the masstransfer coefficient (R) two experiments were done. Both carried out under the same conditions, the only variation being the velocity of

the magnetic stirrer. In the first experiment the stirrer was run at the highest possible velocity, without creating turbulence at the water surface. In the second experiment the stirrer was run at a low velocity, but still guaranteeing a good mixing of the water body. The water temperature in both experiments was quite stable at 23°C . It varied a little approximately + 1°C due to the energy introduced by the magnetic stirrer through the duration of the experiment.

There was water loss during the experiment. For each sampling point a volume of 250ml for Winkler and a volume of approximately 190ml for the headspace analysis were taken. The water loss was not considered in the calculation. It was assumed that the exchange rate was independent of the water volume and the waterbody was homogenous.

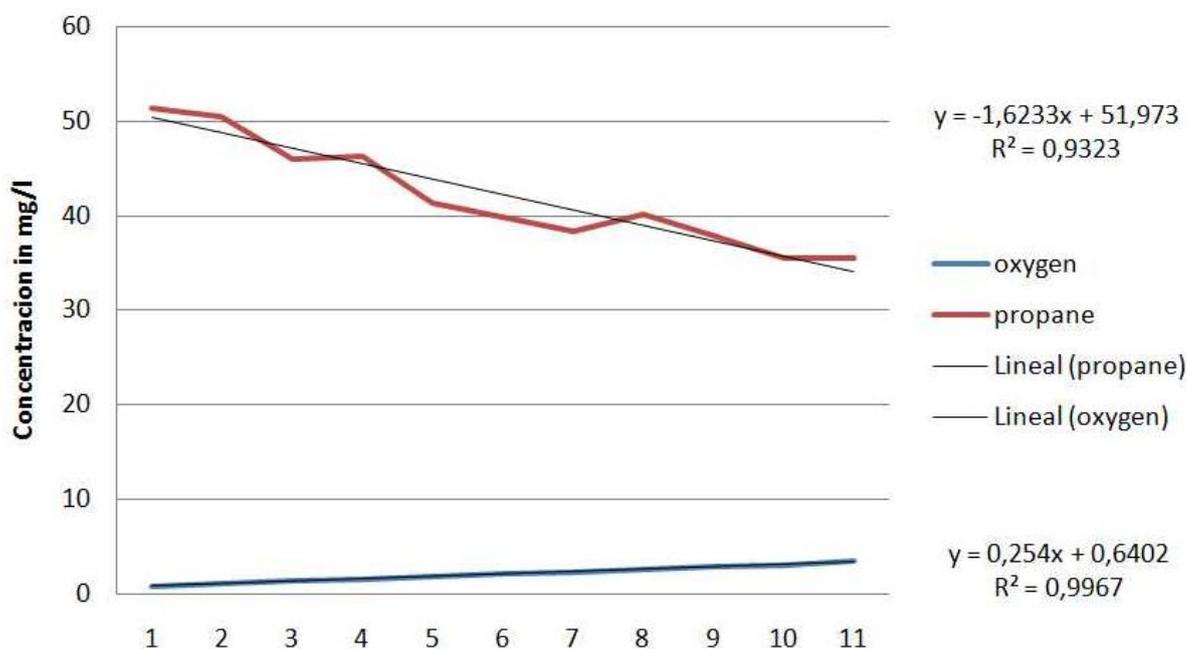


Figure 5.2: Graph reflecting the displacement of propane by oxygen with the time in the first experiment, 30 minutes between each sampling

In the first experiment with the higher stirring velocity, the propane displacement was faster than in the second experiment. Better mixing caused a higher concentration gradient and a faster diffusion. Samples were taken every half an hour and the experiment lasted 6 hours. The results and calculation for propane are presented in Appendix 2 figure (7.4) and (7.5). The values obtained for oxygen measured with the sensor coincided quite well with the values obtained with winkler, see Appendix 2 figure (7.2) and figure (??). The results of the winkler titration were used for the calculation of K .

In the second experiment the displacement of propane was slower, samples were taken every hour and the experiment lasted nine hours. The values measured with Winkler were used for the calculation of K_{oxygen} .

