

# Destroying the indestructible: photocatalytic degradation of forever chemicals

## Background

Per- and polyfluoroalkyl substances (PFAS) are a class of synthetic organic pollutants characterized by multiple carbon-fluorine bonds along a carbon backbone. The C-F bond is one of the strongest organic bonds, and make PFAS **chemically inert**, **thermally resistant**, and **hydrophobic** (2).

Without intervention, PFAS can persist in the environment for decades, earning them the nickname “**forever chemicals**”. Their widespread industrial and consumer usage has led to global distribution and long-term accumulation in water sources and wildlife (2).

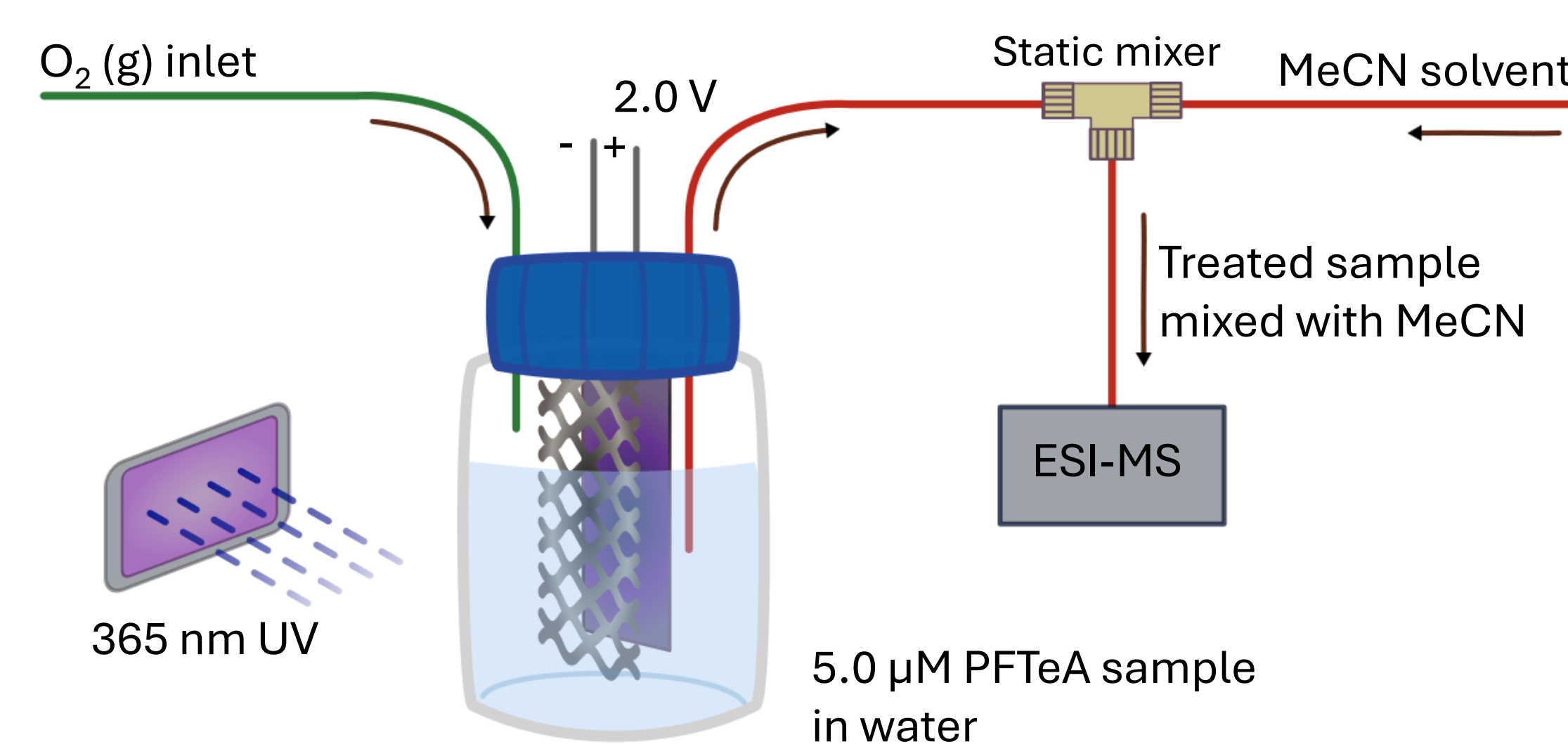
Humans worldwide are **exposed to PFAS through contaminated drinking water** (1). PFAS have been associated with increased risks of cancer, immune system disruptions, and endocrine effects, although **the full extent of harm is relatively unknown** (2).

