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Investigation of the transport of gaseous H_2O_2, HNO_2, NO_2, and O_3 into the bulk water and the electrosprayed microdroplets

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Atmospheric air plasmas in contact with water create so-called “plasma-activated water (PAW)”, containing various reactive oxygen and nitrogen species (RONS). These RONS include long-lived species, e.g., hydrogen peroxide (H_2O_2), nitrite (NO_2-) and nitrate (NO_2-) anions, and ozone (O_3), and other short-lived species. PAW is effective in killing and inactivating various microorganisms, having potential applications in biomedicine [1] and agriculture [2]. Reactive species in PAW (H_2O_2, NO_2- and NO_3-) have the antimicrobial capacity and can promote seed germination and plants growth. PAW is the outcome of plasma-liquid interaction, where gaseous RONS created by plasma are transported into the water. The solubility of the gas species in liquids under the equilibrium conditions is given by Henry’s law solubility coefficient (K_H). Gaseous H_2O_2 and HNO_2 dissolving in water have K_H: ~10^3 and 10^{-1} mol/m^3 Pa, respectively, while K_H of NO_2 and O_3 are much lower: ~10^{-4} mol/m^3 Pa. Thus, the solubility of the gaseous RONS varies markedly and even if their gas phase concentrations are similar, the achieved concentration for each species dissolved in the aqueous phase is significantly different. In this work, the transport of gaseous H_2O_2, HNO_2, NO_2, and O_3 into the bulk water and the electrosprayed (ES) microdroplets is investigated. Gaseous H_2O_2, HNO_2, NO_2, and O_3 species are provided by several external sources. Air containing ~100 ppm of H_2O_2 or HNO_2 is achieved by bubbling through a vessel with 9.8 M H_2O_2 or 20 mM HNO_2 solution, respectively. 250 ppm NO_2 is obtained from a pressure tank by mixing with air. O_3 generator is used to make O_3, which is mixed with air to get ~450 ppm of gaseous O_3. UV-Vis spectroscopy colorimetric methods are used for the chemical analysis of the dissolved species (H_2O_2, O_3, NO_2- and NO_3-) in the aqueous phase. In the gas phase, the concentration of $H_2O_2$and O_3 is measured using electrochemical gas sensors. For HNO_2 and NO_2, the UV-Vis absorption spectroscopic technique is used.

We found that the solvation of the gaseous H_2O_2, HNO_2, NO_2, and O_3 into water is enhanced by the increasing gas-water interface surface area obtained during the ES process. compared to the transport into the bulk which has a fixed surface area regardless of the water volume. H_2O_2 was solvated in water with 4 orders of magnitude more efficiently than O_3, despite the 7 orders of magnitude larger Henry’s law coefficient. This is because of the insufficient amount of gaseous H_2O_2 next to the gas-water interface area: H_2O_2 is completely depleted from the gas, unlike O_3 molecules [3]. HNO_2 is well solvated into the water, making aqueous NO_2-, with 3 orders of magnitude higher efficacy than O_3, which corresponds well with the ratio of HNO_2 and O_3 Henry’s law coefficients. While NO_2 is solvated in water also making aqueous NO_2-, with 2 orders of magnitude higher efficacy than O_3 despite similar Henry’s law coefficients. Our results provide a comparison of the highly soluble H_2O_2 with the medium soluble HNO_2 and weakly soluble NO_2 and O_3 gaseous species that can lead to a better understanding of the transport mechanism of gaseous RONS generated in the plasma into the water and will enable optimization of the plasma liquid interaction systems.

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[1] Machala et al., J. Phys. D. Appl. Phys. 52, 034002 (2019)
[2] Kučerová et al., Appl. Sci. Vol. 11, 1985 (2021)
[3] E. Hassan et al., Water 13, 182 (2021)

Investigation of the Transport of Gaseous H_2O_2, HNO_2, NO_2, and O_3 into the Bulk Water and the Electrosprayed Microdroplets

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Introduction and Motivation

- Atmospheric air plasmas in contact with water create "plasma-activated water" (PAW) solution, which contains various reactive oxygen and nitrogen species (RONS) e.g., H_2O_2, NO_2^-, NO_3^-, and O_3 [1].
- PAW has potential applications in biomedicine and agriculture [2,3].
- PAW results from plasma-liquid interaction, where gaseous RONS created by plasma are transported into water.
- Our motivation is to better understand the transport mechanism of various plasma gaseous RONS into the bulk water and electrosprayed (ES) water microdroplets.
- The solubility of the gas species in liquids under equilibrium conditions is given by Henry's law solubility coefficient (K_H) [4].
- A comparison of highly soluble H_2O_2 with medium soluble HNO_2 and weakly soluble O_3, NO_2, and NO gaseous species is presented here. HNO_2, NO_2, and NO transported into water lead NO_2^- ions.

