PAPER

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Prospects for finding Junge variability-lifetime relationships for micropollutants in the Danube river†

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Persistence of chemical pollutants is difficult to measure in the field. Junge variability-lifetime relationships, correlating the relative standard deviation of measured concentrations with residence time, have been used to estimate persistence of air pollutants. Junge relationships for micropollutants in rivers could provide evidence that half-lives of compounds estimated from laboratory and field data are representative of half-lives in a specific system, location and time. Here, we explore the hypothesis that Junge relationships could exist for micropollutants in the Danube river using: (1) concentrations of six hypothetical chemicals modeled using the STREAM-EU fate and transport model, and (2) concentrations of nine micropollutants measured in the third Joint Danube Survey (JDS3) combined with biodegradation half-lives reported in the literature. Using STREAM-EU, we found that spatial and temporal variability in modeled concentrations was inversely correlated with half-life for the four micropollutants with half-lives ≤90 days. For these four modeled micropollutants, we found Junge relationships with slopes significantly different from zero in the temporal variability of concentrations at 88% of the 67 JDS3 measurement sites, and in the spatial variability of concentrations on 36% out of 365 modeled days. A Junge relationship significant at the 95% confidence level was not found in the spatial variability of nine micropollutants measured in the JDS3, nor in STREAM-EU-modeled concentrations extracted for the dates and locations of the JDS3. Nevertheless, our model scenarios suggest that Junge relationships might be found in future measurements of spatial and temporal variability of micropollutants, especially in temporal variability of pollutants measured downstream in the Danube river.

Environmental significance

This manuscript addresses a classic problem in environmental chemistry: how to infer persistence of chemicals from field measurements of concentrations. We use modeling and field data to examine the hypothesis that Junge relationships between variability of concentrations and persistence, observed for atmospheric contaminants, could also exist for micropollutants in the Danube river. The linear flow of the river constrains the applicability of Junge relationships in a way that is not observed for the atmosphere, and relationships can only be expected for chemicals degraded on shorter time scales than the residence time of water in the river. Analysis of available field data from the Danube did not reveal Junge relationships, but model results indicate that Junge relationships for micropollutants in rivers might be waiting to be discovered.

Introduction

Pharmaceuticals, personal care product ingredients, hormones and industrial chemicals are examples of organic micropollutants of emerging concern in water. Micropollutants can be considered persistent in fresh- or estuarine water according

to European Union regulation if their degradation half-lives exceed 40 days. Degradation half-lives in aquatic systems are thus important in environmental assessment of micropollutants.[1,2]

The rate of biodegradation determines the persistence of many micropollutants in natural waters.[3–5] Biodegradation rates can be measured in laboratory experiments and/or estimated from field studies using mass balance or benchmarking approaches.[6–8] However, determining biodegradation rates in the environment is challenging. Dissipation or attenuation rates observed in laboratory or field experiments are typically the sum of all removal processes, which include biodegradation, hydrolysis, photolysis and volatilization. Consequently,

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the contribution of biodegradation to measured attenuation cannot be readily discerned. Furthermore, the absolute and relative rates of competing removal processes vary according to the nature of the pollutant and the physical, chemical and biological conditions of the environment.[9]

Relating biodegradation rates of micropollutants determined in the laboratory or estimated from field studies to rates in rivers is particularly challenging due to high temporal and spatial variability in river systems. Experimental methods may not fully reflect the influences of variability of river conditions on degradation rates,[1,10] and assumptions such as complete mixing and steady state, which are required for estimating degradation rates in static lake systems with inverse multi-media modeling and benchmarking are also not well suited for rivers.[11,12]

Estimating the persistence of atmospheric pollutants from field observations and relating field observations to laboratory studies poses many similar challenges. In 1974, Junge[13] proposed a concept that provides an empirical approach to estimate the half-lives of gases in the atmosphere. Junge postulated that due to incomplete mixing of gases in the atmosphere and transient transport events, persistent gases with long half-lives have more homogeneous concentrations than non-persistent gases, and hence the residence time of a gas in the atmosphere could be empirically related to variability in measured concentrations.