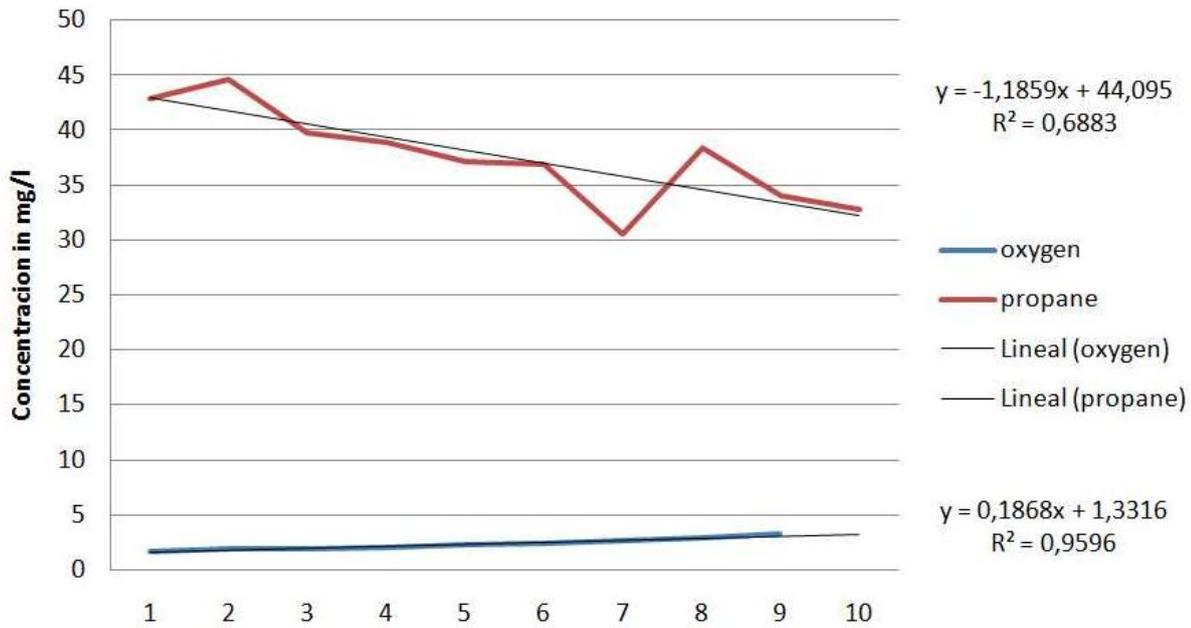


Figure 5.3: Graph reflecting the displacement of propane by oxygen with the time in the second experiment, 1 hour passed between each sampling point

5.2.2 Results obtained for the masstransfer coefficient

With the tendency line obtained in the experiment, two different concentrations for the propane and the oxygen were calculated. With these concentrations the transfer coefficient K was determined. Oxygen was calculated with formula (3.31) and for propane it was calculated with formula (3.33). With the $K_{propane}$ and K_{oxygen} the R was calculated applying formula (3.30).

Table 5.1: Values obtained for masstransfer coefficient K of oxygen and propane and for R , the ratio between the two coefficients

coefficient	First experiment	Second experiment
$K_{propane}$	0,223	0,178
K_{oxygen}	0,230	0,186
R	1,032	0,954

The values obtained for R are in a range that is comparable to values determined in other studies:

Rathbun et al. determined R for propane and oxygen in a study in 1978. The experiment was repeated 34 times and the value for R was found to be $1,39 \pm 0,028$. The ratio was independent of mixing condition in the water and independent of the water temperature varying between 20 and 30 °C [RAS⁺78]

In a study by Bourmansour et al. in 1995, the value for R was $1,389 \pm 0,024$. [BV98]

Madsen et al. obtained a value of 1,52 with a reliability factor of 95% and R was shown to be independent on turbulence and temperature.

The gas mixture used in this study consisted of 87,48% propane. Because of that the R found for this gas mixture had a slightly different value to the R determined in the studies mentioned above. In these studies pure propane was used. The range of the value was comparable to the values obtained in the other experiments, that made it more reliable. Both R found in the two experiments were very close. The value used for the later calculation was the arithmetic mean of them, $R = 0,99354$.

5.3 Determination of the oxygen transfer rate

In order to determine the oxygen transfer rate, three long running experiments were made. They were modified subsequently due to the experience with the preceding experiment. The first experiment had a different experimental set up. The other two experiments were run under the same conditions but one was batch operated the other had a continuous inlet flow.

