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Temperature-Resolved Element Release from Municipal Solid Waste (MSW)

Eight minor and trace elements in four fractions of Munich residual waste measured by an Electrothermal Vaporisation Unit connected to Inductively Coupled Plasma Optical Emission Spectrometry (ETV-ICP-OES)

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Motivation

3.8 Gt/a of MSW by 2050

A growing world population increases both the waste volume and the emissions of its treatment [1].

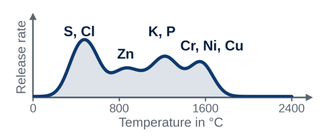
Inorganics limit every thermal process

S, K, Cl, P and **heavy metals** enter the gas phase and cause deposits, corrosion, emissions and poor residue quality [2].

Release data exist only for biomass

Temperature-resolved data for the individual fractions of municipal waste are largely missing [3].

ETV-ICP-OES



Fraction-resolved release profiles

Database serves as a foundation for optimisation of **waste incineration**, **pyrolysis** and **gasification**.

Approach

Sorting (AWM)*



Munich residual municipal solid waste, manually sorted into 15 fractions

Analysed MSW fractions

- **Paper** 10.2 %
- **Organic** 39.2 %
- **Plastic** 10.2 %
- **Composites** 6.2 %

Mass shares of Munich residual household waste in 2016 [4]; these four fractions carry 65.8 % in total

* Abfallwirtschaftsbetrieb München

Sample preparation

Cutting of the fractions into small pieces by hand

Milling in a rotor beater mill, which yields a coarse and a fine sample fraction

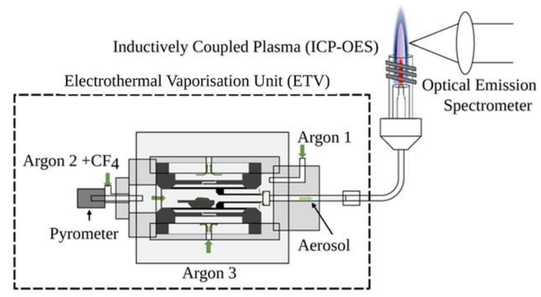
Splitting of coarse and fine fractions according to standard to reduce the sample amount

Weighing-in of 1 to 5 mg into a graphite boat, which is heated in the ETV

4 samples per fraction

× 5 replicates

ETV-ICP-OES measurement



[5]

- ETV 4000d graphite tube furnace, 5 kW, inert Ar, ≤ 2400 °C; CF_4 keeps refractory elements volatile; the aerosol passes into the plasma [6]
- **Heating programme:** 10 °C/s to 2400 °C within 240 s, 60 s hold, bake-out after every sample
- **Validation** of every measurement run with $(NH_4)_2SO_4$ (280 °C) and Ag (2212 °C) for the temperature and certified reference materials for the concentration determination
- **Evaluation** of eight elements (P, S, Cl, K, Cr, Ni, Cu, Zn); emission lines smoothed by a moving mean, the temperature signal by a Savitzky-Golay filter; 1.34 s transport delay corrected

release rate: $r(t) = \frac{I(t)}{\int I(t)dt} \cdot c$

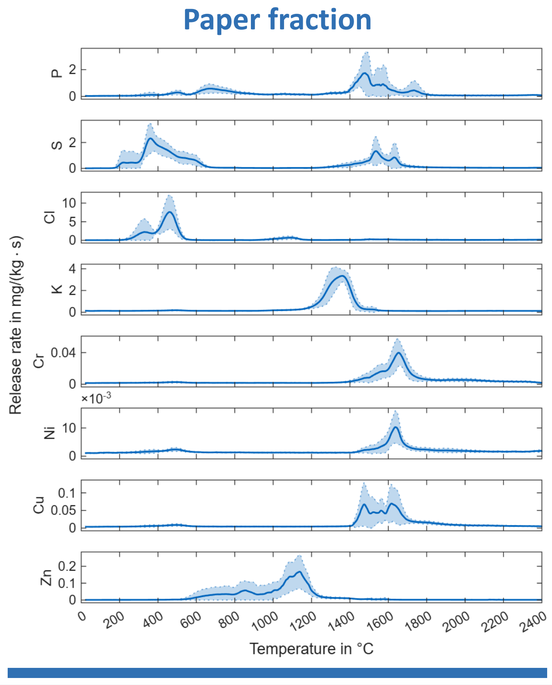
I … *signal intensity of emitted radiation in cps*
c … *measured concentration in mg/kg*

Results

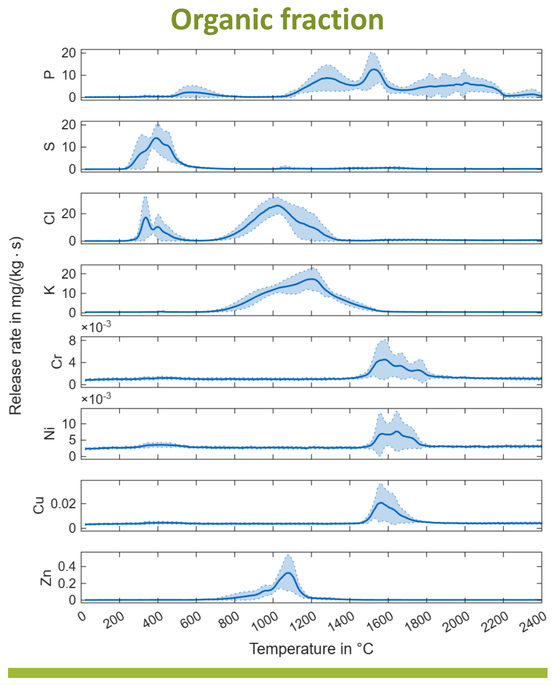
Temperature-resolved release rates of elements in mg/(kg·s)