## Research Objectives

This research aims to:

1. Explore the **degradation mechanism** of forever chemicals under  $\text{TiO}_2$  photocatalytic conditions.
2. **Predict further reaction outcomes** using the kinetic modeling software COPASI.

## Pressurized Sample Infusion



## Acknowledgements and references

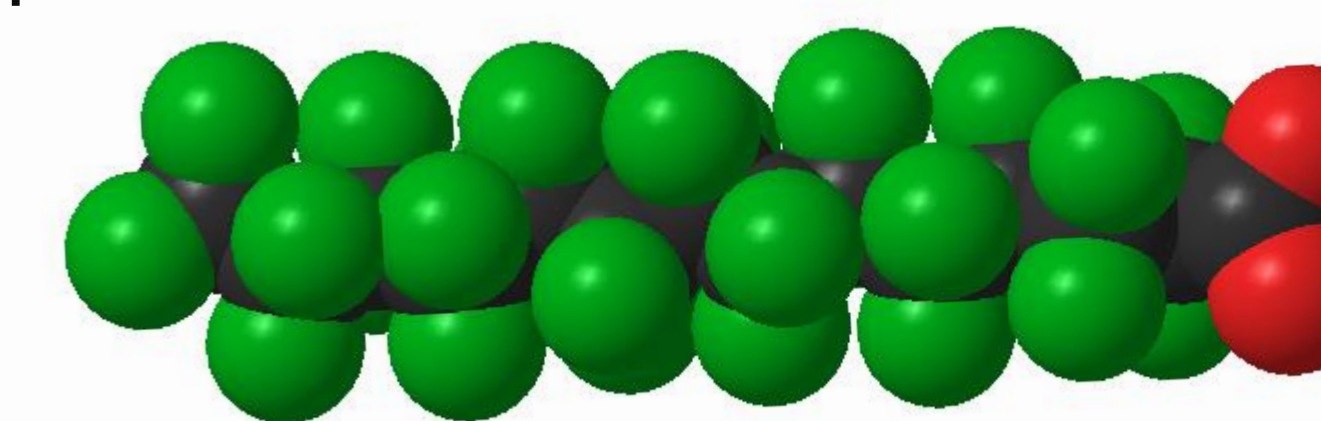
This research was conducted on the unceded lands of the Ləkʷəŋən and W̱SÁNEĆ peoples.

