

## Efficiency of removing emerging contaminants from wastewater using electron beam

Dilara Turkel Agacik<sup>1</sup>, Mark S. Driscoll<sup>1,2</sup>, Alexander B. Artyukhin<sup>1</sup>, Fred B. Bateman<sup>3</sup>

<sup>1</sup>*Department of Chemistry, State University of New York College of Environmental Science and Forestry, Syracuse, NY 13210, USA*

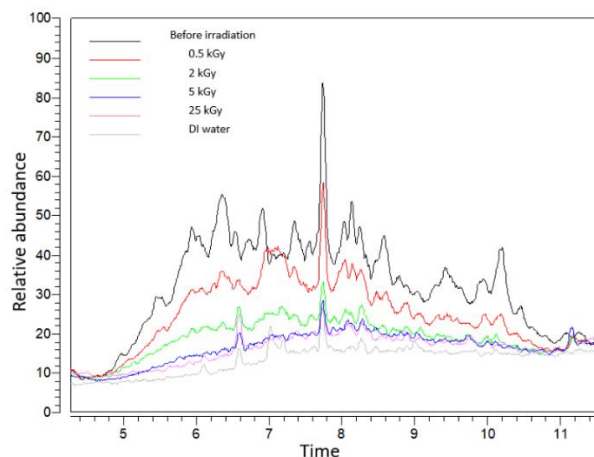
<sup>2</sup>*UV/EB Technology Center, State University of New York College of Environmental Science and Forestry, Syracuse, NY 13210, USA*

<sup>3</sup>*National Institute of Standards and Technology, Gaithersburg, MD 20899, USA*

**Purpose:** The purpose of the project was to assess the superiority of irradiation technology over conventional wastewater treatment methods with respect to the efficient removal of a wide range of emerging contaminant compounds. Despite regulated approaches, wastewater remains a reservoir for various pollutants, including pesticides, pharmaceuticals, plasticizers, and corrosion inhibitors. Recognizing the shortcomings of conventional methods, the study explored the integration of radiation technology, a novel and effective approach gaining prominence in wastewater treatment. The primary objective was to achieve significant degradation of organic compounds in wastewater effluent. Employing carefully determined doses of electron beam irradiation, the project utilized samples from the Syracuse Metro Wastewater Treatment Plant (WWTP) across different seasons. Analysis using untargeted high-resolution liquid chromatography/mass spectrometry revealed that the electron beam treatment substantially degraded contaminants, demonstrating effectiveness by reducing at least 80% of individual contaminant species up to 84.52%. This research underscores the potential of electron beam treatment as a robust strategy for wastewater treatment, offering enhanced efficiency in addressing emerging contaminants and contributing to environmental sustainability.

**Methods:** Approximately 500 mL of wastewater was collected in a clean, amber-colored glass bottle from the outflow of the Metro WWTP in the early morning on May 20, 2022, and again on July 19, 2022. The collected wastewater was divided into 20 mL vials and securely placed inside a polystyrene foam container to maintain proper thermal insulation. Subsequently, the samples were shipped to the National Institute of Standards and Technology (NIST) in Maryland, USA for electron beam irradiation analysis at various doses. Treated samples were aliquoted into 10 mL vials and put into EQUAN autosampler for large volume injections, and analyzed with Thermo Scientific Orbitrap LC-MS, which is capable of producing precise and high-resolution data, resulting in increased sensitivity for detecting, characterizing, and quantifying trace analytes. The first batch underwent irradiation at doses of 0.1, 0.5, 2, 5, 15, and 25 kGy, while the second batch received irradiation at doses of 0.05, 0.1, 0.2, 0.5, 1, and 50 kGy, respectively. All the samples were analyzed in full scan mode and the spectra were recorded over the range of  $m/z$  100-1200 in both positive and negative mode by electrospray ionization (ESI) probe. In negative ion mode, the analyte is charged through deprotonation, while in positive ion mode, it is charged through protonation upon reaching the detector. The obtained results exhibited a range between 1 and 0, indicating the presence and absence of the corresponding masses in the wastewater sample. Recorded data was processed through the MZmine 2 software which is one of the most used and free software help to preprocess untargeted LC/MS raw data.

