An experimental study of cold atmospheric plasma for plasma medicine research and applications, using the μAPPJ rf-driven plasma source, was performed in this work. A reactive plasma in helium with small admixture of reactive gas have been generated at atmospheric pressure with a gas temperature close to room temperature. By using different diagnostic techniques, the generated fluxes of ROS, RNS, and VUV radiation in the gas phase have been studied. Moreover, the transport of ROS from the gas phase into the liquid phase has been studied since the therapeutic application of CAP usually involves liquid layer as an interface. The effect of ROS on the etching profile of a deposited a-C:H films on a silicon wafer has been investigated in this work as well to obtain more information about the radical transport from the plasma to the surface and about the interactions of O atoms with the a-C:H layer. Additionally, a 2D axially symmetric fluid model of the gas flow and species transport combined with the basic kinetic model of the reaction of O atoms with O\textsubscript{2} molecules has been solved to study the transport and surface reactivity of O atoms. Additionally, the effect of ROS on some biological targets such as leukemia cells has been investigated. The most important findings of this study are briefly summarized in the following.

Regarding the plasma etching experiments, where the remote μAPPJ with He/O\textsubscript{2} gas mixture has been used to etch a model hydrogenated amorphous carbon layer, I can conclude the following. The comparison of the plasma-etched profiles into the a-C:H film, measured by means of ISR, with the simulated loss rates of O atoms have revealed that O atom surface loss probability under our conditions is $\beta = 0.2 - 0.6 \%$. This low surface loss probability allows O atoms to travel along the surface to the larger radial distances, which are mainly limited by their recombination lifetime in the reaction with O\textsubscript{2} molecules in the gas phase. The maximum surface-integrated etching rate is therefore obtained for lower O\textsubscript{2} admixture of 0.4% than the admixture of 0.6%, which provides the largest O atom density on the jet axis. This information is important for processes where the surface-integrated etching rate or surface-integrated radical
flux to the surface, for example by treatment of liquids, are the most important parameters for the treatment result. Additionally, these experiments demonstrated that low surface reactivity does not limit the surface processes significantly under atmospheric pressure conditions, because the species becomes many more chances to react at the surface (very slow diffusion) compare to low-pressure plasma. Additionally, The presented results demonstrate that ISR is a powerful diagnostic technique providing 2D maps of the thickness and optical film properties of the analyzed films, which can provide valuable information about surface processes during cold atmospheric plasma etching.

The VUV spectra of the constricted mode jet with helium as feed gas were measured by the VUV monochromator, where the emission features of He excimer, both the first and the second continua, clearly appeared together with atomic oxygen, hydrogen and nitrogen lines. It was observed that the intensity of He excimer continuum is independent of the normal level of impurities and no additional gas purification steps are needed to maximize the yield of this emission. Additionally, the effect of $\alpha$ to contracted mode transition of our plasma on the emission was studied. The VUV spectra of these two operation modes are showing difference between intensity of the first and second excimer continuum.

By means of MBMS, the absolute densities of the most relevant RONS (such as O, N, NO$_2$, O$_3$, NO, and N$_2$O) were measured and investigated. The effect of variation of distance from the jet on the density of these species has been studied to optimize the height above the targeted surface in any future plasma treatment. Also, the effect of the variation of nitrogen and oxygen admixtures has been studied, where the distance from the electrode was fixed at 4 mm and the applied voltage at 230V$_{RMS}$, on their densities.