The Junge variability-lifetime relationship is:

$$\sigma/\mu = a\tau^b \quad (1)$$

where μ and σ are the mean and standard deviation of the measured concentrations of the chemical in air, σ/μ is the corresponding relative standard deviation (also known as coefficient of variation), τ is the chemical's residence time in air, and a and b are empirical fitting parameters. The parameter b represents the slope of the variability-lifetime relationship on a logarithmic scale and thus the strength of the empirical relationship between variability and lifetime. The slope b can take values between 0 and -1, with -1 being the theoretical minimum value of a strong Junge relationship. Atmospheric transport modeling has demonstrated that linear Junge relationships can only be expected over limited ranges of half-lives, and that the minimum value of $b = -1$ is only approached for substances with long atmospheric half-lives (between 1000 to 10 000 days).[14] The parameter a depends on the relative location of emissions and measurement sites, but has no firmly established physical meaning.[13] The ratio σ/μ can represent variability in time (when concentrations are repeatedly measured in the same location) or variability in space (when measurements are performed in different locations simultaneously).[15]

The Junge variability-lifetime relationship for atmospheric gases has been established both theoretically and empirically, and correlations between measured variability in atmospheric concentrations and atmospheric residence time or rate constants for specific degradation pathways (*e.g.* hydroxyl radical oxidation) have been reported in multiple studies.[14,16–18] Calibrated Junge relationships have even been extrapolated to

estimate degradation rates for chemicals not included in the calibration set. Examples include studies of the atmospheric lifetime of cyclic siloxanes,[16] and halocarbons.[19]

Here, we test the hypothesis that Junge variability-lifetime relationships of the form of eqn (1) can be found for micropollutants in a river system, by analogy to gases in the atmosphere. Unlike the atmosphere, rivers have boundaries defined by banks and a dominant direction of transport, which means that micropollutants emitted to rivers can only mix within a limited space and can only degrade within the limited travel time from the location of emissions to the observation point. The restricted space and time available for degradation and mixing will restrain the reduction in variability in measured concentrations with increasing persistence compared to the atmosphere. Further, variability in concentrations of substances that are not appreciably degraded during the travel time between major sources along the river will not be correlated with persistence. Therefore, Junge relationships in rivers are expected to be weaker than those in the atmosphere and only to exist for substances that are degraded on time-scales shorter than the travel time of flowing water between major emission sources in the river.

Junge relationships in river systems must conform to several constraints that have been identified in applications of the Junge theory to atmospheric pollutants. One constraint is that the chemicals included in the relationship should have covariate sources and sinks.[13,14] Therefore, to examine micropollutants with correlated emission patterns in river systems, we selected micropollutants that are mostly emitted from Waste Water Treatment Plants (WWTPs).[20,21] To comply with the requirement of covariate sinks we chose micropollutants for which biodegradation was likely to be the dominant removal process. We therefore assume that the rates of biodegradation of the micropollutants are covariate, which does not imply that the magnitude of the biodegradation rate needs to be the same, but rather that it should have similar spatial and temporal variability for all micropollutants. Another constraint is that measurements of micropollutant concentrations should be remote from emission sources. Considering these restrictions, existing sets of micropollutant concentration measurements in rivers that are optimal for the application of Junge relationships are not widely and readily available.

We selected the Danube river as a case study because it offers conditions that conform at least approximately to the aforementioned constraints of the Junge relationship. Most WWTPs on the Danube, which are likely sources of micropollutants, are located upstream in the river where population density is higher and monitoring sites remote from emission points are thus potentially found downstream in the river. The residence time of rainwater that flows over the surface in the upper Danube river basin has been estimated to be 10 months[22] based on tritium concentrations measured in Vienna. Although the residence time of water in the Danube river itself is likely shorter, it will be longer than the half-life of many organic micropollutants. Furthermore, organic micropollutants in the Danube have been measured in the Joint Danube Surveys (JDS), by the International Commission for the Protection of the Danube

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river,[23] and we could simulate micropollutant concentrations in the river using the STREAM-EU model.[24,25]

Using the Danube as a case study, and recognizing the shortcomings of available empirical data and lack of strict conformity to constraints on the Junge relationship, we explore the potential for Junge relationships to exist in both modeled and measured concentrations of micropollutants in the river. The parameters a and b are unique and have to be calibrated for each measurement location and time.[14,26] Thus our study includes analysis of Junge relationships in spatial and temporal variability of (1) STREAM-EU model-predicted concentrations of hypothetical micropollutants with known properties, and (2) monitoring data of concentrations of micropollutants in the Danube river.

