

Supporting Information for
“Relating degradation of pharmaceutical active ingredients in a stream network to degradation in water-sediment simulation tests”

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S1 Phase separation

Assume that the parent compound can be in 3 different states:

1. aqueous phase in water column (M_{aq}),
2. sorbed to a suspended sediment particle in water column (M_{susp}),
3. being in the settled sediment (M_{settl}), including both aqueous state in porewater and being sorbed onto settled particles.

Transitions between the states are governed by processes:

- A Desorption from M_{susp} to M_{aq} ,
- B Sorption from M_{aq} to M_{susp} ,
- E Settling from M_{susp} to M_{settl} ,
- F Resuspension from M_{settl} to M_{susp} ,

The behaviour of each molecule of the compound can be simulated by a Markov chain having these finite number of states (M_{aq} , M_{susp} , and M_{settl}) and continuous time (Fig. S1). Phase transformation rates are denoted by symbols A , B , E , and F (C and D are not used as they denote different quantities, namely concentration and diameter).

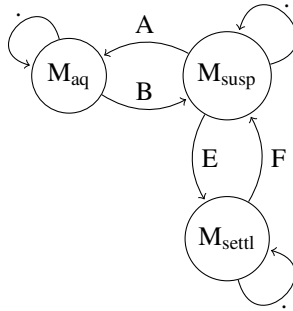


Figure S1. Markov chain of partitioning. Dots denote return rates.

The probabilities of being in a certain state reach an equilibrium as $t \rightarrow \infty$. Keeping in mind that the sum of transition probabilities from a single node must sum up to 1, the transition matrix assuming a state vector of $[M_{aq} \ M_{susp} \ M_{settl}]$ based on Figure S1 is:

$$P = \begin{bmatrix} 1 - B & B & 0 \\ A & 1 - A - E & E \\ 0 & F & 1 - F \end{bmatrix} \quad (S1)$$

The equilibrium probability distribution $\phi = [\phi_1 \ \phi_2 \ \phi_3] = \left[\frac{M_{\text{aq}}}{M_{\text{total}}} \ \frac{M_{\text{susp}}}{M_{\text{total}}} \ \frac{M_{\text{settl}}}{M_{\text{total}}} \right]$ doesn't change when multiplied with P :

$$\phi P = \phi \quad (S2)$$

This means:

$$\phi_1 = (1 - B)\phi_1 + A\phi_2$$

$$\phi_2 = B\phi_1 + (1 - A - E)\phi_2 + F\phi_3$$

$$\phi_3 = E\phi_2 + (1 - F)\phi_3$$

so

$$\frac{\phi_1}{\phi_2} = \frac{A}{B} \quad (S3)$$

and

$$\frac{\phi_3}{\phi_2} = \frac{E}{F} \quad (S4)$$

Since $\phi_1 + \phi_2 + \phi_3 = 1$:

$$\phi_2 = \frac{1}{\frac{A}{B} + 1 + \frac{E}{F}} \quad (S5)$$

Thus, just like reaction constants of opposing reactions determine the equilibrium state in chemistry, A/B and E/F completely determine the equilibrium state of phase separation in the system. The two ratios represent general sorption and sediment (e.g. resuspension-settling) equilibria, respectively.

A/B directly describes the sorption equilibrium in the water phase:

$$\frac{A}{B} = \frac{\phi_1}{\phi_2} = \frac{M_{\text{aq}}}{M_{\text{susp}}} = \frac{1}{K_d \cdot SSC} \quad (S6)$$

where K_d is the distribution or sediment-water partitioning coefficient [$\text{m}^3 \text{kg}^{-1}$] and SSC is the suspended sediment concentration [kg m^{-3}].

E/F is the sediment mass ratio between the active sediment layer and the suspended sediment:

$$\frac{E}{F} = \frac{S}{\text{SSC} \cdot Z_w} \quad (\text{S7})$$

where S is the sediment mass in the active sediment layer [kg m^{-2}], and Z_w is the water depth [m].

S1.1 Partitioning in the presence of biotransformation

When the parent compound is subject to degradation into transformation products (TP) from any of the previously mentioned states, the system's only equilibrium is when all parent compound has degraded to TP (as TP is an "absorbing state" in a mathematical sense, there is no exit process from it, Fig. S2). This means that in a strict sense "partitioning equilibrium" doesn't exist anymore for the parent compound.

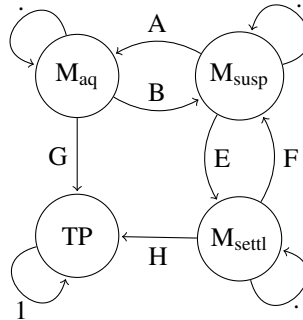


Figure S2. Markov chain of partitioning when M_{aq} and M_{settl} degrade with rate constants of G , and H , respectively. Dots denote return rates.