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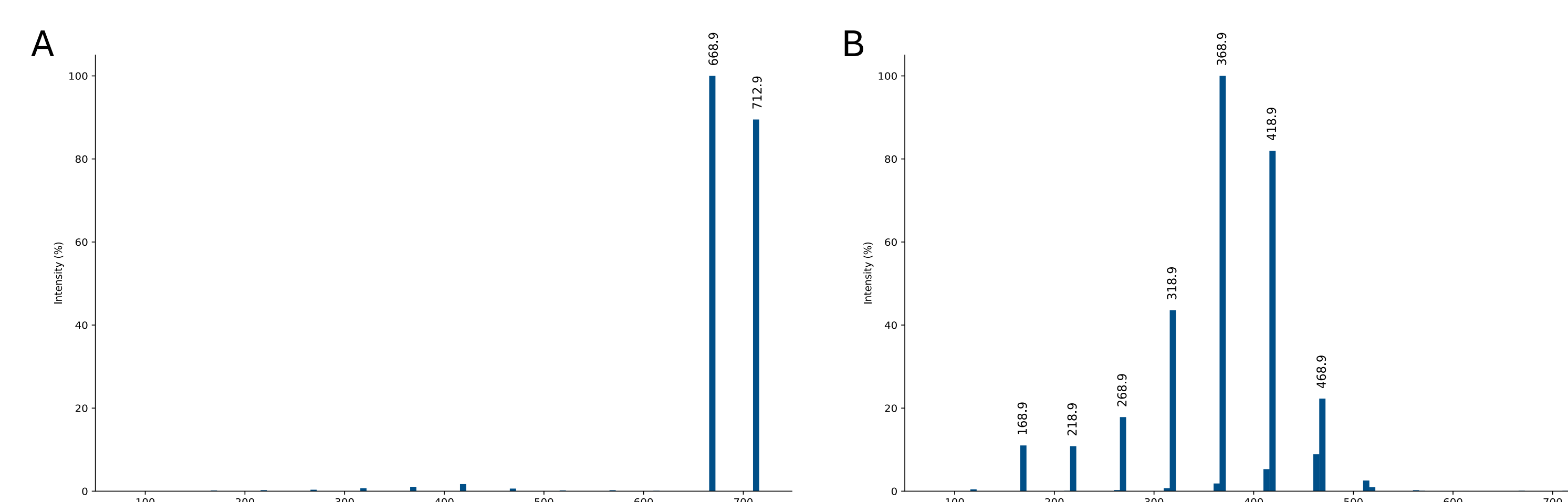
- (1) Health Canada. *Per- and polyfluoroalkyl substances (PFAS) and your health*. 2023.
- (2) Health Canada, Water Quality – Reports and Publications. *Water Talk: Per-and Polyfluoroalkyl Substances (PFAS) in Drinking Water*. 2023.

## Mass Spectrometry Analysis

**Perfluorotetradecanoic acid (PFTeA or C14)**: a common forever chemical with a 14-carbon backbone. In Canada, the manufacture, use, and sale of PFTeA containing products is prohibited (1) with a maximum daily consumption limit of  $3.0 \times 10^{-5}$  parts per million (2).