Materials and methods

Evaluation of modeled micropollutant concentrations in the Danube river

Our first step to test our hypothesis that Junge relationships might exist for micropollutants in the Danube river was to employ the STREAM-EU fate and transport model[25] to predict concentrations of hypothetical micropollutants with known half-lives in the river. The STREAM-EU model rationale and application to the Danube river have been described in detail by Lindim *et al.*[24,25] We applied the model to calculate daily concentrations of six hypothetical micropollutants for one year at 68 sampling locations along the length of the Danube river that coincide with the locations used in the JDS monitoring survey (see the locations in Fig. S1†).

The STREAM-EU model represents an idealized scenario for the Junge variability-lifetime relationship and allows biodegradation to be modeled as the only relevant removal process. We selected hydrological conditions from 2013 (the year of the JDS3 survey) as input, and otherwise used the same model conditions as described previously.[25] The six hypothetical micropollutants have identical properties except they were assigned fixed biodegradation half-lives of 7, 15, 30, 90, 180 and 360 days, respectively. The micropollutants were otherwise modeled as tracers of water flow in the Danube river by setting the rates of all other removal processes in STREAM-EU to negligible values. The partition coefficient log K_{OW} of all six micropollutants was set to 1.0 to represent very low sorption to particles because modeling studies of atmospheric transport have demonstrated that multimedia exchange of pollutants leads to deviations from the Junge relationship for chemicals that remain in the mobile medium.[14] The six chemicals were each assigned a constant per capita emission rate of 10 ng s^{-1} and concentrations were extracted after a 4 year model spin up period. Modeled data at the Rackeve-Soroksar Danube stagnant lateral arm in Hungary (station S23), were excluded from further evaluations as average concentrations were 10 times higher than at any other station.

Junge relationships in both spatial and temporal variability of concentrations (of the form of eqn (1)) were initially examined graphically, then determined using least-squares linear fit from the modeled concentrations of only four micropollutants

with the lowest biodegradation half-lives (7, 15, 30 and 90 days). Specifically, 67 Junge relationships were calculated for *temporal* variability in chemical concentrations at each of the 67 locations included in the analysis by computing the relative standard deviation of concentrations (σ/μ) over the 365 days of the model simulation, and, 365 Junge relationships were calculated for *spatial* variability in chemical concentrations for each day of the model scenario from the σ/μ of modeled concentrations at the 67 locations. In addition, we calculated a Junge relationship for variability in STREAM-EU modeled concentrations of the four hypothetical model substances with half-lives less than or equal to 90 days at locations and times that correspond to sampling conducted in the JDS3 survey.

Evaluation of empirical monitoring data from JDS3

Developing an empirical Junge relationship for micropollutants in the Danube river requires two inputs; first, monitoring data of micropollutants for which a relative standard deviation (σ/μ) for spatial and/or temporal variability can be calculated and, second, estimated biodegradation half-lives for those micropollutants, ideally in the Danube river itself.

For the first requirement, we used the measured concentrations of micropollutants in surface water that have been reported in the third JDS monitoring campaign (JDS3).[23] The micropollutant concentrations were measured in 68 water samples taken during August and September of 2013 at the same 68 locations along the river that were modeled in STREAM-EU.[27] Several institutions performed measurements during the JDS3, but only measured concentrations by the Laboratories of Croatian Waters (CW) were used in this study because they reported a large set of target substances (168), with relatively low limits of quantification (LOQ).[27] Nevertheless, most of the micropollutants in the JDS3-CW data set included concentrations below LOQ at more than one of the 68 stations. Micropollutants with measurements below the LOQ at more than 28 of the 68 locations were excluded.

For the second requirement, we reviewed the literature for measured biodegradation half-lives of micropollutants in the JDS3 dataset with minimal removal by photolysis, hydrolysis and volatilization. Very few studies in the literature report biodegradation rates and half-lives from field or experimental conditions in rivers, and to our knowledge none were based in the Danube river. Most of the data we collected were for biodegradation, dissipation and overall attenuation half-lives from diverse studies where biodegradation was considered the main driver of chemical loss. Half-lives estimated from QSAR or single degradation pathways other than biodegradation (*e.g.* photolysis and hydrolysis) were discarded. To limit our analysis to micropollutants for which biodegradation is dominant, micropollutants from JDS3-CW were screened for their potential for volatilize or sorb to soil/sediment, and the micropollutants included in our analyses were limited to those with log $D_{OW} \leq 4$ and log $K_{AW} \leq -5$ (ref. 12) and with negligible photolysis or hydrolysis reported in previous studies with relevant environmental conditions. The potential for sorption of cationic pharmaceuticals to soil/sediment was examined to