5.3.1 First experiment, batch operation

Experimental set up and condition

In the first experiment, the set up was assembled in a way that allowed the experiment to run over an infinite time. This was possible because small 10 liter tanks were used for the inlet. The inlet was batch operated. Every 4 hours, 20 liters flowed into the wetland. For each supply the tank was filled again and oxygen was displaced with propane. Balloons were connected for the pressure compensation. For this procedure a constant vigilance was necessary. The retention time was 18,9 hours. A common retention time for a wetland is 48 hours. The shorter time was selected because the experiment should be run at least two or three times the hydraulic retention time. The experiment was run for 50 hours. The temperature varied between 15 °C at night and 26 °C during the day. Appendix 3 shows a graph of the temperature variation.

Samples were taken every two hours. The sampling was made at three points: the entrance, middle and outlet. Propane was measured with headspace analysis and calculated as described above in the chapter 4.2.2. The detailed data obtained for the propane concentration is represented in Appendix 3.

Parameter	Value for the CW
Pore water volume, l	85
Flow volume, l/d	120
Batch operation, l/4h	20
HRT, h	18,9

Development of the propane concentration at the run time of the first experiment

A varying propane concentration was expected at the inlet while a stable propane concentration was expected at the outlet of the wetland. The propane concentration at the outlet was expected to reach equilibrium after the expiration of the HRT. To be sure that the concentration became stable and to obtain enough interpretable data, the experiment was run for 2 1/2 times the HRT.

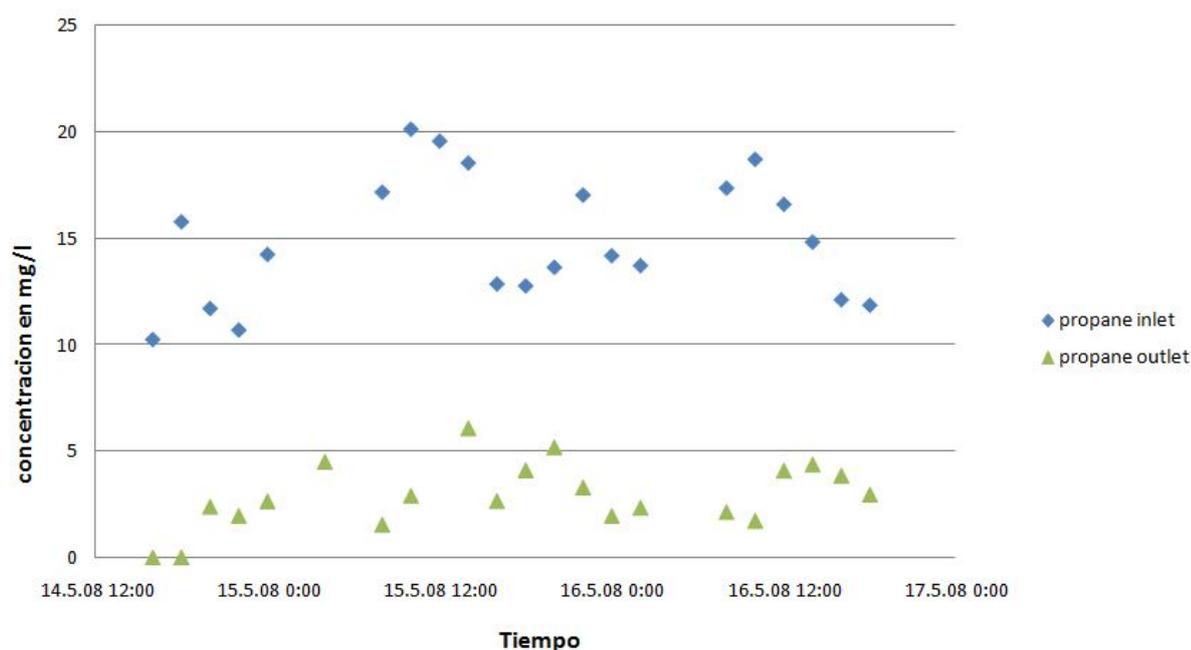


Figure 5.4: Graph that showing the propane concentration in the first experiment over time

Concentration in the inlet Due to the batch operating, the concentration at the inlet varied. The samples were taken every two hours and the batch operation was conducted every four hours, each supply lasted between one and two hours. Some samplings coin-

cided with the feeding of the wetland. These higher concentrations represent the inlet and were taken for the calculation. A medium propane concentration of 17,66 mg/l was obtained. See Appendix 3 figure (7.12),(7.13),(7.14),(7.15);