However, when biotransformation is slow compared to phase transformation (e.g. G and H is small compared to A , B , E , and F), an approximate, relative equilibrium exists for the parent compound: ratios of $M_{\text{aq}}/M_{\text{susp}}$ and $M_{\text{settl}}/M_{\text{susp}}$ remain close to constant and Eqs. S3 and S4 are still good approximations.

Numerical simulations and the analysis of transient partitioning in the absorbing Markov chain suggest that the applicability criteria for these approximations is $E/H > 200$

for the range of A/B and E/F of the Rhine dataset. When this is fulfilled, ϕ_1 , ϕ_2 , and ϕ_3 are approximated with a mean relative error of 4% via Eqs. S3 and S4.

The typical range of E can be easily estimated, as it is closely bound to sediment particle settling. For a typical suspended sand particle with 0.5 mm diameter the mean settling velocity is about 7 mm per second. In a stream with 2 m mean depth E becomes 3069 [d^{-1}]. This means that the partitioning approximations can be used for any compound with $H < 15$ [d^{-1}] (half-life in sediment < 1 hours). For the finest sand ($d=0.0625$ mm) the threshold sediment half-life is longer, but is still only 1 day.

S2 Total-system degradation

? derived first-order degradation rate constants in water and sediment as functions of a second-order degradation rate constant k'_{bio} . The first-order degradation rate constant is the product of k'_{bio} [$\text{d}^{-1} (\text{kg OC})^{-1} \text{m}^3$] and the total particulate organic carbon concentration (POC [kg OC m^{-3}]) as a proxy for the degrader biomass and the aqueous (bioavailable) fraction (f_{aq} [-]) of the compound:

$$k_{\text{deg}} = k'_{\text{bio}} POC f_{\text{aq}} \quad (\text{S8})$$

where k_{deg} is the first-order degradation rate constant [d^{-1}].

In a specific compartment the degradation rate at any moment ($\text{Deg}(t)$ [kg d^{-1}]) is the product of the compartment-specific degradation rate constant and the mass of the parent compound in the given compartment ($M(t)$ [kg]):

$$\text{Deg}(t) = k_{\text{deg}} M(t) \quad (\text{S9})$$

If relative separation remains constant among the compartments, the total system degradation will be first-order as well¹:

$$\text{Deg}_{\text{total}}(t) = k^* M_{\text{total}}(t) \quad (\text{S10})$$

where $\text{Deg}_{\text{total}}$ is the total system degradation rate [kg d^{-1}], M_{total} is the mass of the parent compound in the entire system [kg], and k^* is the system-level degradation rate constant [d^{-1}].

Total-system degradation is composed of two first-order mechanisms:

$$\text{Deg}_{\text{total}}(t) = k_{\text{w}} M_{\text{w}}(t) + k_{\text{sed}} M_{\text{sed}}(t) \quad (\text{S11})$$

where k_{w} and k_{sed} are the first-order degradation rate constants in water and sediment [d^{-1}], respectively, and M_{w} and M_{sed} are the masses of the parent compound in water and sediment [kg], respectively. By expressing both degradation rate constants as functions of k'_{bio} the total system rate can be found.

¹ The total system degradation is really first-order if the ratios between M_{aq} , M_{susp} and M_{settl} remain constant. Here we assume this on the basis that for slowly degrading compounds a single river reach isn't lasting long enough to remove significant proportions via degradation. If degradation is significant inside a reach, mass distribution among the compartments changes slightly from the pure sorption equilibrium.

In the water phase the following equations apply²:

- Mass of compound in water column [kg]:

$$M_w(t) = M_{aq} + M_{susp} = M_{total}(t) (\phi_1 + \phi_2) = M_{total}(t) \frac{\frac{A}{B} + 1}{\frac{A}{B} + 1 + \frac{E}{F}} \quad (S12)$$

- Particulate OC concentration in water column [kg m⁻³]:

$$POC_w = f_{oc, sed} SSC \quad (S13)$$

where $f_{oc, sed}$ is the organic carbon content of the sediment [-].

- Aqueous fraction in water column [-]:

$$f_{aq, w} = \frac{M_{aq}}{M_w} = \frac{1}{1 + \frac{B}{A}} \quad (S14)$$

Thus, the first-order degradation rate constant in water is:

$$k_w = k'_{bio} f_{oc, sed} SSC \frac{1}{1 + \frac{B}{A}} \quad (S15)$$

In the sediment the corresponding quantities are:

- Mass of compound in sediment [kg]:

$$M_{settl}(t) = \phi_3 M_{total}(t) = M_{total}(t) \frac{\frac{E}{F}}{\frac{A}{B} + 1 + \frac{E}{F}} \quad (S16)$$

- Particulate OC concentration in sediment [kg m⁻³]:

$$POC_{sed} = f_{oc, sed} \frac{S}{Z_a} \quad (S17)$$

where Z_a is the depth of the active sediment layer [m].