Regarding the liquid treatment, the remote $\mu$APPJ with He, He/H$_2$O, He/O$_2$, and He/O$_2$/H$_2$O gas mixtures has been used to study the transport of reactive species from the gas phase into the liquid and the following aqueous phase chemistry. The effects induced by $\mu$APPJ in water were quantitatively studied by HPLC using phenol as a chemical probe and by measuring H$_2$O$_2$ concentration and pH change. Additionally, the possible effect of high-energy VUV photons on the aqueous chemistry was checked by specially designed plasma jet modifications, whereas no measurable effect of these photons was, however, observed. The fastest phenol degradation of $-4.9 \times 10^{15}$ phenol molecules s$^{-1}$ has been measured for the He/O$_2$. The absolute phenol degradation rate for the He/O$_2$ treatment has been compared to the absolute flux of reactive oxygen atoms to the liquid as determined from the fluid model and absolute density measurements of O atom density. It could be shown that the transport of O atoms from the plasma into the liquid is an efficient process, where more than fifty percent of O atoms, which are leaving the jet nozzle, end up inside the liquid even at surface loss probability much lower than one. The recent reports of Kusalik et al [178, 179] and the analysis of our data strongly indicate that the solvated O atoms O$_{(aq)}$ do not react with the water molecules and can, therefore, directly oxidize phenol and its products. The primary aromatic hydroxylated products of phenol were detected and measured quantitatively: CC, HQ, 2-HBQ, and RS. There are no indications that ozone, generated in this plasma, is influencing the aqueous chemistry, mainly due to its very low solubility in water. The concentration of H$_2$O$_2$ in the treated solutions is clearly correlated to the addition
of water vapor into the gas mixture, with only a small effect of $O_2$ in the gas or phenol in the DI water. $H_2O_2$ in He and He/$H_2O$ treatments is most probably generated in the gas phase and then transformed into the liquid phase according to Henry’s law. The fact that no additional $H_2O_2$ is generated in the DI water without phenol is evidence of $O_{(aq)}$ generation, where its most probable loss channel will be its mutual recombination into $O_2$ and $O$ recombination with dissolved $O_2$. The pH-value decrease of the treated liquid could only be observed when phenol was dissolved in the DI water due to the formation of organic acids as ring-cleavage degradation products of phenol. These results help to understand in a quantitative way the complex interaction of CAPs with aqueous solutions and will allow a better understanding of the interaction of these plasmas with solutions containing biological macromolecules, microorganisms, or even eukaryotic cells.

These findings have been employed to study the reaction mechanism of plasma-generated oxygen atoms in aqueous solutions, where He/0.6%$O_2$ gas mixture was used since it is the most reactive plasma condition of the above-mentioned four conditions. The gas mixture with $O_2$ leads in preferential production of $O_{(gas)}$ atoms in the plasma. The plasma-generated $O_{(gas)}$ atoms enter the aqueous solution facing the gas flow emanating from the plasma and initiate there chemical reactions. The experiments with $^{18}O_2$ isotope demonstrated that the phenol molecules react directly with $O_{(aq)}$, without any intermediate reactions, without reactions with $H_2O$ molecules and generating OH radicals. Additionally, the used atmospheric plasma source demonstrates its potential to be an effective source of $O_{(aq)}$ atoms without any chemical precursors in the liquid phase and the necessity of its photolytic activation. The atmospheric plasma-based sources have, therefore, a very large potential being used in future studies of $O_{(aq)}$ reactivity in solutions and in future applications based on reactions of $O_{(aq)}$ radicals such as waste remediation or therapeutic treatments.

Regarding the biomedical applications of my work, I can conclude the following. Cold physical plasma has been suggested to be an option for cancer therapy, but some cancers are highly resistant to plasma-induced peroxide stress such as THP-1 leukemia cells. By using the COST-Jet with He/$O_2$, it was demonstrated that the chemistry can be tuned towards other species such as hypochlorous acid. With similar treatment times, this condition severely hampered cell activity and growth by inducing apoptosis whereas plasma treatments dominated by hydrogen peroxide did not. Additionally, immune stimulatory proteins were found to be elevated. Understanding the biological impact of gas and liquid phase plasma chemistry will help to improve the plasmas’ efficacy in order to tailor them to the therapeutic applications’ needs. These findings are in line with the above-mentioned findings of the liquid treatments and the following aqueous phase chemistry.