Concentration in the middle of the wetland In this experiment samples of the middle of the wetland were taken to see how the concentration would vary over the length of the wetland. The results are shown in a graph in Appendix 3. The concentrations were not used for later calculations but they confirm the validity of the concentrations of the inlet and the outlet, as they lie just in between both values. The effect of the batch operation could still be seen because the values did vary. The medium propane concentration obtained was 7,11 mg/l. See Appendix 3 figure (7.18),(7.17),(7.18),(7.19);

Concentration in the outlet The experiment was run for more than two times the HRT and the outlet was expected to reach a stable state after one HRT. But the values still varied with a standard deviation of 1,01. The medium propane concentration was 3,47 mg/l. Beside the propane peaks for CO₂ were measured. Gas was produced in the system but it was assumed not to affect the experiment. See Appendix 3 figure (7.20),(7.21),(7.22),(7.23);

5.3.2 Second experiment, batch operation

The main problem of the first experiment was that the outlet concentration did not become very stable. It was assumed that there would be a problem in the inlet propane concentration. Another problem was that the first experiment was very time intensive and needed a constant supervision.

Changes in the experimental conditions

To avoid these problems the set up and the method were changed. A stable entrance was reached using a huge water tank of 250 liters that was saturated once at the beginning of the experiment. The water mass which left was compensated for propane gas. As it was difficult to close the tank hermetically, the water was bubbled with propane throughout the whole experiment. The exiting gas was substituted by the entering gas. This guaranteed a stable concentration of propane in the inlet water.

The concentration of propane in the tank was determined to be 63,9 mg/l. For pure propane the saturation concentration is 74 mg/l at 20°C. The saturation concentration of the gas mixture used in this study, makes up a 86,4% of the saturation concentration for pure propane. This value matches exactly with the percentage of propane in the gas mixture of 87,48 %.

Using a bigger tank had the advantage that the experiment could be run automatically with a perestraltic pump regulating the entrance. No permanent attendance was necessary. The saturation of the big tank lasted one day. A disadvantage of this set up was

that the run time of the experiment was limited by the volume of the tank.

Parameter	Value for the CW
Pore water volume, l	85
Flow volume, l/d	151
Batch operation, l/4h	25
HRT, h	15

In this experiment two samples were taken for the inlet. Two different points were chosen to get a more balanced and reliable value.

Development of the propane concentration at the run time of the second experiment

As in the first experiment a varying propane concentration was expected at the inlet and a stable propane concentration was expected at the outlet of the wetland. The propane concentration of the outlet was expected to reach equilibrium after the expiration of the HRT. To be sure that the concentration became stable and to obtain enough interpretable data, the experiment was run for 2 times the HRT. Samples were taken during the day. No samplings were made over night but the feeding continued automatically.

Concentration in the inlet The inlet concentration varied due to the batch operating. Feeding with the peristaltic pump was more precise and the maxima in the graph (5.5) coincided exactly with the feeding of the wetland. The samples were taken every two hours and the batch operation was conducted every four hours, each supply lasted 1 1/2 hours. The medium propane concentration was 10,27 mg/l. The arithmetic mean of the three maxima, obtained during the feeding, was 12,95, it was taken for the later calculation of K. See Appendix 4 figure (7.24),(7.25),(7.26),(7.27);

Concentration in the outlet The experiment was run for two times the HRT and the outlet reached a stable state after one HRT. The medium propane concentration was very stable 1,7 mg/l. The variation coefficient was low, 4,4%. Beside the propane, CO₂ was measured. See Appendix 4 figure (7.28),(7.29);

5.3.3 Third experiment, continuous operation

The experimental set up of the second experiment was good because the values obtained for the outlet were stable and the propane concentration in the tank was reliable. The automatic feeding worked well. To compare the data a different operation mode was