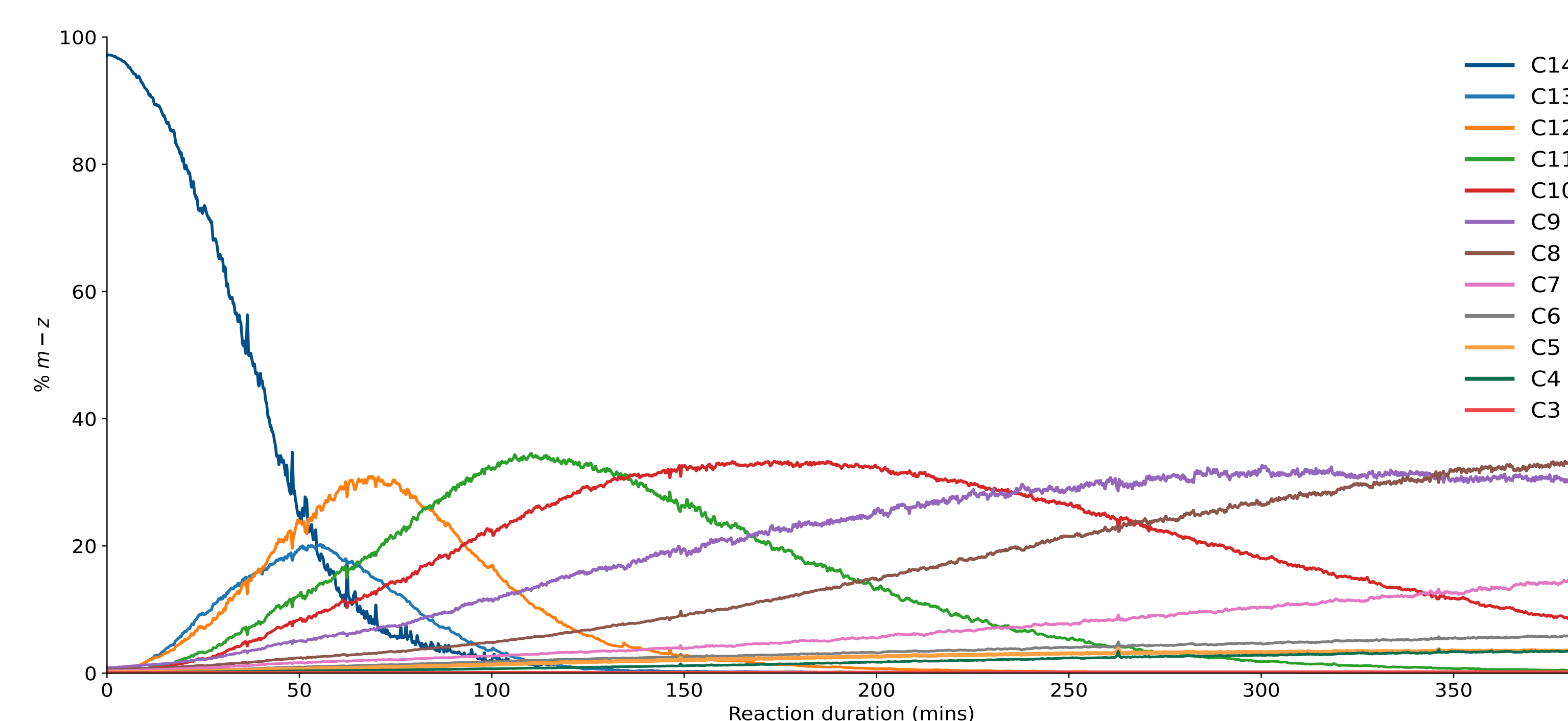
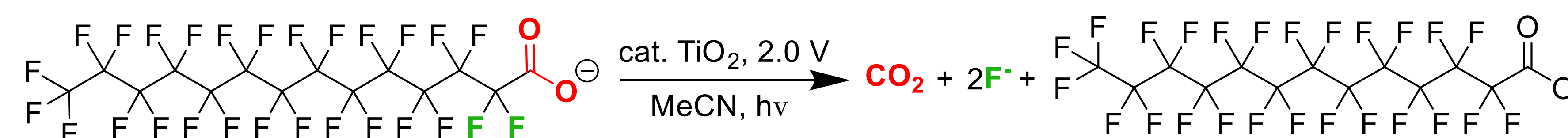


