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Spraying ozonated water: mass transfer characterization from the atomizing liquid film to the cloud of droplets

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Summary

The present work proposes a fully characterization of the mass transfer occurring in a spray. First, a global method that relies on the collection and the titration of the sprayed liquid along the spray is presented. Ozone desorption and dioxygen absorption rates are determined and found to be equal. Moreover, for both solutes, most of the mass transfer ($\approx 70\%$) occurred in the atomizing liquid film that form the droplets at the direct exit of the nozzle. General correlations allowed to predict the desorption occurring in the already formed droplets, but not during their formation in the liquid film.

Then, an original local method based on light absorption through a dioxygen sensitive dye (resazurin) has been developed to locally assess the mass transfer in this atomizing liquid film. Measurements confirmed that the transfer occurring in the small region is quite strong.

From the complementarity of both the global and local approaches, the mass transfer of ozone can be fully predicted, from the direct exit of the nozzle (2-3cm) to the cloud of droplets (80cm-1m) produced by a spray. This understanding allows to prepare adequate ozone doses for plants treatments and would allow propositions of technical solutions to create anti-desorption devices for the spraying of OW.

Keywords: Agriculture – O₃ desorption – O₂ absorption – Light absorption – Resazurin dye

Introduction

For their controversial effects on the health and the environment, the use of pesticides in agriculture must be reduce to face increasing regulatory and societal pressures. The ozone molecule has been identified as a good candidate to substitute those chemicals partially or fully, especially thank to its biocide properties and its low persistence in the environment. A wide range of microorganisms related to the agrifood industry has been inhibited by ozonated water, giving hope for the development of crops protection with OW. But the process of spraying has been showed to induce strong mass transfer phenomenon between the sprayed liquid and the air (Canado et al., 2020; Fujiwara & Fujii, 2004). This ozone desorption dramatically reduces the effect of ozonated water since low residual ozone doses are then applied to the plant.

Studies that characterized the mass transfer occurring in a spray seemed to highlight that most of the measured mass transfer is located right after the nozzle, e.g. for the ozone desorption, 70% of the dissolved ozone is lost within the 3cm after the nozzle. This seems to be due to the atomizing phenomenon occurring right after the nozzle: the liquid exits the orifice and takes the configuration of a thin liquid film that undergoes instabilities due to the frictions with the surrounding air. These instabilities then reach a critical amplitude that break the liquid film in droplets for the spraying application. This liquid film configuration before the formation of the droplet seems to be suitable for strong mass transfer (Canado et al., 2020; Lin et al., 1977; Simpson & Lynn, 1977; Yeh & Rochelle, 2003).

However, the methods used for the mass transfer characterization in sprays have been global methods that lack of local accuracy to rigorously attribute such a mass transfer to the atomizing liquid film. To quantify the mass transfer enhancement in this liquid film, solute measurements must be made in the region where the droplets are formed. The difficulty of such measurements lies in avoiding any disturbances of the liquid flow in order to measure the composition of the liquid

correctly. Although many titration methods exist to quantify a given solute in a liquid, methods giving direct access to the solute quantification without liquid collection, such as Raman scattering spectroscopy, rainbow refractometry, or laser induced fluorescence, are rare or difficult to implement (Lebrun et al., 2021; Lemoine & Castanet, 2013; Li et al., 2020). Liquid collection methods report the global behavior of the mass transfer process, but they lack spatial and time resolution since the liquid collector volume varies with the collection of liquid and the titration is delayed with respect to the moment of collection. Moreover, they involve end effects such as wall collisions, splashes and eddies that can lead to overestimation of the mass transfer. Although various methods are reported in the literature for measuring the temperature of droplets (Brübach et al., 2006; Strizhak et al., 2020; Volkov & Strizhak, 2018) and their composition (Shao et al., 2012; Srinivasan & Aiken, 1988), no reliable techniques have been proposed for in situ measurement of the mass transfer in the region of the liquid film that produces the droplets.