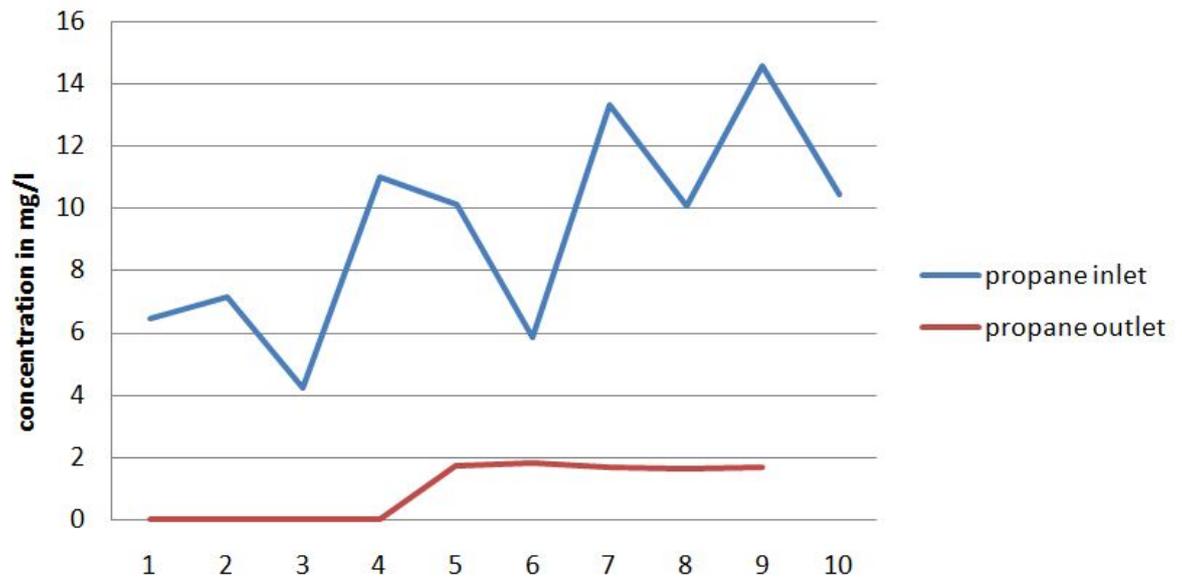


Figure 5.5: Graph showing the propane concentration in the second experiment over time, two hours between each measuring point, a 12 hour break between point four and five was made

chosen for this experiment. Instead of batch operation this time the water supply was conducted continuously.

Changes in the experimental conditions

The only change in the set up was that the perestraltic pump now ran continuously with a flow volume of 0,1 l/min.

Parameter	Value for the CW
Pore water volume, l	85
Flow volume,l/d	151
Continous operation,l/min	0,1
HRT, h	15

Development of the propane concentration at the run time of the second experiment

A stable propane concentration was expected at the inlet and at the outlet of the wetland. The propane concentration of the outlet was expected to reach equilibrium after

the expiration of the HRT. Sampling started a short time before finishing the HRT in order to observe the equilibration in the graph.

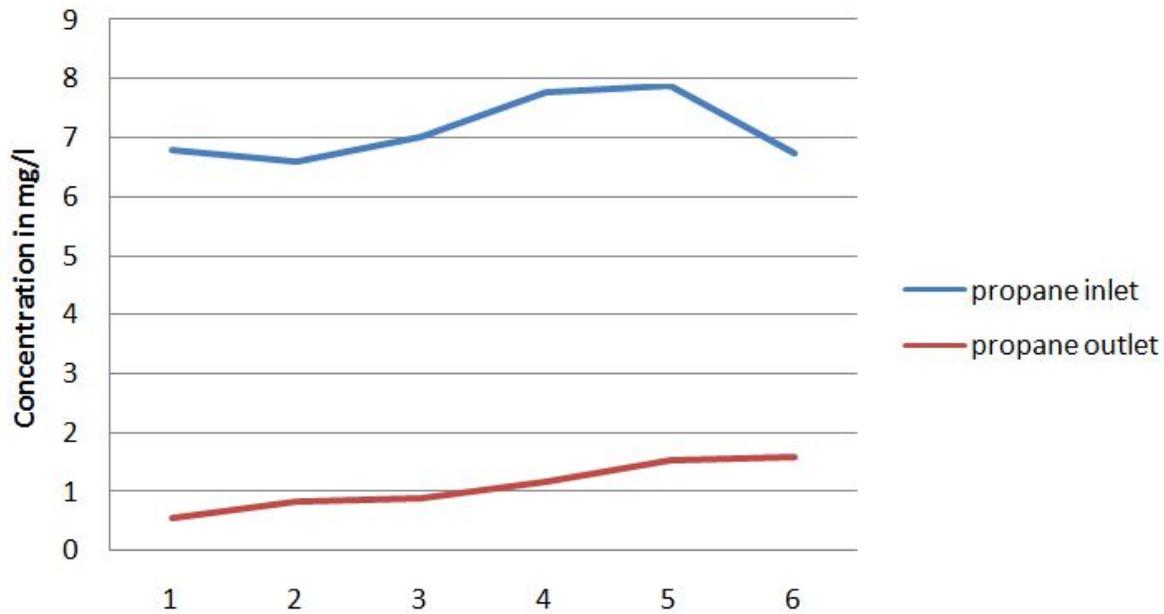


Figure 5.6: Graph that shows the propane concentration in the third experiment over time, between two hours are between each measuring point, the first sample was taken 14 hours after the start of the water supply