**PFTeA**  
( $\text{C}_{13}\text{F}_{27}\text{COOH}$ , 712.95 g/mol)



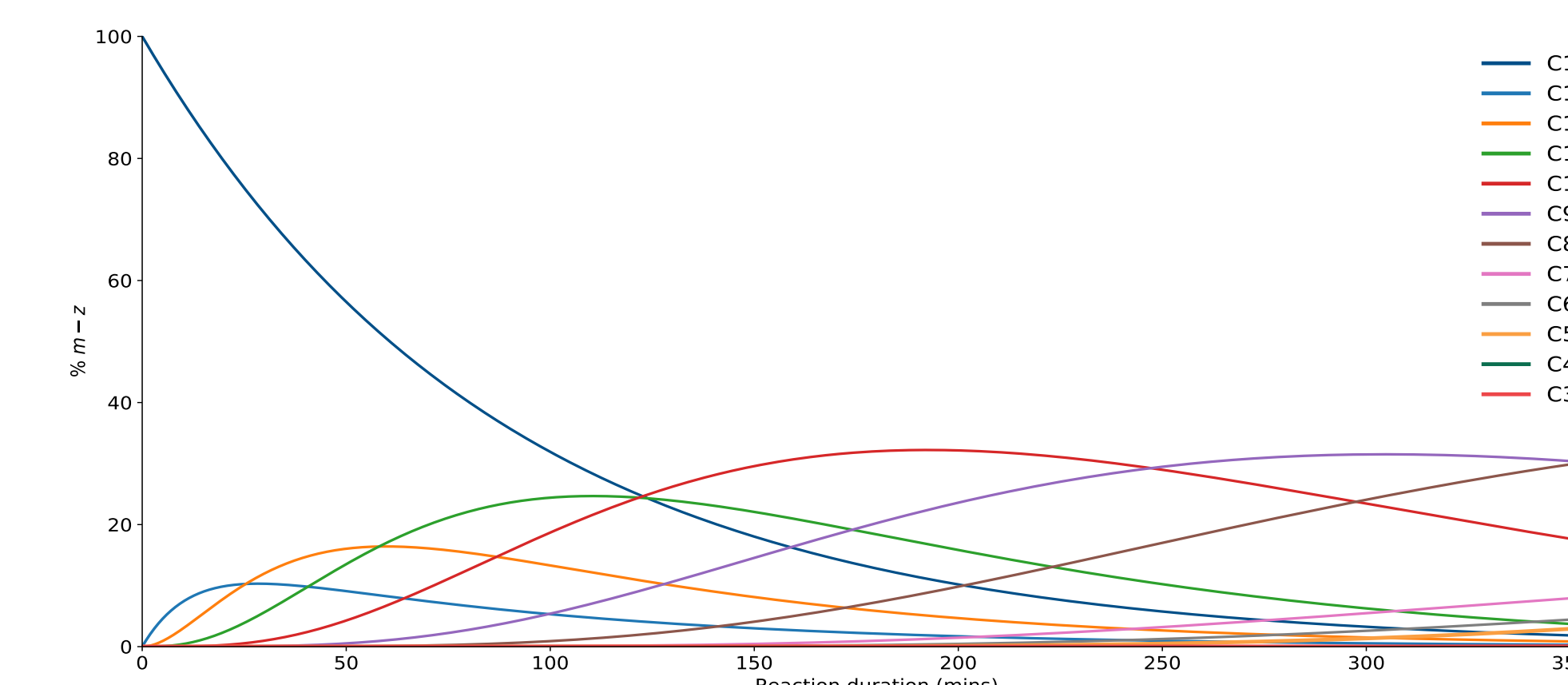
**Figure 1:** Electrospray ionization mass spectra of 5.0  $\mu\text{M}$  PFTeA before (a) and after (b) 360 minutes of  $\text{TiO}_2$  photocatalytic treatment (2.0 V, 365 nm UV). The decrease in the C14 peak and appearance of shorter chain products demonstrate progressive degradation.

The experimental data support a **stepwise breakdown mechanism**. The original C14 compound steadily decreases, while C13 first increases and then decreases. This same rise-and-fall pattern is then observed for C12, then C11, and so on. This sequential appearance and disappearance of each shorter chain compound shows the molecule **does not break apart randomly**, but is instead **shortened one carbon at a time**.