A recent method for oxygen mass transfer visualization and measurement has been successfully applied to several gas-liquid-solid contactors (Dietrich et al., 2013, 2019; Dietrich & Hebrard, 2018; Kherbeche et al., 2020). It relies on the light absorption of a dioxygen sensitive dye called dihydroresorufin. In presence of glucose and sodium hydroxide, the dye can be oxidized (e.g., by dissolved dioxygen), and this oxidation leads to a new form of the dye, the resorufin, which absorbs light from a different wavelength. Then, from light absorption, the quantity of oxidized dye, and thence the quantity of dioxygen that has been transferred and has reacted with the dye, can be determined. This method provides solute quantification without disturbing the flow and offers a fun way to visualize the mass transfer.

The objective of this study is to fully characterize the mass transfer in an entire spray: from the liquid film to the cloud of droplets. First a global characterization of the spray using liquid collection is made to obtain ozone desorption and dioxygen absorption profiles along the spray. Then, the latter method relying on the oxygen sensitive dye is implemented in the liquid film to measure the mass transfer during dioxygen absorption. Finally, the experimental results obtained are extrapolated to make an ozone desorption prediction along the whole spray.

Materials and methods

- Global characterization of the mass transfer in the whole spray

Figure 1 detailed the experimental set-up used for the global measurement of the mass transfer along the spray. A solution in a liquid tank can be pumped (WT3000-1JA, Longer precision pump CO.Ltd, China) and sent through a nozzle to produce a spray. Beakers can be placed under the spray to collect some liquid to perform some composition measurements. Two nozzles were tested : the ADX-120-02 (Nozal, France) nozzle which works with air suction and produce a flat liquid film, and the AFX-080-02 nozzle which also produce a flat liquid film but without air suction. A camera (APX Photron) and a LED panel (LitePad HO LED, Rosco) are placed at each side of the spray to obtain images of the sprayed droplets.

Two configurations of the set-up can be run: an ozone desorption configuration, where an ozone generator produce (CFS1, Ozonia) an ozone gas stream which is sent for bubbling in the liquid tank to produce ozonated water. An dioxygen absorption configuration is made by bubbling a nitrogen gas stream in the water instead of ozone, to produce a dioxygen free water. By spraying ozonated water in ambient air, ozone desorption is expected. When spraying the dioxygen free water in the air, dioxygen absorption is expected.

Dissolved ozone concentration are determined by filling the collecting beakers with 5mL indigo reagent and by performing the gravimetric indigo method after the sprayed ozonated water collection (Bader & Hoigne, 1982). Dissolved dioxygen concentration are determined with an oxygen optical probe (HACH – Intellical LDO101 Lab Luminescent DO Sensor). Those dissolved concentrations determined at different distances from the nozzle allow to determine a concentration profile along the spray, which will be use for the mass transfer analysis.