Concentration in the inlet The propane concentration at the inlet was almost stable. The medium propane concentration of 12,95 mg/l was used for later calculations. The variation coefficient was 8,15%. See Appendix 5 figure (7.30);

Concentration in the outlet Although the experiment lasted longer than the HRT, the concentration kept rising. The gradient of the last two values was very small. It was assumed that these two points represented the equilibrium. The value used for later calculations was 1,5 mg/l. To obtain better values the experiment should have lasted a bit longer. Beside the propane, CO₂ was measured in the outlet. See Appendix 5 figure (7.31);

5.4 Comparison of the results

The oxygen transfer was determined with a tracergas method, using propane as a tracer. The same method was used in studies reflected in table (5.2).

Unlike to other studies, the tracer gas in our study was not pure propane but a gas mixture, with propane as the main component. Due to this the mass transfer ratio R was determined for the specific gas mixture used in this study (see chapter 5.2). R relates the mass transfer coefficient of propane to the mass transfer coefficient of oxygen. The value obtained for R was 0,99354 for the specific gas mixture used in this study. With the obtained mass transfer coefficient for oxygen, the oxygen transfer to the wetland was determined.

Table 5.2: Studies on the oxygen transfer with a propane tracer gas method

Study	Summary	Reference
Rathbun et al. in 1977	study on reaeration rates under laboratory condition	[RAS ⁺ 78]
Rainwater et al. in 1984	study on certain factors necessary for the field application of the tracer method; the dependency of R on temperature and the adsorption of propane on soil.	[RAHA84]
Vasel and Schrobiltgen in 1989	study on oxygen transfer in trickling filters	[VS91]
Thene et al. in 1990	oxygen transfer at weirs	[TG90]
Boumansour et al. in 1997	oxygen transfer on RBC	[BV98]
Hebrard et al. in 1999	determination of the water quality correction factor	[HDR ⁺ 00]
Huisman et al. in 2001	study on reaeration in sewers	[HWG04]
Madsen et al. in 2006	study on the influence of temperature, turbulence and impurities on the oxygen transfer in wetlands	[MVHJ06]
Santa, 2007	study on the oxygen transfer to a unplanted gravelbed	[San07]

5.4.1 Determination of the masstransfer coefficient

To calculate the masstransfer coefficient for propane ($K_{propane}$) samples of the inlet and the outlet of the wetland were taken. An important component in the calculation of $K_{propane}$ is the hydraulic residential time (HRT). In this study the theoretical HRT was calculated and used for the determination of $K_{propane}$. The wetlands were run with waste water for several years, so a variation in the retention time, due to clogging and sludge accumulation is possible. K_{oxygen} was calculated with the value for R and $K_{propane}$. The K_{oxygen} was not standardized to 20°C because the temperature varied (from 15°C to 26°C) during the experiment, see graph Appendix 3 figure (7.11)

Table 5.3: Masstransfer coefficients of the three experiments in comparison

Parameter	1.Exp. batch operated	2.Exp., batch operated	3. Exp. continuous
HRT, h	18,9	15	15
$C_{inlet}, mg/l$	17,66	12,95	6,8
$C_{outlet}, mg/l$	3,47	1,71	1,5
$K_{propane}, 1/h$	0,086	0,135	0,101
$K_{oxygen}, 1/h$	0,085	0,133	0,099

The values for K_{oxygen} determined in the three experiments were in a range of 0,08 to 0,13. The identicalness of the results matches with the fact that the retention time was the same or almost the same in the three experiments.

In a study of Santa in 2007 the relation of the retention time and the oxygen mass transfer was shown. With a increasing hydraulic retention time, the mass transfer decreased. For a very retention times of 1,08, 2,19, 3,47 and 47,78 he obtained values of 0,27, 0,25, 0,18 and 0,03, respectively for a K_{oxygen} standardized to 20°C [San07]

To confirm the reliability of the values obtained for K_{oxygen} they were compared with the results of others studies.