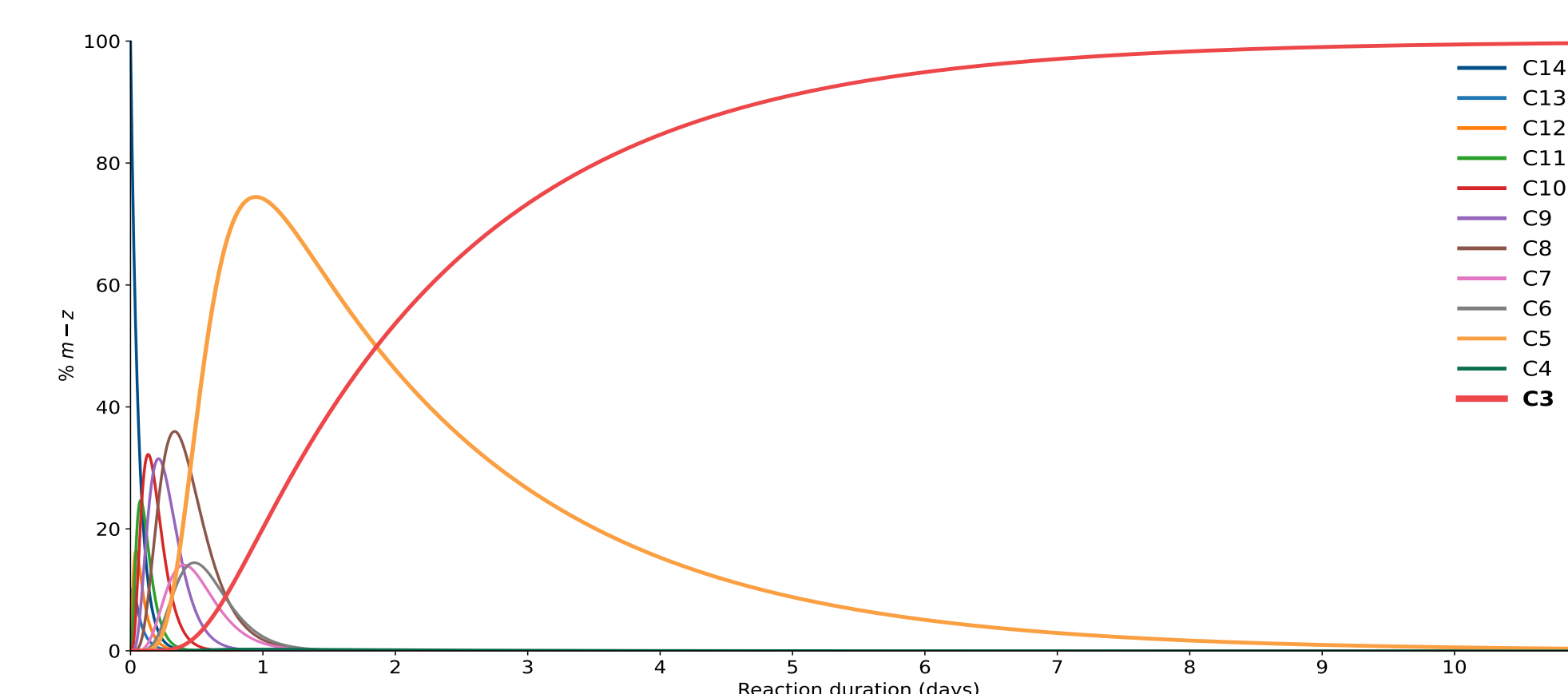
**Figure 2:** Electrospray ionization mass spectra 5.0  $\mu\text{M}$  PFTeA in the presence of  $\text{TiO}_2$  photocatalyst with applied potential of 2.0 V and irradiation with a 365 nm UV LED. Ion traces are reported as percentages of total detected PFAS signals as a function of reaction time. C14 corresponds to  $\text{C}_{13}\text{F}_{27}\text{COO}^-$ ; C13 to  $\text{C}_{12}\text{F}_{25}\text{COO}^-$ ; and subsequent labels indicate stepwise shortening of the fluorinated carbon backbone.

## COPASI Predictive Simulation



**Figure 3:** Simulated 6-hour degradation of PFTeA breakdown products generated in COPASI under photocatalytic treatment (2.0 V, 365 nm UV). The model was parameterized using experimental ESI-MS data.

The experimental concentration data and associated reaction parameters were implemented in the **kinetic modelling software COPASI**. The validated model (Figure 3) was then used to extrapolate the reaction beyond the 360-minute experimental window to **predict the time required for complete PFTeA decomposition**.



**Figure 4:** Simulated long-term degradation of PFTeA breakdown products generated in COPASI. The model predicts that under the same reaction conditions, complete degradation to C3 species would occur within 11 days.

Simulation results indicate that under the same reaction conditions, **PFTeA would fully degrade** in approximately **11 days** (Figure 4).

## Conclusion

This study shows that:

1.  $\text{TiO}_2$  photocatalysis enables **stepwise shortening of PFTeA** rather than random fragmentation.
2. Kinetic modeling allows prediction of long-term treatment performance. The model indicated that **complete PFTeA degradation could occur within 11 days** under the studied conditions.