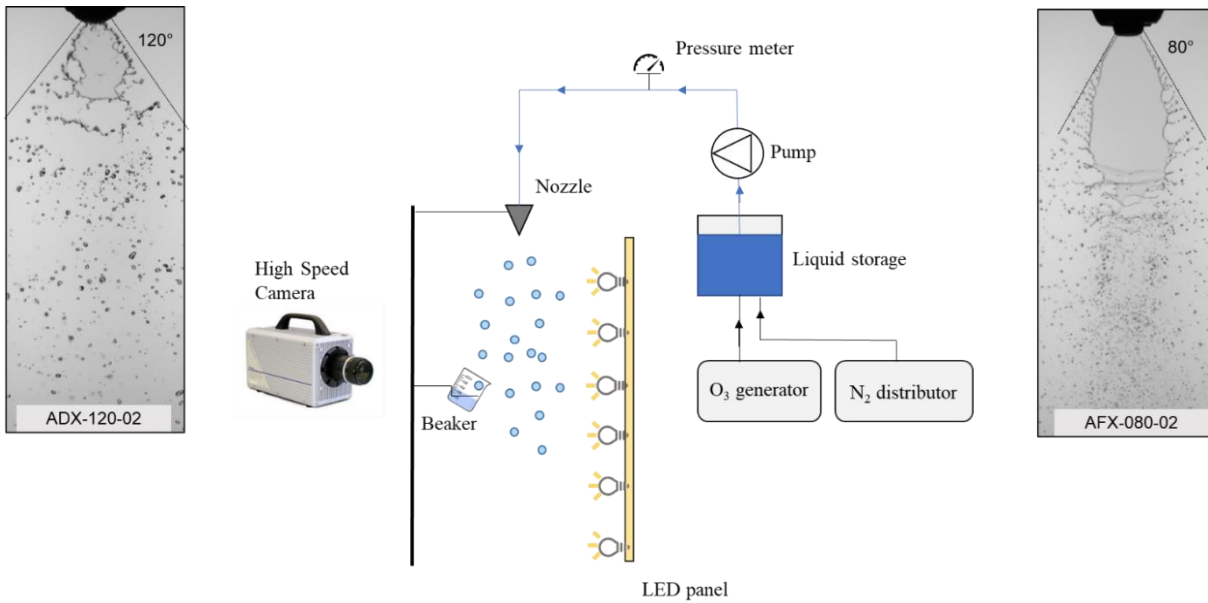


Figure 1: Experimental set-up for the global determination of the mass transfer along a spray.

- Local characterization of the mass transfer in the atomizing liquid film

Figure 2 shows the experimental set-up used for the characterisation of the mass transfer inside the liquid film. A dihydroresorufin (DHR) solution contained in a tank is pumped to be sent through an AFX nozzle to produce a flat liquid film. This liquid film is placed on the focal plane of a CMOS camera (acA9120 – Basler AG, Germany), and is enlightened with a LED panel equipped with a 550nm filter. The camera allows to take pictures of the liquid film with the aim to track light intensity variation along the liquid film. This light intensity variation is due to the coloration of the solution caused by the absorption of dioxygen in the liquid and the oxidation of the colorless DHR to form the pink resorufin (RSO).

From the light intensity computed with the images, an absorbance profile through the liquid film is defined, along a vertical Z axis:

$$A(z) = \log\left(\frac{I(z)}{I_0(z)}\right) = \varepsilon \delta(z)[RSO](z)$$

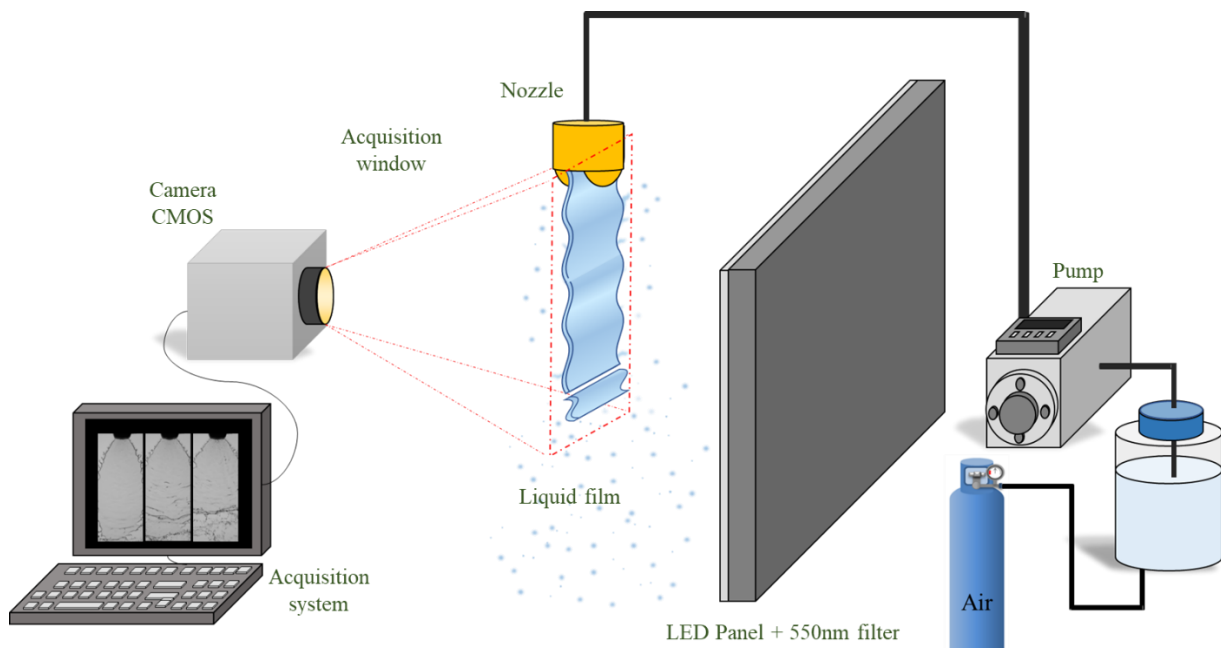


Figure 2: Experimental set-up for the local determination of the mass transfer within the liquid film.

After a validation procedure (not detailed here), the Beer-Lambert law can be used for this optical system. By spraying a RSO solution of known concentration, and by recording the absorbance through the liquid film, its thickness can be determined:

$$\delta(z) = \frac{A_{RSO}(z)}{\varepsilon [RSO]}$$

Then, the spraying of a DHR solution allow to determine the concentration of appearing RSO due to oxidation along the film:

$$[RSO](z) = \frac{A_{DHR}(z)}{\varepsilon \delta(z)}$$

And from the knowledge of the stoichiometry of the oxidation reaction, the concentration profile of dioxygen that have transferred in the liquid film can be determined :

$$[O_2](z) = \frac{[RSO](z)}{2}$$

- Mass transfer analysis

For the global mass transfer characterization, the volumetric liquid side mass transfer coefficient is determined from the dissolved concentration measured along the spray:

$$k_L a = \ln \frac{[O_x]_z^* - [O_x]_z U}{[O_x]_0^* - [O_x]_0 Z}$$

The interfacial area is determined from the droplets diameters measured by image analysis:

$$a = \frac{6}{d}$$

For the local mass transfer characterization, the liquid side mass transfer coefficient is determined from the dioxygen profile obtained along the liquid film :

$$k_L = \frac{d[O_2]}{dz} \frac{Q}{2 w(z)[O_2]^*}$$

And the interfacial area of the liquid film has been defined as :

$$a_{film} = \frac{2}{\delta}$$

Results and discussion

- Global characterization of the mass transfer in the whole spray

Figure 3 exhibits the dissolved concentration profiles obtained with the liquid collection and titration method. As expected, the dissolved concentration of ozone decrease along the spray, denoting the desorption occurring when spraying ozonated water in air. The dioxygen profile shows an increase of the dioxygen within the sprayed liquid along the distance of collection. For both profile, a strong variation is recorded in the first centimeters of the spray, as already observed in previous studies (Canado et al., 2020; Fujiwara & Fujii, 2004; Lin et al., 1977).