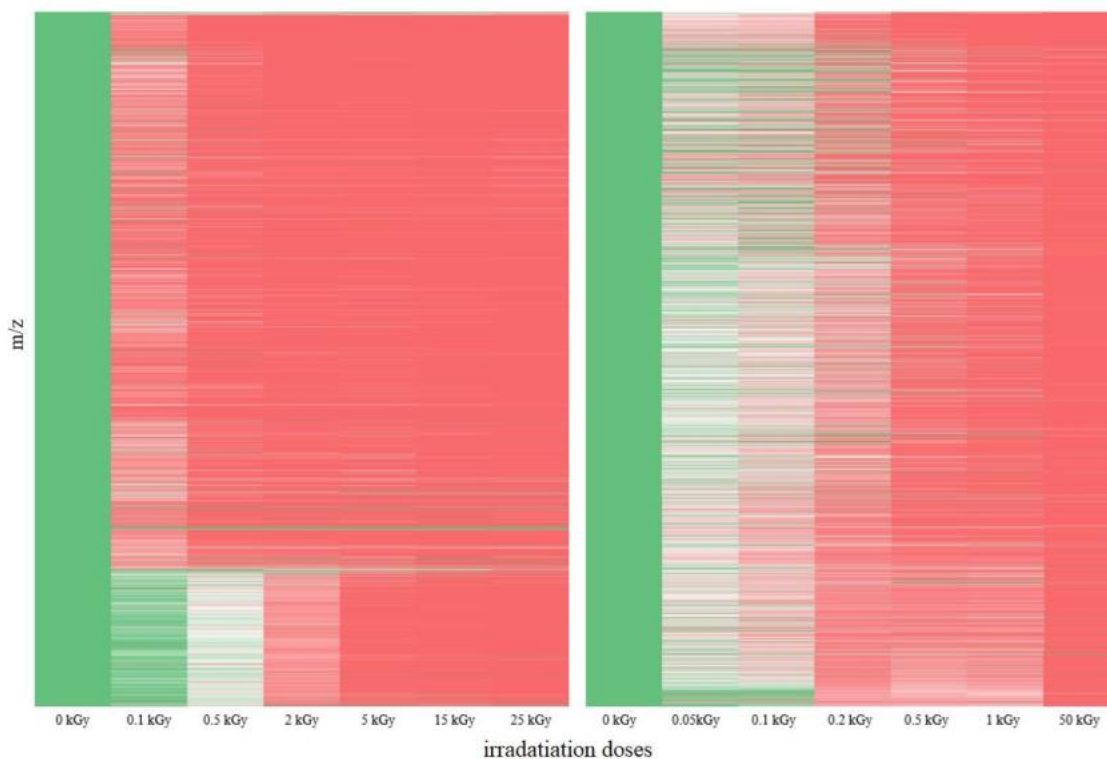
**Results:** The findings indicate a noticeable trend of increasing degradation with increasing irradiation doses. Figure 1 illustrates chromatograms corresponding to various irradiation doses, along with the sample before the irradiation process and distilled water. The area under the chromatograms refers to the total ion amount in the wastewater sample. As the electron beam (EB) irradiation dose increases, there is a notable reduction in the area under the chromatograms. This decrease in the area is directly associated with the decrease in the total ion amount. The non-irradiated sample exhibits the highest ion count, while the sample irradiated at 25 kGy displays the lowest total ion count, closely resembling the trend observed in the DI water sample.



**Figure 1.** LC/MS total ion chromatogram (TIC) in the negative ion mode of DI water, nonirradiated, and irradiated wastewater samples for the first batch of samples.

At a dose of 0.5 kGy, approximately 72% of the pollutants underwent degradation, which further increased to 92% at a dose of 2 kGy. Following these results, we collected additional wastewater samples in July to assess the degradation percentage at interval doses, of 0.05, 0.2, and 1 kGy, and raising the highest dose to 50 kGy. The results for the two control doses, 0.1 and 0.5 kGy, exhibited differing degradation percentages. In comparison to the first batch, 84% of the pollutants were degraded at a dose of 0.5 kGy.

The two heatmaps given in Figure 2 present the comprehensive degradation profile of the two batches, corresponding to varying irradiation doses. A total of approximately three thousand features, i.e., distinct compounds, were found in the wastewater samples.



**Figure 2.** The heatmaps depict the distinct degradation patterns, highlighted by a spectrum of colors, changing from green to red, of various organic compounds present in the wastewater samples: first batch (left) and second batch (right).

In the tables, the first column denotes the non-irradiated samples, while the subsequent columns exhibit data pertaining to the electron beam (EB) treated samples. The color scheme employed in the heatmaps depicts the presence and changes in organic compound levels. These degradation patterns are visually represented by a spectrum of colors transitioning from green to red. The green color signifies the presence of the compound, whereas the red color signifies a reduction or an absence of the compounds at different EB irradiation doses. Both heatmaps provide compelling evidence that as the treatment doses of wastewater increase, there is a corresponding escalation in the overall degradation level.

**Conclusions:** This study highlighted the extensive effectiveness of utilizing electron beam radiation in wastewater treatment to eliminate emerging contaminants. Steering away from exclusive emphasis on individual identification, our focus centered on the collective removal of these contaminants. The objective of our research was to contribute to a broader comprehension of the potential of electron beam treatment as a holistic approach to wastewater remediation, addressing a spectrum of emerging pollutants. By utilizing HRLC-MS Untargeted Analysis, we could effectively survey a broad range of chemical species, enabling a thorough investigation of emerging contaminants in the wastewater samples. The study confirmed that electron beam treatment method is quite effective and untargeted analysis also provides comprehensive results for the study.

**Relevance to CIRMS:** This study constitutes a segment of the doctoral research conducted by the primary author, centering on the removal of emerging contaminants from wastewater through the utilization of the electron beam irradiation technique. The direct alignment with the CIRMS mission lies in the intention to integrate irradiation techniques alongside traditional methods for wastewater treatment. Additionally, this work underscores the significance of radiation steps by providing a comprehensive analysis of wastewater. The primary author aspires to pursue an academic career, with a research focus on the diverse applications of electron beam radiation in various fields.

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