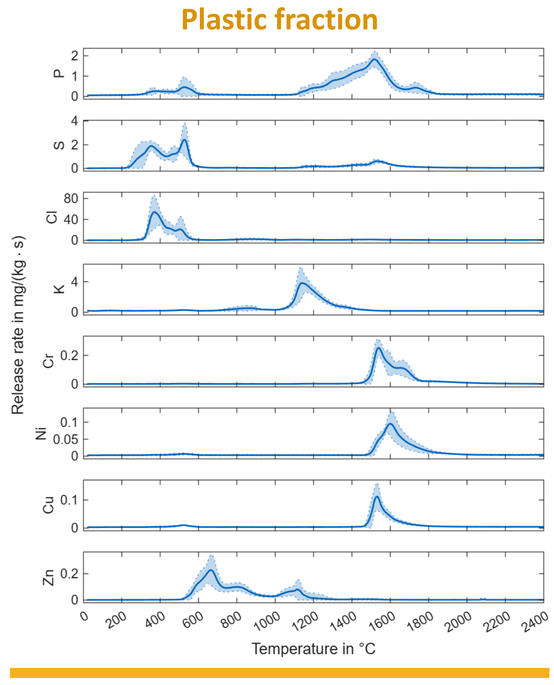
Paper fraction



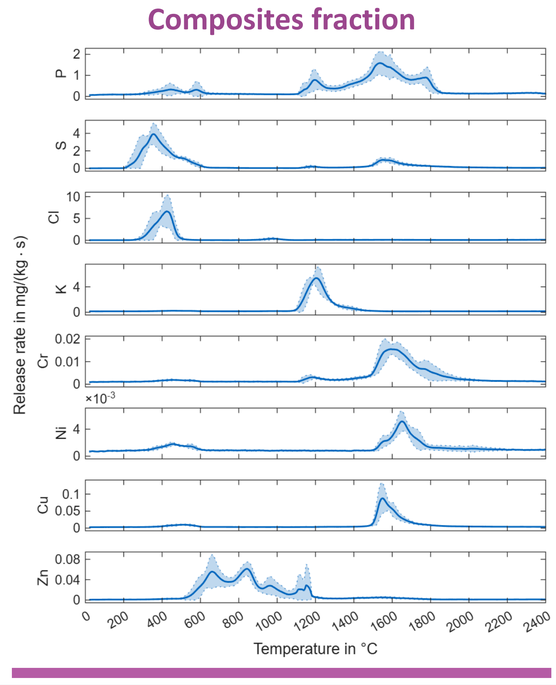
Organic fraction



Plastic fraction



Composites fraction



Validation & Limitations

- **Temperature validation:** 281 °C for $(NH_4)_2SO_4$ (ref. 280 °C) and 2175 °C for Ag (ref. 2212 °C) → axis confirmed, no correction applied.
- **Concentration validation:** recoveries of reference material scatter; deviations from the microwave digestion used as reference: −100 % to > 1300 % (due to: background at low contents, carry-over, matrix-free liquid standard, 1–5 mg against an inhomogeneous material).
- **Consequences:** K, S and Cl are quantitatively reliable, Cr, Ni, Cu and Zn within a factor of two, P semi-quantitative. Positions and shapes of the release curves are unaffected by concentration uncertainty.
- **Best agreement** with data from **pyrolysis processes**/thermal treatment in inert atmospheres.

Conclusion

Release common to all four fractions: sulphur and chlorine start below 600 °C; phosphorus and potassium mainly above 1100 °C; chromium, nickel and copper only above 1400 °C

What sets the fractions apart?

- **Paper** releases zinc mainly above 1100 °C and potassium at the highest temperatures of all fractions.
- **Organic** shows a second and larger chlorine stage at 1000 °C together with potassium, and more than 80 % of its sulphur release below 600 °C.
- **Plastic** releases chlorine almost completely below 600 °C in two steps at 350 °C and 500 °C and shows the lowest zinc maximum at 650 °C.
- **Composites** emit chlorine in one narrow step at 400 to 500 °C and their zinc release spreads from 600 °C to 1200 °C.

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[2] Peng Lu, Qunxing Huang, A.C. (Thanos) Bourtsalas, Nickolas J. Themelis, Yong Chi, and Jianhua Yan. Review on fate of chlorine during thermal processing of solid wastes. Journal of Environmental Sciences, 78:13–28, 2019. DOI: 10.1016/j.jes.2018.09.003.

[3] Hendrik Mörtenkötter, Carolin Heilmeier, Thorben de Riese, Sebastian Fendt, and Hartmut Spliethoff. Temperature resolved release of inorganic compounds from biomass. Fuel, 357: 129939, 2024. DOI: 10.1016/j.fuel.2023.129939.

[4] Martina Heller and Jens Langhein. Analyse des Münchner 3-Tonnen-Systems für den Abfallwirtschaftsbetrieb München. *Münchner Statistik*, 2. Quartalsheft:24–33, 2018.

[5] Hendrik Mörtenkötter, Dominik Grünwald, Sebastian Fendt, and Hartmut Spliethoff. Validation of electrothermal vaporization for the analysis of biomass samples and comparison with other methods of analysis. Waste and Biomass Valorization, 14(10):3489–3502, October 2023. DOI: 10.1007/s12649-023-02129-0.

[6] Albena Detcheva, Peter Barth, and Jürgen Hassler. Calibration possibilities and modifier use in etv icp oes determination of trace and minor elements in plant materials. Analytical and Bioanalytical Chemistry, 394(5):1485–1495, 2009. DOI: 10.1007/s00216-009-2835-4.

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