Materials and Methods

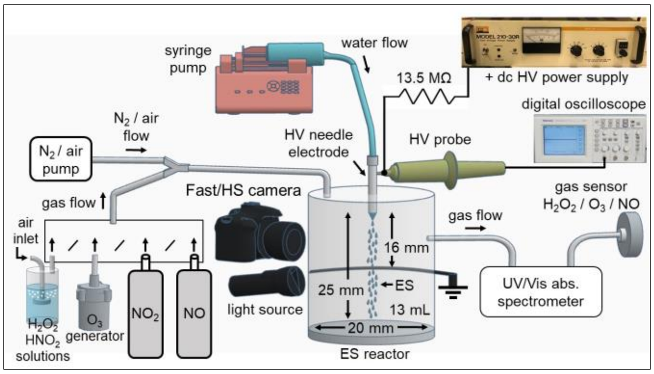

Fig 1. Schematic of the experimental setup: studying Transport of gaseous H_2O_2, HNO_2, O_3, NO_2, and NO into the electrosprayed (ES) water microdroplets

- Air/H_2O_2 (~100 ppm) or air/HNO_2 (~100 ppm) is created by bubbling air through a vessel with 9.8 M H_2O_2 or 20 mM HNO_2 solution, respectively.
- Diluted output from O_3 generator is used to make air/O_3 (~450 ppm).
- Air/NO_2 (~250 ppm) and N_2/NO (~600 ppm) are provided by pressure tanks.
- In the gas phase, the concentration of H_2O_2, O_3, and NO is measured by electrochemical gas sensors. For HNO_2 and NO_2, the UV-Vis absorption spectroscopic technique is used.
- UV-Vis spectroscopy colorimetric methods are used for the quantitative analysis of the dissolved H_2O_2, O_3, and NO_2^- (key product formed in the liquid phase after solvation of HNO_2, NO_2, and NO) in the aqueous phase.
- Fast (60 fps) and High-Speed (25,000 fps) cameras with exposure time 25 and 7.5-20 µs, respectively, are used to visualize the electrosprayed water microdroplets and analyse their surface area.

Results

- Total surface area of ES water microdroplets (Fig 2) is increased with applied voltage and water flow rate [5].
- Solvation into ES microdroplets is enhanced significantly compared to solvation into bulk water (Fig 3).
- Solvation of H_2O_2 (µ mol) is limited with respect to K_H due to its fast depletion from the gas. Solvation of O_3 (n mol) is limited due to its slow diffusion into water microdroplets [6].
- Solvation of HNO_2 (n mol) which is ionized to H^+ and NO_2^- once entering water, corresponds well with its Henry's law coefficient [7].
- NO_2 (n mol) seems better soluble than predicted by its K_H, which may be because it is ionized into NO_2^- once entering water and as ion NO_2^- is quickly diffused into the volume.
- NO (n mol) also seems better soluble than predicted, especially at higher voltages (11 and 13 kV) where a weak corona discharge may be ignited: OH radicals are generated and interact with NO to produce the highly soluble HNO_2.
- Solubility is not determined purely by Henry's law, as indicated by comparison of relative K_H coefficients normalized to K_H of O_3 compared with values derived from our experimental results (see table below).

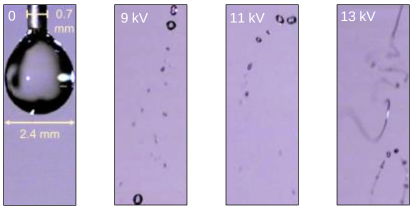

Fig 2. Microdroplets photographs at water flow rate: 500 µL/min

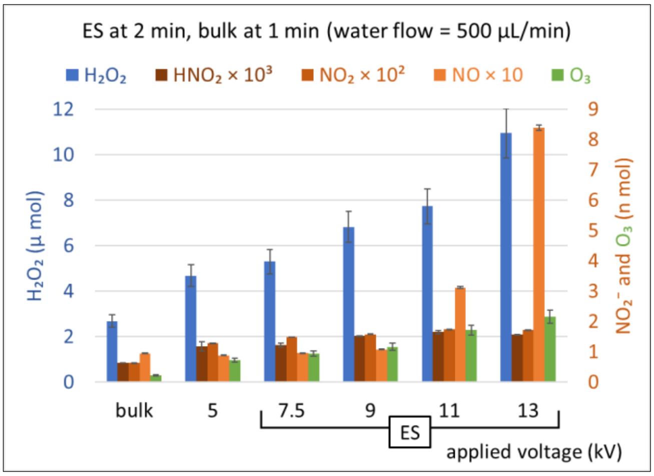

Fig 3. The amount of dissolved H_2O_2 , O_3 and NO_2^- from (HNO_2, NO_2, and NO) in bulk vs ES

Species	~ K_H (mol/m³ Pa)	Relative K_H normalized to K_H of O_3	Experimental values normalized to O_3
H_2O_2	10^3	10^7	10^4
HNO_2	10^{-1}	10^3	10^3
NO_2	10^{-4}	1	10^2
NO	10^{-5}	10^{-1}	10
O_3	10^{-4}	1	1

Conclusions

The obtained results can lead to a better understanding of the transport mechanism of gaseous RONS generated in the plasma into the water and will enable optimization of the plasma liquid interaction systems and tuning of PAW chemical composition.

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[7] Janda, M. et al., Appl. Sci. Vol. 11, 7053 (2021)

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[5] [6] [7]