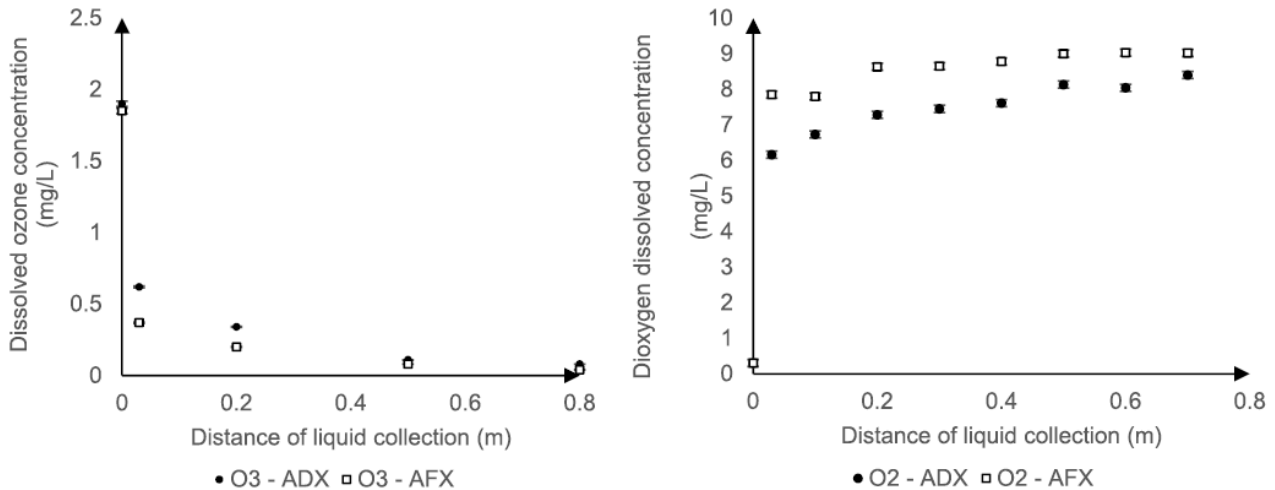


Figure 3: Dissolved concentration at different distance from the nozzle for two nozzle (ADX and AFX) for the ozone desorption (left) and dioxygen absorption (right)

By normalizing those profile with the theoretical saturation concentration of each solute in air, it is possible to see that the mass transfer is identical for both solute along the spray (figure 4). Figure 4 denotes the strong mass transfer occurring in the liquid film region and the smoother mass transfer when droplets are formed. The mass transfer that occurs within the liquid film is such strong that it brings the dissolved concentration to about 70% of the saturation concentration

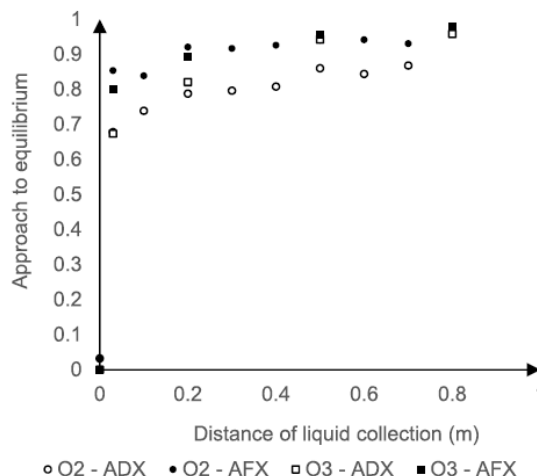


Figure 4: Normalized dissolved concentration profiles for both solutes and nozzle

- Local characterization of the mass transfer inside the liquid film

The original method implemented in this study allowed to obtained local and accurate dissolved O_2 concentration profiles along the liquid film. Profiles have been obtained for 3 different flowrates and 3 different region in the liquid film. The profiles obtained are plotted in figure 5.