Table 5.4: Literature overview of values for K_{oxygen} obtained in different studies

Study	K_{oxygen} , 1/h	experimental conditions
Foree et al.; in 1976 [FA76]	0,015 - 0,97	Reaeration in small streams of different flow characteristics, determination of K_{la} with the radioactive tracer krypton-85 and tritium at a temp of 25°C
Rathbun et al.; in 1977 [RAS ⁺ 78]	0,42 - 0,28	Laboratory study at a small scaled water tank, determination of K_{la} with the ethylene and propane as tracer; test on different mixing conditions and on the presence of phenol, detergent and oil on the surface at a temp of 25°C
Gelda et al.; in 1989 [GAE ⁺ 96]	0,11 and 0,0625	Measurement of oxygen transfer to a whole lake, taking a watercolumn as representative for the lake condition, estimation of the reaeration coefficient by a mass balance on oxygen, K_{la} was calculated for a temp of 20°C
Banks et al.; in 1983 [BAW ⁺ 84]	0,023 - 0,036	Laboratory study at a small scaled water tank to see the effect of artificial rain with different characteristics on the oxygen concentration, K_{la} was calculated for a temp of 20°C
Rainwater et al.; in 1984 [RAHA84]	0,49 - 0,72	Laboratory study at a small scaled water tank to see if a changing temperature or adsorption on soils has an effect on the tracer method, K_{la} was calculated for a temp of 20°C
Hebrard et al.; in 1999 [HDR ⁺ 00]	38 - 156	Study on the difference of the oxygen mass transfer in a bubble column filled with clear or with wastewater. Determination of the water quality factor

Study	K_{oxygen} , 1/h	experimental conditions
Huisman et al.; in 2001 [HWG04]	0,33 - 10,6	Field study on the reaeration in sewers applying a tracer method with sulphur hexafluoride as tracer gas.
Santa; in 2007 [San07]	0,03 - 0,27	Laboratory study on the oxygen transfer in a gravelbed with varying hydraulic retention times; K_{la} was calculated for a temp of 20°C

Many studies have been made on rotating biological contactors, some results are represented in the following table.

Table 5.5: Overview of values for K_{oxygen} , all obtained in studies on rotating biological contactors, modified table of Chavan and Mukherji in 2008 [CM08]

Study	K_{oxygen} , 1/h	Notes and Reference
Bintaja et al.; in 1975	2,58 - 17	-
Zeevalkink et al.; in 1979	2,76 - 13	-
Kim and Molof; in 1982	29 - 95	-
Paolini; in 1986	3,72 - 13	-
Vasel and Schrobiltgen; in 1989	9 - 63	Study on OTR with and without biofilm and with different hydraulic retention times; [VS91]
Boumansour et al.; in 1997	2 - 20	Measured K_{oxygen} applied a tracer gas method with propane as tracer [BV98]

Study	K_{oxygen} , 1/h	experimental conditions
Kubsad et al.; in 2004	1,68	Determined the K_{oxygen} by measuring the DO [KCG04]
Chavan and Mukherji; in 2007	0,66 - 4,0	[CM08]
Vasel and Schrobiltgen; in 1989 [VS91]	9 - 63	Study on the oxygen transfer at trickling filters with and without biofilm and with different hydraulic retention times

The values for K_{oxygen} vary a lot with the experimental set up. Studies with similar conditions were made by Foree et al. (1976), Rathbun et al. (1977), Gelda et al. (1989), Banks et al. (1983), Rainwater et al. (1984), Huisman et al. (in 2001) and Santa; (2007). In comparison to the values obtained in these studies the results of K_{oxygen} were in the same range, which confirms the validity of the determined mass transfer coefficients. The scale of the values in the studies was between 0,015 and 10,6. With values in between 0,08 and 0,13 the results obtained in this study were low.

The K_{oxygen} determined in the studies on rotating biological contactors, trickling filters and bubble column were higher. This is due to the fact that all these systems were especially designed for a huge air - water contact, guaranteeing a high oxygen transfer. A subsurface flow constructed wetland is a system with few contact between air and water. The fact that the values obtained in this study were much lower than the values of the optimized systems is further proof of their reliability.

5.4.2 Oxygen transfer rate

According to Kadlec and Knight, subsurface flow constructed wetlands, with the air - water interface below ground, have a special mixing mechanism and a different turbulence scale. The oxygen transfer rates (OTR) to water are extremely low so the OTR for subsurface flow constructed CWs are expected to be low. [KK96]

There is no specific study of the oxygen transport from air to water moving in a gravelbed. (Kadlec and Knight, 1996)

In this study the oxygen transfer to a planted gravelbed was measured. To determine the OTR the obtained values for K_{oxygen} were put in the formula (3.39). The calculation is described in chapter 4.5.6. The values for the maximum oxygen transfer rates found in this study are represented in table tbl:resultsotr .

