Prize-winning thesis: oxidation done properly!

July 17, 2024 | Andri Bryner
Topics: Drinking Water | Wastewater | Pollutants | Organisation & Staff

Environmental chemist Joanna Houska has received an award for her doctoral thesis from the German Water Chemistry Society. She conducted her research at Eawag and EPFL, demonstrating both theoretically and experimentally how oxidative water treatment using ozone or chlorine can be more efficiently utilized when there is a precise understanding of the organic substances dissolved in the water to be treated.

"This work is a milestone along the road to advancing our understanding of the role of dissolved organic matter in oxidative water treatment," stated Joanna Houska's supervisor, Urs von Gunten, who is a professor at EPFL and head of the Drinking Water Chemistry Group at Eawag. According to von Gunten, Houska possesses "a remarkable ability to tackle complex scientific questions both theoretically and experimentally, successfully resolving issues with great independence.” Her experiments and modelling have produced and interpreted exciting new data, offering insights that can be employed to improve oxidative water treatment methods.

Inefficient and hazardous without accurate analysis

What is the underlying issue? When chlorine or ozone are used for water disinfection/oxidation, the primary goal is to render pathogens and micro-pollutants harmless. However, a substantial proportion of the oxidants reacts with water matrix components such as dissolved organic materials. This not only reduces the efficiency of the treatment process, but, in the worst-case scenario, can also lead to the formation of toxic by-products. For efficient oxidation, it is therefore crucial to have a precise understanding of the dissolved substances in the water being treated. Traditional approaches have hitherto relied mainly on aggregate parameters derived, for example, from UV absorption. However, Houska addressed this gap in her thesis, firstly developing methods to measure the concentrations of relevant compounds, and then characterising and evaluating the compounds as to whether and to what extent they could form problematic by-products. Lastly, she revealed insights into oxygen isotopes in hydrogen peroxide, demonstrating how the problematic precursor substances can be distinguished from one another. Notably, in her research, Houska went beyond the disinfection/oxidation of drinking water to also investigate the formation of ozone by-products at a wastewater treatment plant and their subsequent degradation in biological post-treatment of treated wastewater.

A first for Switzerland

The doctoral prize in the field of water chemistry has been awarded every year since 1992, and carries with it EUR 1,500. 2024 sees it being awarded for the first time in Switzerland. Joanna Houska already knows how she will use the prize money: "My bicycle urgently needs an upgrade, so the prize money will likely be invested in that.” She currently works in the environmental department at Roche, in the area of wastewater and water protection.

Cover picture: Joanna Houska at the award ceremony with Prof. Thomas Ternes, at the Annual Meeting of the German Water Chemistry Society in Limburg (photo: Nina Hermes, BfG).