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ensure cationic compounds comply with our sorption restriction, the details can be found in the ESI.†

Our final empirical dataset includes nine micropollutants: amitriptyline, caffeine, carbamazepine, codeine, hydrocodone, lidocaine, nicotine, tramadol and venlafaxine. The relative standard deviation σ/μ of concentration measurements in the Danube from JDS3-CW, biodegradation half-lives in the Danube estimated from our literature review and physicochemical properties of these nine substances are summarized in Tables S1 and S6 of the ESI.†

A single arithmetic mean, standard deviation and corresponding σ/μ, were calculated for the nine micropollutants using concentration measurements above the LOQ combined with imputed data for measurements reported below the LOQ[28,29] to avoid bias in the estimation of means and standard deviations. A detailed example of the method for the imputation can be found in the ESI.† The resulting σ/μ obtained for each compound reflects both the *spatial* variability between the 68 stations, and the *temporal* variability over the duration of the JDS3 sampling campaign.

The biodegradation half-lives of the nine micropollutants estimated from literature data[6,7,30–41] were summarized as a geometric mean with uncertainty estimated with a confidence factor (Cf)[42] where 95% of expected values lie between the geometric mean × Cf and the geometric mean ÷ Cf.

The Junge relationship of the form of eqn (1) was fitted to the σ/μ obtained from monitoring data in the Danube and the geometric mean of degradation half-lives for the nine micropollutants using least-squares linear regression.

Results

Variability of modeled concentrations of micropollutants in space and time in the Danube

Graphical analysis of STREAM-EU-modeled concentrations of the six hypothetical micropollutants demonstrates a departure from the Junge relationship, especially for spatial variability of highly persistent substances (Fig. 1).

Junge relationships (eqn (1)) imply that σ/μ should fall monotonically with increasing half-life of the hypothetical chemicals. Monotonic declines in σ/μ are observed in spatial and temporal Junge plots for hypothetical substances with half-lives up to 30 days (Fig. 1). However, in 38 out of 365 (10%) cases, modeled spatial variability of concentrations of the hypothetical micropollutant with $\tau = 90$ days (C90) is greater than spatial variability for the $\tau = 30$ days micropollutant (C30). For the two hypothetical chemicals with longer half-lives ($\tau = 180$ and 360 days, C180 and C360), spatial variability predominantly increases with half-life; in 75% of cases (275/365) σ/μ of C180 is greater than C90, and in 93% of cases (339/365) σ/μ of C360 is greater than C180. Temporal variability declines monotonically more consistently for the hypothetical chemicals. However still 4.5% (3 of 67) of the temporal σ/μ of modeled concentrations of C90 are higher than the corresponding σ/μ of C30. Similarly, 10% (7 of 67) of temporal σ/μ of C180 are higher than C90, and 13% (9 of 67) of temporal σ/μ of C360 are higher than C180.

Junge correlations for modeled concentrations of hypothetical chemicals with half-lives less than or equal to 90 days

Our results above indicate that variability in our modeled concentrations of micropollutants in the Danube consistent with the Junge theory is only observed for chemicals with half-lives less than about 90 days. Using linear regression analysis, we find Junge relationships in both spatial and temporal variability of STREAM-EU modeled concentrations of the four hypothetical model compounds with half-lives less than or equal to 90 days (Fig. 2 and Table S5†).

The temporal variability relationships of the 365 modeled days show a wider variability in slopes at each of the 67 stations (Fig. 2b) than the corresponding variability in the spatial relationships. The lowest b slope value −0.802, was obtained in the temporal variability relationship at station S56 in Bulgaria, near the mouth of the Danube river. The highest b value for a temporal relationship was −0.066, which was calculated for station S29 located in Croatia. The Pearson correlation coefficient (r) between the parameter b and the distance of the station to the mouth of the Danube is 0.75, implying that steeper slopes are observed at stations located close to the mouth of the Danube, which supports the hypothesis that lower reaches of the Danube are more remote from sources of micropollutants. Of the 67 temporal relationships, 59 (88%) have slope values significantly different from zero (two-tailed t-test, p-value ≤ 0.05).