Table 5.6: Results of the three experiments in comparison

Parameter	1.Experiment, batch operated	2.Experiment, batch operated	3.Experiment, continous
HRT, h	18,9	15	15
OTR, $\frac{mg}{m^2 \cdot h}$	86	136	101
OTR, $\frac{g}{m^2 \cdot d}$	2,08	3,26	2,43

The range of these values were compared to values obtained in other studies to proof their reliability. The OTR can be calculated direct or indirectly, described in chapter 3.4.

In this study OTR was measured directly with a tracer gas method with propane. The same method was used in the study of Santa (2007) were it was determined the oxygen transfer to an unplanted gravel bed. Four experiments have been carried out with HRT set at 1.08, 2.70 and 3.17, and 48 h and maximum oxygen transfer rates of 6.16, 5.71, 4.11, and $0.78 \frac{g}{m^2 \cdot d}$, respectively.

Another study where OTR was measured directly was conducted by Brix and Schierup in 1990 (in Kadlec 1996 [KK96]). This study is described more precisely in chapter 3.4.2. In this study the oxygen release through plant roots was measured directly, it was found to be just $0,2 \frac{gO_2}{m^2/d}$. The OTR was determined to be $5,2 \frac{gO_2}{m^2/d}$, measured with an indirect massbalance.

Most studies on OTR apply an indirect measurement, estimating the value with a mass-balance. The values are represented in the following table:

Table 5.7: Values for the oxygen transfer to wetlands reported in literature, obtained with an indirect measurement method, modified table of Cooper, 2005 [Coo05]

Author	OTR, $\frac{g}{m^2 \cdot d}$	Notes
Burka and Lawrence (1990), Cooper (1999)	40 – 79	2 vertical flow and 2 horizontal flow CWs, based on long term averages

Author	OTR, $\frac{g}{m^2*d}$	Notes
Ciupa (1995, 1996)	5,4	1 horizontal flow and 1 vertical flow CW, overall average
Cooper et al. (1996, 1997, 2001)	57 – 71	2 vertical flow CWs, tertiary nitrification only
Weedon (2001)	39,5	1 compact vertical flow CW
Weedon (2002)	28 – 35	1 compact vertical flow CW
Platzer (1998, 1999)	28	vertical and horizontal flow CW, values for vertical flow beds only
Brix et al.(2002)	51– > 100	2 compact vertical flow CW, recommend design at 1,5 m ² /pe
Cooper and Cooper (2003)	30	3 tidal flow CWs

Compared to the indirectly measured OTR, the values obtained in this study were very low. The OTR reported in literature range between 5,4 to > 100 $\frac{g}{m^2*d}$, the OTR obtained in this study was comparatively low in a range from 2,08 - 3,26 $\frac{g}{m^2*d}$. Some reason could be that most of the wetlands observed in the studies shown in table (5.7) were conducted at vertical flow. Vertical flow constructed CWs have a higher oxygen transfer rate than the horizontal flow CW studied in the present work, due to their construction.

If the values are compared to the study carried out by Santa, it can be seen that they are reliable because they lie in exactly the same range. A range of 0,78 to 6,16 $\frac{g}{m^2*d}$ (Santa,2007) respectively 2,08 - 3,26 $\frac{g}{m^2*d}$ of this study.

Regarding the retention time, Santa measured a OTR of $4,71 \frac{g}{m^2*d}$ for a HRT of 3,27 h and a a OTR of $0,78 \frac{g}{m^2*d}$ for a HRT of 47,78 h. The HRT in our study of 15 and 18 hours is in between these two HRT of the study of Santa and the values obtained for OTR of our study, of $2,08 - 3,26 \frac{g}{m^2*d}$, are just in between the values obtained by Santa. The values match very well. The study of Santa was conducted at a unplanted wetland and our study at a planted wetland. The good correlation of the values of these two studies show in their tendency that the influence of plants on the oxygen transfer rate is not very huge.

The three values obtained in this study were so close that they didn't show a direct tendency regarding the operation mode. In a study of Caselles - Osorio y Garcia (2007) the redox condition in batch operated wetlands were higher than the redox condition in a continous operated wetland [COG06]. In our study the OTR of the continously operated wetland is slightly lower than the OTR of the batch operated experiment with the same retention time. Though the difference is too small to reach a clear concclusion. The values obtained for OTR confirm the assumption that the oxygen transfer to sub-surface flow constructed wetlands is very low.