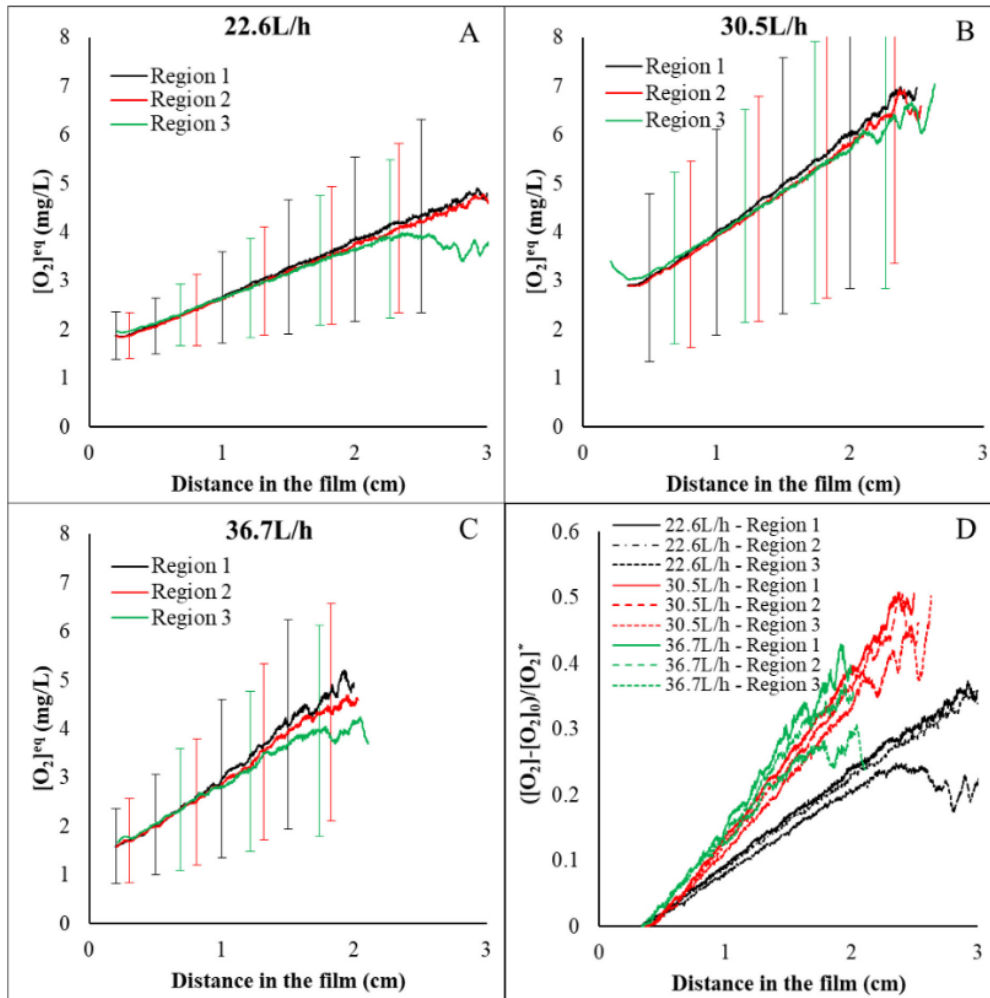


Figure 5: Dissolved O_2 concentration profiles along the liquid film for different flowrate (A,B,C) and normalized dissolved O_2 concentration profiles (D)

Figure 5A,B,C shows that dioxygen absorption do happen in the liquid film since dissolved dioxygen concentration increase with the distance in the film. It seems that curves are steepest for increasing flowrates. This is validated with figure 5D where normalized profiles are plotted together. The profile obtained with the local method is consistent with the profile obtained with the global method as shown on figure 6. That is a way to validate the implementation of this method in the liquid film.

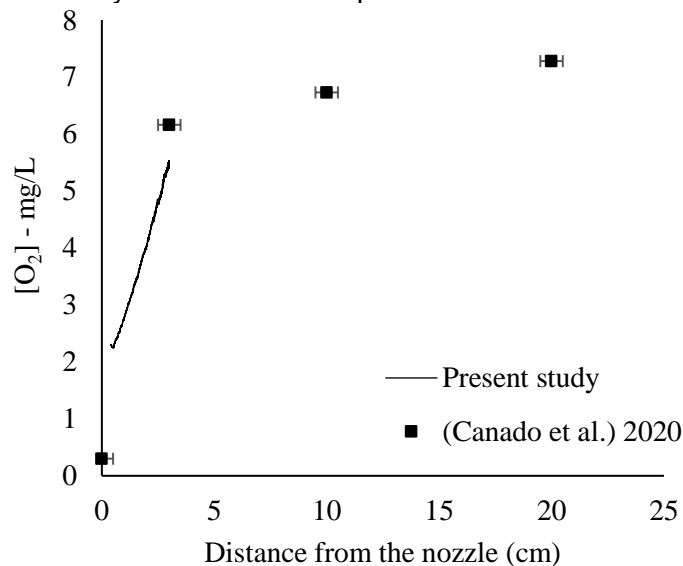


Figure 6: Combination of the global and local dioxygen profiles obtained in this study.