Spatial variability relationships have a narrower range of slope values compared to the temporal relationships, with b values between −0.059 and −0.236 obtained on January 27th and July 13th, respectively (Fig. 2a). Only 133 spatial relationships out of 365 (36%) have slopes that are significantly different from zero (two-tailed t-test, p-value ≤ 0.05). The coefficient of determination (R^2) of our modeled temporal and spatial Junge relationships is generally high (mean spatial and temporal $R^2 > 0.8$, Table S5†). However the existence of a slope that is significantly different from zero is a better indicator of the strength of the Junge relationships since the R^2 values were calculated from just four model scenarios for different assumed degradation half-lives.

Modeled and empirical Junge relationships for concentrations of micropollutants measured in the JDS3 survey

The Junge relationship we constructed for variability in STREAM-EU modeled concentrations of the four hypothetical model substances with half-lives less than or equal to 90 days at locations and times that correspond to sampling conducted in the JDS3 survey has a slope b of −0.034 that is not significant at the 95% confidence level (two-tailed t-test, p-value = 0.5889), and a correlation coefficient (R^2) of 0.169 (Fig. S4†).

There are not robust significant correlations between STREAM-EU-modeled variability of concentrations of the four hypothetical substances and the measured variability of concentrations of the nine selected micropollutants from the JDS3 survey. The strongest correlations between modeled variability of the hypothetical tracers and measured variability of
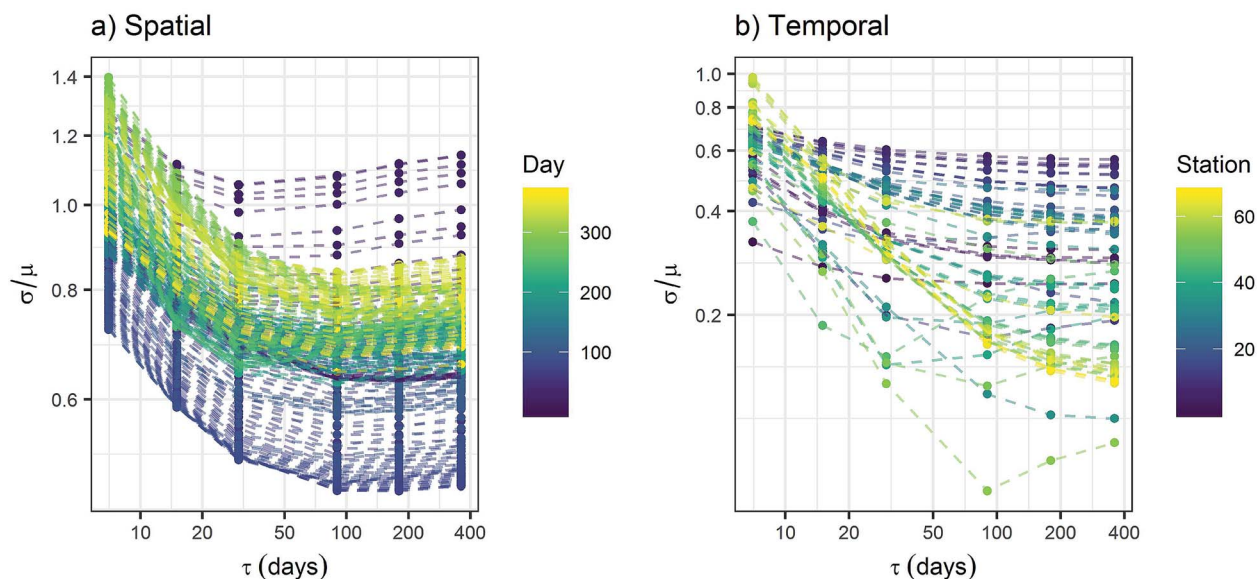
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Fig. 1 (a) Spatial and (b) temporal relative standard deviation (σ/μ) of STREAM-EU-modeled concentrations of six hypothetical chemicals in the Danube river with biodegradation half-lives (τ) of 7, 15, 30, 90, 180 and 360 days.

the real substances have correlation coefficients (R^2) of 0.2 to 0.3 and p-values < 0.05, but in many cases the correlations are weak and not statistically significant. Plots and regression analysis comparing variability in the JDS3 measurement data to variability in the STREAM-EU model concentrations are included in the ESI (Fig. S5–S13†).