Original publication

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        ing drinking water and wastewater treatment is accompanied by oxidation of m
        atrix components such as dissolved organic matter (DOM). To improve predicti
        ons of the efficiency of oxidation processes and the formation of oxidation
        products, methods to determine concentrations of oxidant-reactive phenolic,
        olefinic or amine-type DOM moieties are critical.<br />Here, a novel selecti
        ve oxidative titration approach is presented, which is based on reaction kin
        etics of oxidation reactions towards certain DOM moieties. Phenolic moieties
         were determined by oxidative titration with ClO<sub>2</sub> and O<sub>3</su
        b> for five DOM isolates and two secondary wastewater effluent samples. The
        determined concentrations of phenolic moieties correlated with the electron-
        donating capacity (EDC) and the formation of inorganic ClO<sub>2</sub>-bypro
        ducts (HOCl, ClO<sub>2</sub><sup>?</sup>, ClO<sub>3</sub><sup>?</sup>).
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        ClO<sub>2</sub>-byproduct yields from phenol and DOM isolates and changes du
        e to the application of molecular tagging for phenols revealed a better unde
        rstanding of oxidant-reactive structures within DOM.<br />Overall, oxidative
         titrations with ClO<sub>2</sub> and O<sub>3</sub> provide a novel and promi
        sing tool to quantify oxidant-reactive moieties in complex mixtures such as
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        f disinfection byproducts (DBPs) such as low molecular weight aldehydes and
        ketones from the reactions of ozone with dissolved organic matter (DOM). By
        applying a recently developed non-target workflow, 178 carbonous and nitroge
        nous carbonyl compounds were detected during bench-scale ozonation of two la
        ke waters and three secondary wastewater effluent samples and full-scale ozo
        nation of secondary treated wastewater effluent. An overlapping subset of ca
        rbonyl compounds (20%) was detected in all water types. Moreover, wastewater
         effluents showed a significantly higher fraction of <em>N</em>-containing c
        arbonyl compounds (30%) compared to lake water (17%). All carbonyl compounds
         can be classified in 5 main formation trends as a function of increasing sp
        ecific ozone doses. Formation trends upon ozonation and comparison of result
        s in presence and absence of the <sup>•</sup>OH radical scavenger DMSO in
        combination with kinetic and mechanistic information allowed to elucidate po
        tential carbonyl structures. A link between the detected carbonyl compounds
        and their precursors was established by ozonating six model compounds (pheno
        l, 4-ethylphenol, 4-methoxyphenol, sorbic acid, 3-buten-2-ol and acetylaceto
        ne). About one third of the detected carbonous carbonyl compounds detected i
        n real waters was also detected by ozonating model compounds.<br />Evaluatio
        n of the non-target analysis data revealed the identity of 15 carbonyl compo
        unds, including hydroxylated aldehydes and ketones (e.g. hydroxyacetone, con
        fidence level (CL) = 1), unsaturated dicarbonyls (e.g. acrolein, CL = 1;
         2-butene-1,4-dial, CL = 1; 4-oxobut-2-enoic acid, CL = 2) and also a ni
        trogen-containing carbonyl compound (2-oxo-propanamide, CL =1).<br />Overall
        , this study shows the formation of versatile carbonous and nitrogenous carb
        onyl compounds upon ozonation involving ozone and <sup>•</sup>OH reactions
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of undesired byproducts from ozonation of dissolved organic matte
        r (DOM) such as aldehydes and ketones is currently hampered by limited knowl
        edge of their precursors and formation pathways. Here, the stable oxygen iso
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        ese byproducts was studied to determine if it can reveal this missing inform
        ation. A newly developed procedure, which quantitatively transforms H<sub>2<
        /sub>O<sub>2</sub> to O<sub>2</sub> for subsequent <sup>18</sup>O/<sup>16</s
        up>O ratio analysis, was used to determine the ?<sup>18</sup>O of H<sub>2</
        sub>O<sub>2</sub> generated from ozonated model compounds (olefins and pheno
        l, pH 3-8). A constant enrichment of <sup>18</sup>O in H<sub>2</sub>O<sub>2<
        /sub> with a ?<sup>18</sup>O value of ?59‰ implies that <sup>16</sup>O-
        <sup>16</sup>O bonds are cleaved preferentially in the intermediate Criegee
        ozonide, which is commonly formed from olefins. H<sub>2</sub>O<sub>2</sub> f
        rom the ozonation of acrylic acid and phenol at pH 7 resulted in lower <sup>
        18</sup>O enrichment (?<sup>18</sup>O = 47-49‰). For acrylic acid, enhanc
        ement of one of the two pathways followed by a carbonyl-H<sub>2</sub>O<sub>2
        </sub> equilibrium was responsible for the smaller ?<sup>18</sup>O of H<sub
        >2</sub>O<sub>2</sub>. During phenol ozonation at pH 7, various competing re
        actions leading to H<sub>2</sub>O<sub>2</sub> via an intermediate ozone addu
        ct are hypothesized to cause lower ?<sup>18</sup>O in H<sub>2</sub>O<sub>2<
        /sub>. These insights provide a first step toward supporting pH-dependent H<
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        rbonyl compounds (aldehydes, ketones and ketoacids), a main class of organic
         disinfection byproducts (DBPs). However, the detection of carbonyl compound
        s in water and wastewater is challenged by multiple difficulties inherent to
         their physicochemical properties. A non-target screening method involving t
        he derivatisation of carbonyl compounds with <em>p</em>-toluenesulfonylhydra
        zine (TSH) followed by their analysis using liquid chromatography coupled to
         electrospray ionisation high-resolution mass spectrometry (LC-ESI-HRMS) and
         an advanced non-target screening and data processing workflow was developed
        . The workflow was applied to investigate the formation of carbonyl compound
        s during ozonation of different water types including lake water, aqueous so
        lutions containing Suwannee River Fulvic acid (SRFA), and wastewater. A high
        er sensitivity for most target carbonyl compounds was achieved compared to p
        revious derivatisation methods. Moreover, the method allowed the identificat
        ion of known and unknown carbonyl compounds. 8 out of 17 target carbonyl com
        pounds were consistently detected above limits of quantification (LOQs) in m
        ost ozonated samples. Generally, the concentrations of the 8 detected target
         compounds decreased in the order: formaldehyde &gt; acetaldehyde &gt; glyox
        ylic acid &gt; pyruvic acid &gt; glutaraldehyde &gt; 2,3-butanedione &gt; gl
        yoxal &gt; 1-acetyl-1-cyclohexene. The DOC concentration-normalised formatio
        n of carbonyl compounds during ozonation was higher in wastewater and SRFA-c
        ontaining water than in lake water. The specific ozone doses and the type of
         the dissolved organic matter (DOM) played a predominant role for the extent
         of formation of carbonyl compounds. Five formation trends were distinguishe
        d for different carbonyl compounds. Some compounds were produced continuousl
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Houska, J.; Salhi, E.; Walpen, N.; von Gunten, U. (2021) Oxidant-reactive carbonous moieties in dissolved organic matter: selective quantification by oxidative titration using chlorine dioxide and ozone, *Water Research*, 207, 117790 (11 pp.), doi:10.1016/j.watres.2021.117790, Institutional Repository

Houska, J.; Manasfi, T.; Gebhardt, I.; von Gunten, U. (2023) Ozonation of lake water and wastewater: identification of carbonous and nitrogenous carbonyl-containing oxidation byproducts by non-target screening, *Water Research*, 232, 119484 (17 pp.), doi:10.1016/j.watres.2022.119484, Institutional Repository

Houska, J.; Stocco, L.; Hofstetter, T. B.; Gunten, U. von (2023) Hydrogen peroxide formation during ozonation of olefins and phenol: mechanistic insights from oxygen isotope signatures, *Environmental Science and Technology*, 57, 18950-18959, doi:10.1021/acs.est.3c00788, Institutional Repository

Manasfi, T.; Houska, J.; Gebhardt, I.; von Gunten, U. (2023) Formation of carbonyl compounds during ozonation of lake water and wastewater: development of a non-target screening method and quantification of target compounds, *Water Research*, 237, 119751 (14 pp.), doi:10.1016/j.watres.2023.119751, Institutional Repository

Related Links

Doctoral prize

Eawag Research Group Drinking Water Chemistry

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