- Mass transfer analysis

From the dissolved profiles obtained for each method of characterization, mass transfer parameters have been assessed and presented in table 1:

	Film region	Droplets region
a (m^2/m^3)	170 000	10 000
k_L (m/s)	6.6×10^{-3}	8.84×10^{-4}
$k_L a$ (s^{-1})	1.12×10^3	8.84

Table 1: Mass transfer parameters obtained with a global method (droplets region) and for a local method (film region)

The mass transfer analysis highlights that the transfer in the liquid film region is much higher than the one occurring in the droplets. That is due to a better interfacial area, mainly caused by the micrometric thickness of the liquid film. The hydrodynamic inside the liquid film also seems to enhance the mass transfer compared to the droplets as demonstrates the higher value of k_L for the liquid film. Both this contributions explain why a stronger mass transfer occurs during the formation stage of the droplets : the atomizing liquid film.

- Extrapolation to ozone desorption

The purpose of this study was to study the mass transfer during spraying processes to understand the phenomenon limiting the efficiency of ozonated water spraying to perform pest management in crops. From the common knowledge of the sprays and droplets, a model based on the correlation of Saboni (Saboni, 1991) allowed to correctly predict the mass transfer occurring from 3cm to 1m in a spray. However, this correlation did not succeed in predicting the mass transfer in the first 3cm after the nozzle. A model based on mass balances and on the experimental k_L obtained for dioxygen with the local experiments allowed to obtain a good match between the prediction of ozone desorption and the experimental one obtained with the global method, as shown on figure 7.

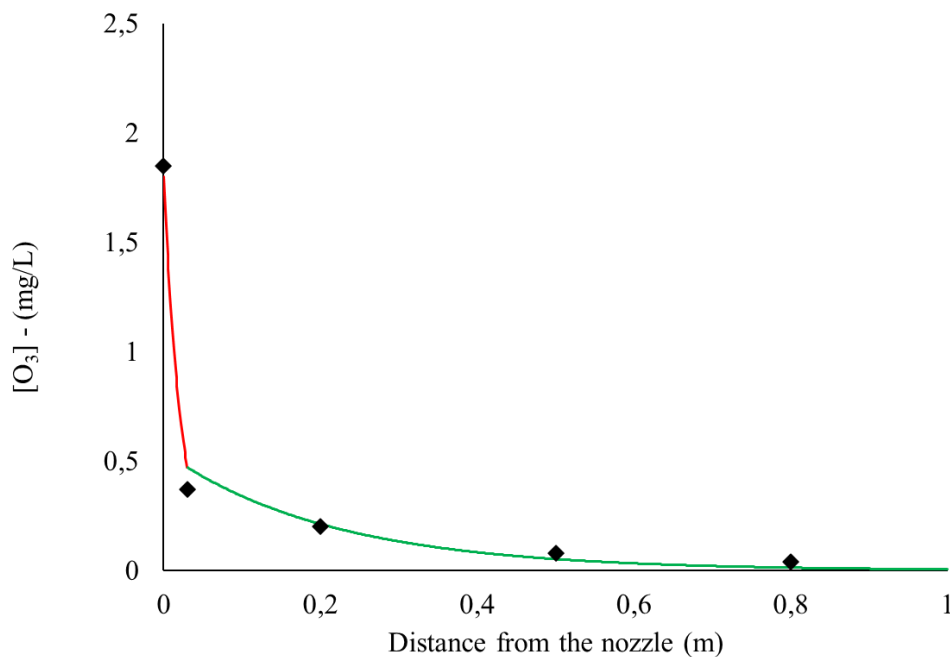


Figure 7: Experimental dissolved ozone concentration (squares) and prediction (curves)

Conclusions

A strong mass transfer occurs in the spray processes. A new method based on the use of a dioxygen sensitive dye allowed for the first time to perform a local mass transfer analysis on an atomizing liquid film that exits a spraying nozzle. This method highlighted that most of the mass transfer is located in the liquid film region, due to a better interfacial area and hydrodynamic than the droplets. From the results obtained for dioxygen experiments, the prediction of the ozone desorption along the whole spray (film + droplets) have been successfully made. This prediction could be used to find the parameters on which act to propose an efficient way to spray ozonated water for pest management in agriculture.

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