The spatial Junge relationship constructed for nine micropollutants (amitriptyline, caffeine, carbamazepine, codeine, hydrocodone, lidocaine, nicotine, tramadol and venlafaxine) from JDS3 monitoring data and half-life estimates from literature has a negative slope ($b = -0.045$) (Fig. 3), but a low correlation coefficient ($R^2 = 0.069$) and the 95% confidence interval of the slope b is wide and included positive values,
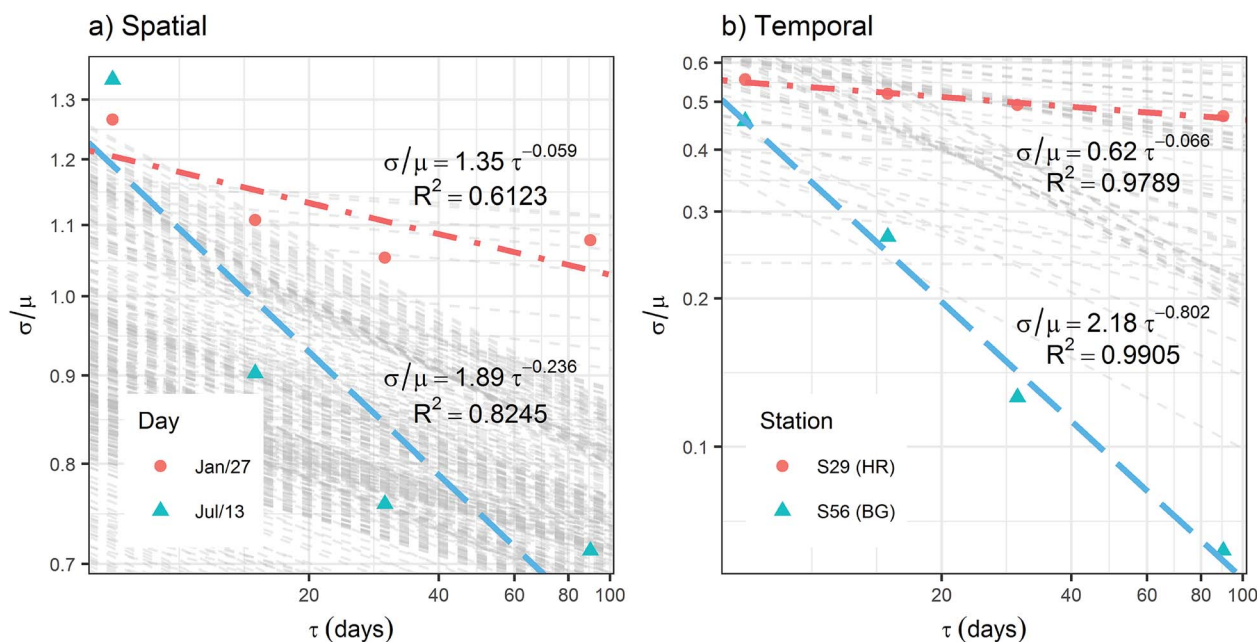

Fig. 2 Examples of Junge relationships obtained from STREAM-EU modeled data of four hypothetical chemicals with half-lives less than or equal to 90 days. (a) Spatial variability relationships for 365 days in 2013. (b) Temporal variability relationships for 67 monitoring stations in the Danube. σ/μ is the relative standard deviation of modeled concentrations and τ is the biodegradation half-life in days. The relationship in red (dash-dot line) corresponds to the highest value of the slope b (on 27 Jan for spatial and on station S29 in Croatia-HR for temporal), in blue (dash line) the minimum value of b (on 13 Jul for spatial and station S56 in Bulgaria-BG for temporal) and in light grey the remaining relationships.
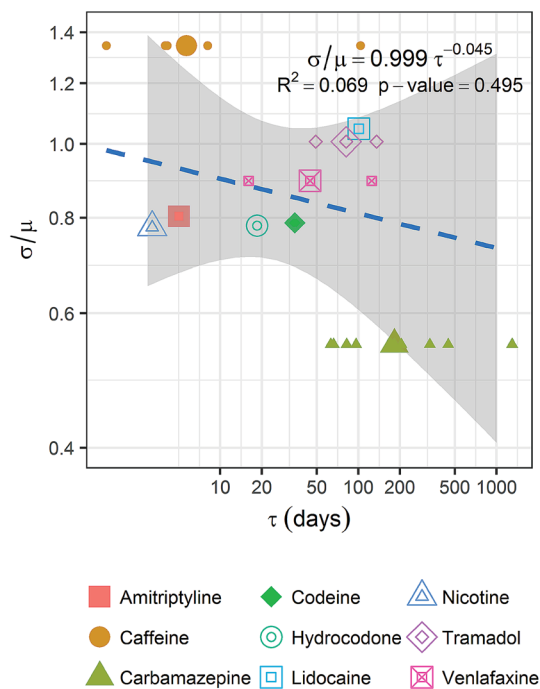
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Fig. 3 Empirical Junge relationship for nine micropollutants using degradation half-lives (τ) estimated from literature sources and relative standard deviations (σ/μ) calculated from the concentrations measured in the JDS3-CW monitoring campaign. The half-lives found in literature are shown in small vignettes, the geometric means of these values are plotted with the largest vignette and are used for the linear regression. The 95% confidence interval of the regression line is shown in gray shade.

