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Characterization and assessment of industrial water recycling processes by non-target screening

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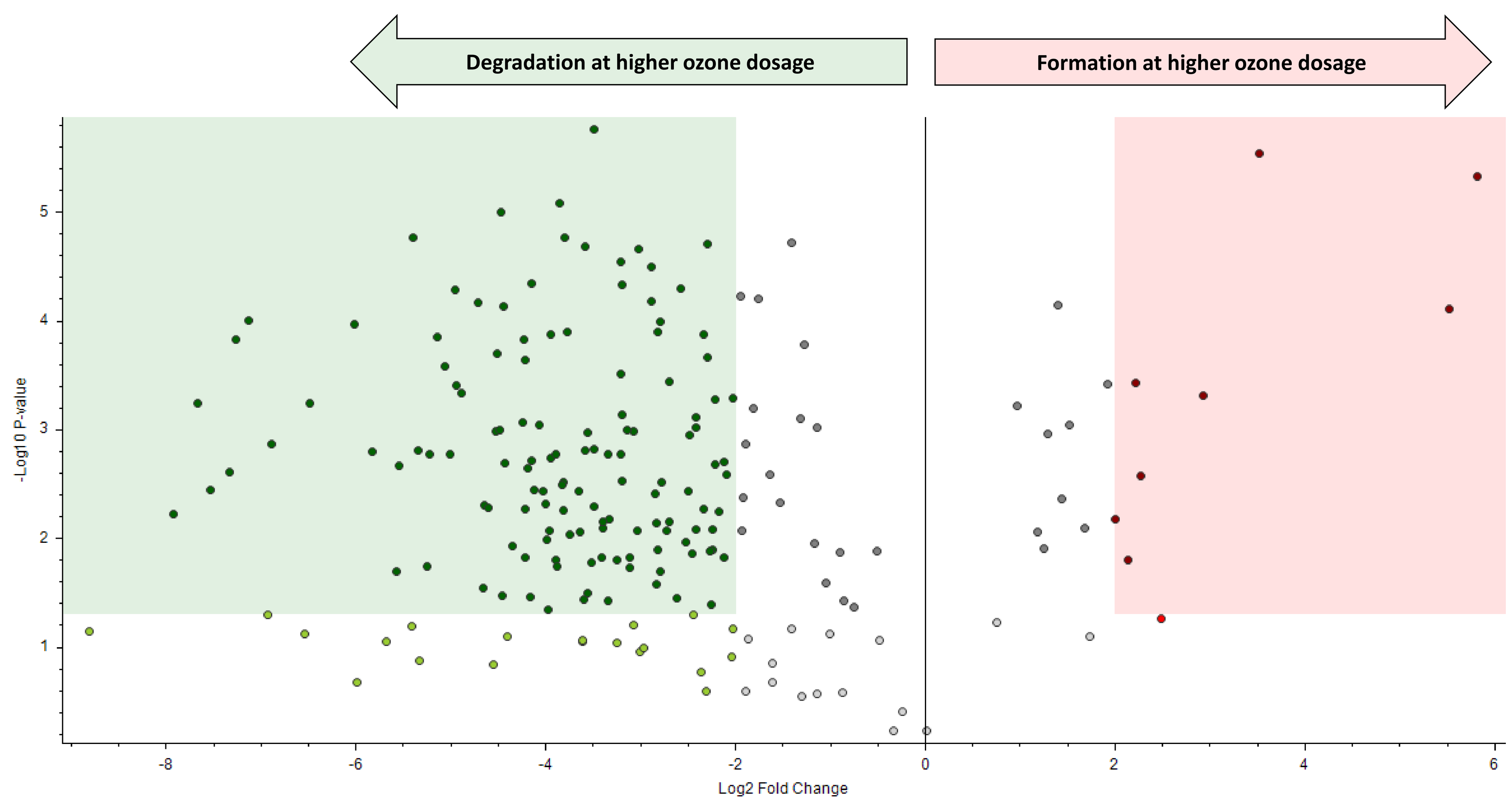
Introduction – The recycling and reuse of waste and wastewater of industrial processes is likely the most impacting measure to save and protect natural resources and reduce energy consumption in industrial processes. In the chemical industry, raw materials often have to meet very specific quality criteria. As a consequence, recycling processes of production wastes have thoroughly be monitored and assessed to ensure a sufficient quality of reuse materials. In this study, a recycling process for industrial wastewater with high salt content was evaluated by polarity extended mass spectrometric non-target screening (NTS). In combination and comparison with process parameters and online measured physical parameters, NTS allows a comprehensive process assessment.