which indicates that the slope is not significantly different from zero at the 95% confidence level. The σ/μ of the concentrations, geometric mean (τ) and confidence factor (Cf) of the half-lives of the nine micropollutants that are used to derive the empirical Junge relationship are reported in Table S6.†

Caffeine and carbamazepine are the most studied micropollutants in our literature review. Degradation of these two compounds is mostly quantified as overall dissipation rates in laboratory studies or on mesocosm scale using different substrates and conditions. The range of caffeine and carbamazepine degradation half-lives reported in literature span over 3 orders of magnitude and the 95% confidence interval for the half-life (obtained with Cf[42]) is 1.7 to 19.3 days and 76.6 to 430.78 days respectively. The wide confidence intervals of caffeine and carbamazepine half-lives are thus an indication of the wide variation that could be expected for the five micropollutants for which only a few degradation rate studies could be found in literature (Fig. 3). Caffeine and carbamazepine are also among the most ubiquitous micropollutants in the JDS3-CW. Caffeine was detected in all 68 sampled locations, whereas carbamazepine was measured in 65 out of 68 samples.

Discussion

We found examples of both spatial and temporal Junge relationships with slopes that are significantly different from zero at

the 95% confidence interval in modeled concentrations of four hypothetical micropollutants with degradation half-lives less than 90 days using the STREAM-EU model for the Danube river. This finding is significant because it implies that Junge relationships that have, to our knowledge, only been observed for pollutants in the atmosphere might also be found in river systems and in other aquatic systems. Our model results demonstrate that Junge relationships can only be expected in river systems for pollutants that have degradation half-lives that are shorter than the residence time of water in the river, such that degradation contributes to variability in concentrations along gradients of remoteness from sources in the river despite the directional flow and restricted mixing in rivers.

Modeled concentrations of the four hypothetical micropollutants with half-lives less than 90 days extracted at the same locations and times as sampling in the JDS3 survey exhibited a weak Junge relationship ($b = -0.034$) that was significant only at the 41% confidence level. Further, in our analysis of monitoring data from the JDS3 survey of the Danube river, we did not find evidence of a Junge relationship in the variability of concentrations of nine micropollutants with a similar range of estimated biodegradation half-lives. Our attempt to find Junge relationships in empirical measurement data from the JDS3 survey illustrates several important considerations for data analysis and/or design of monitoring programs that seek to find Junge relationships for micropollutants in rivers.

The empirical data we selected for this study (JDS3-CW) was collected at locations and times where our model analysis indicates a weak and non-significant Junge relationship. Modeled Junge relationships based on temporal variability at fixed monitoring sites had steeper slopes with a high percentage of slopes that were significantly different from zero in the model scenarios (Fig. 2), especially at stations downstream in the Danube. Monitoring of micropollutant concentrations at stations downstream might therefore produce temporal Junge relationships that are statistically significant. However the existence of modeled Junge relationships in the STREAM-EU scenarios might not translate into similar relationships in reality due to a lack of agreement between the model and the real system in both the relative standard deviation of concentrations (the vertical axis of a Junge plot) and in degradation half-lives (the horizontal axis of a Junge plot).