Methods – Aqueous samples were obtained from a water treatment process, which included ozonation with different doses of ozone followed by chlorine-alkali electrolysis. The sodium chloride content of the samples could go up to 20% (w/v). To prepare the samples for chromatographic analysis, a solid phase extraction was conducted to lower the salt content below 0.1%. The samples where then analyzed by supercritical fluid chromatography (SFC) with enhanced polarity range coupled to high resolution, highly accurate mass spectrometry (here 'Orbitrap') with electrospray ionization. For the data analysis, a comprehensive workflow was established, which allowed to assess the changes in the process on molecular level.

Results – The data evaluation workflow was adjusted to address different analytical questions. By comparing samples which were applied to ozonation with different doses of ozone, significant differences in the composition of the samples could be shown. These were monitored through the following treatment process. In the electrolysis step, changes of 'feature' signal intensities could be correlated with observed process parameters, such as electric current. In addition, the removal and/or decrease of a subset of 'features' could be observed. By combining the results of the data evaluation of ozonation and electrolysis samples, optimized process conditions could be selected and tested.
As a consequence, this allows to implement a more efficient water recycling process, which supports are more sustainable production process.

Ozonolysis

Effects of ozone dosage on the chemical composition of an industrial wastewater

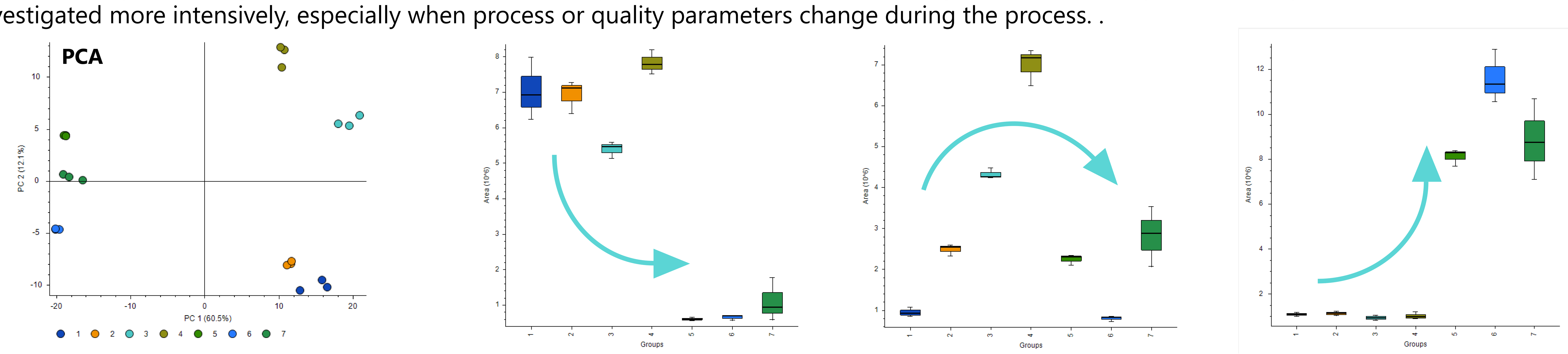


The effects of different ozone dosages on the degradation and formation of chemical compounds in industrial wastewaters can be assessed by volcano-plots. By plotting the change of signal intensities (log 2 basis) and the p-value (log 10 basis), analytical features can be grouped by their signal behavior in the different treatments. Features, which show a significant decrease in signal intensity (negative log2 Fold Change values) and a significant p-value (>~1.2 log10) are (partly) degraded by higher ozone dosages. Features with increased signal intensities (positive log2 Fold Change values) and significant p-values (>~1.2 log10) are (partly) formed by higher ozone dosages. These might be transformation products of the degraded compounds or ozonation byproducts. Features inbetween these two groups are not significantly affected by the increased dosage of ozone. These could be ozone persistent compounds or transformation products which have been formed at the lower dosage and not further been degraded.

Electrolysis

Correlation of feature intensities and process parameters

The applied water-treatment process contained an electrolysis step in order to reach a sufficient water quality to recycle the water back into the production process. This continuous electrolysis was sampled at seven time points. An NTS data evaluation workflow was used to assess the performance of the electrolysis. The principal component analysis (PCA) shows a trend between sampling times, where samples 1 and 2 seem to positively correlated but strongly different from positively correlated samples 3 and 4 and 5 to 7. Among investigated features different trends could be found: Features with decreasing intensities along the electrolysis process might be degraded, those with highest intensities in the middle of the observed time-window could be correlated with intermediate compounds, which are formed in the process and later degraded again. Finally, features with constantly increasing intensities could represent newly formed compounds. These might impact the long-time stability of the process and should be investigated more intensively, especially when process or quality parameters change during the process. .



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