Variability of concentrations of micropollutants are on the vertical axis of a Junge plot. Concentration variability of the nine micropollutants from the JDS3 survey was not robustly correlated to STREAM-EU-modeled variability of the tracer substances (Fig. S5–S13 in the ESI†), which indicates that the model scenarios are not representative of the measured contamination in the real system. Deviations between the model scenario and measurements could be caused by many factors. A notable factor is that in the model scenarios we assumed that emissions are constant and correlated with population density. In reality the level of emissions may be more complex. Micropollutants included in our analysis are expected to have approximately constant emission rates from WWTPs, but could in fact have seasonal or weekly peaks due to episodic usage.[43,44] Spatially, emission of micropollutants into rivers are

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influenced by differences in removal efficiencies in WWTPs, inflow emissions from untreated sewage, and dilution by runoff after precipitation events, which are not correlated to population density.[24,45,46]

Estimated biodegradation half-lives of micropollutants are on the horizontal axis of a Junge plot. In our model scenarios we used a set of defined biodegradation half-lives for the hypothetical chemicals that could be directly transferred to the horizontal axis of our Junge plots, all other removal processes were set to negligible values. In contrast, our empirical Junge relationship is based on degradation half-lives estimated from literature data, and mainly from measured dissipation half-lives rather than studies that measured only biodegradation. It is also important to note that none of the half-lives found in literature was determined specifically for the Danube river, and the experimental or environmental conditions in the studies measuring dissipation/degradation could be different from those in the Danube. Thus, we made several assumptions to extrapolate half-lives from the literature to the Danube river, which adds uncertainty to our empirical variability-lifetime relationship. Most importantly, the uncertainty in the values on the horizontal axis of our empirical Junge plot (Fig. 3) is practically unquantifiable.

Empirical Junge relationships could also be weaker (*i.e.* with slope *b* closer to zero) than corresponding modeled relationships because the ideal conditions for the relationship to hold are not fully met in reality. Stroebe, *et al.*[14] and Becker, *et al.*[18] emphasize three theoretical or practical limitations on the strength of Junge relationships. These are (1) emission and sinks for the compounds in the relationship should be covariate, (2) variability in nearby sources should not determine variability in concentration measurements and (3) variability induced by measurement errors should be small compared to variability in the concentration due to variable source-to-measurement location transport time. The variability-lifetime relationships obtained from STREAM-EU modeled concentrations are robust against these three limitations due to the idealized model conditions and using hypothetical chemicals with fixed removal processes and identical emission distribution. However, each of these three limitations are expected to affect Junge relationships constructed from empirical data and likely will contribute to weaker slopes compared to those from the model scenarios.

The first limitation is that micropollutants in the Danube river do not have perfectly covariate sources (as discussed above) nor perfectly covariate sinks. Sinks for the micropollutants and most importantly the biodegradation rates, can be highly variable in space and time.[4,47] Micropollutants which are not easily biodegraded by a wide variety of microbial communities, could for instance have higher variability of biodegradation in a river, while biodegradable compounds in turn, would have more evenly distributed degradation rates along a river.[48]

The second limitation is that variability in measurements taken near point sources will be strongly determined by variability in the source strength, which will make Junge relationships weaker. Several monitoring stations in the Danube river

are near large cities in Germany, Austria and Hungary and are thus impacted by urban WWTP discharges. The temporal Junge relationships from modeled STREAM-EU concentrations demonstrate this limitation, as the strongest relationships (*i.e.*, relationships with strongly negative *b* slopes) were found mostly at the end of the Danube, which is remote from most emissions in the model scenarios (Fig. 2).

The third limitation is that variability in concentrations associated with measurement errors can positively bias the calculation of the σ/μ. In their study of atmospheric pollutants, Becker, *et al.*[18] could only find Junge relationships when measurements within a factor of three of the LOQ were removed. In this study, the JDS3-CW dataset includes many reports of concentrations that are below LOQ for the micropollutants of interest. Data imputation allowed us to construct σ/μ that represent all sampling sites, but introduces the risk of over or underestimating the lower tail concentrations and therefore distorting the σ/μ. Thus, high quality analysis is particularly important since compounds with short degradation half-lives are optimal for Junge relationships in rivers, but will tend to have more concentrations close to and below LOQ.

Prospects for finding Junge relationships for micropollutants in the Danube or other river systems

Our STREAM-EU model scenarios demonstrate that Junge relationships may exist in rivers for micropollutants with short degradation half-lives relative to transport times in the river. Finding Junge relationships in monitoring data for micropollutants in rivers would be important as it would constrain assumptions on the emission sources and half-lives of the pollutants included in the relationship. Junge relationships in empirical monitoring data in rivers are most likely to be found for a suite of micropollutants with covariate sources and sinks measured over time at a monitoring station as far downstream from sources as possible. Prospects for finding Junge relationships in empirical data will be strengthened if more data on degradation half-lives become available through new lab and field studies.

Conflicts of interest

The authors declare no conflicts of interest.

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