- Aqueous fraction in sediment [-]:

$$f_{aq, sed} = \frac{1}{1 + K_{oc} POC_{sed}} = \frac{1}{1 + \frac{E}{F} \frac{B}{A} \frac{Z_w}{Z_a}} \quad (S18)$$

where K_{oc} is the sediment organic carbon-water partitioning coefficient [m³ kg⁻¹].

Note that $K_{oc} = K_d / f_{oc, sed} = \frac{B}{A} \frac{1}{f_{oc, sed} SSC}$, and $POC_{sed} = \frac{f_{oc, sed} S}{Z_a} = f_{oc, sed} SSC \frac{E Z_w}{F Z_a}$.

Therefore, the first-order degradation rate constant in sediment is:

$$k_{sed} = k'_{bio} f_{oc, sed} \frac{S}{Z_a} \frac{1}{1 + \frac{E}{F} \frac{B}{A} \frac{Z_w}{Z_a}} \quad (S19)$$

² assuming that the compound does not bind to DOC

The ratio between sediment and water degradation rate constants is the following:

$$\frac{k_{\text{sed}}}{k_w} = \frac{POC_{\text{sed}} f_{\text{aq,sed}}}{POC_w f_{\text{aq,w}}} \quad (\text{S20})$$

where

$$\frac{POC_{\text{sed}}}{POC_w} = \frac{S}{SSC Z_a} = \frac{E}{F} \frac{Z_w}{Z_a} \quad (\text{S21})$$

and

$$\frac{f_{\text{aq,sed}}}{f_{\text{aq,w}}} = \frac{1 + \frac{B}{A}}{1 + \frac{E}{F} \frac{B}{A} \frac{Z_w}{Z_a}} \quad (\text{S22})$$

With full substitution of dimensionless ratios:

$$\frac{k_{\text{sed}}}{k_w} = \frac{E}{F} \frac{Z_w}{Z_a} \frac{1 + \frac{B}{A}}{1 + \frac{E}{F} \frac{B}{A} \frac{Z_w}{Z_a}} = \frac{\frac{A}{B} + 1}{\frac{A}{B} \frac{E}{F} \frac{Z_a}{Z_w} + 1} \quad (\text{S23})$$

The total system degradation rate constant is:

$$k^* = k_w \frac{M_w}{M_{\text{total}}} + k_{\text{sed}} \frac{M_{\text{sed}}}{M_{\text{total}}} \quad (\text{S24})$$

Normalising with k_w yields:

$$\frac{k^*}{k_w} = \left(1 - \frac{S}{M_{\text{total}}}\right) + \frac{k_{\text{sed}}}{k_w} \frac{M_{\text{sed}}}{M_{\text{total}}} \quad (\text{S25})$$

We already know that

$$\frac{S}{M_{\text{total}}} = \phi_3 = \frac{\frac{E}{F}}{\frac{A}{B} + 1 + \frac{E}{F}} \quad (\text{S26})$$

so

$$\frac{k^*}{k_w} = \frac{\frac{A}{B} + 1}{\frac{A}{B} + 1 + \frac{E}{F}} + \frac{\frac{A}{B} + 1}{\frac{A}{B} \frac{E}{F} \frac{Z_a}{Z_w} + 1} \frac{\frac{E}{F}}{\frac{A}{B} + 1 + \frac{E}{F}} = \frac{\frac{A}{B} + 1}{\frac{A}{B} + 1 + \frac{E}{F}} \left(1 + \frac{\frac{E}{F}}{\frac{A}{B} \frac{E}{F} \frac{Z_a}{Z_w} + 1}\right) \quad (\text{S27})$$

In rivers water and suspended sediment move with the flow, while settled sediment remains. Without phase separation the compound would always stay in M_{aq} and the following equation would connect the fluxes at the upstream and downstream ends of the reach:

$$F_{\text{out}} = F_{\text{in}} \exp(-k_w \tau_w) \quad (\text{S28})$$

where F_{in} and F_{out} are the incoming and outflowing fluxes of the parent compound [kg d^{-1}], respectively, and τ_w is the mean water residence time in the reach [d].

When phase separation is present, system-wide degradation rate constants and residence times apply:

$$F_{\text{out}} = F_{\text{in}} \exp(-k^* \tau^*) \quad (\text{S29})$$

where τ^* is the mean system-level residence time of the compound in the reach [d].

Instead of calculating the reach-specific k^* , it is easier to calculate with degradation rate constant (k_w) and residence time (τ_w) of the water and introduce the influence of settled sediment via a dimensionless modification factor (δ):

$$F_{\text{out}} = F_{\text{in}} \exp(-\delta k_w \tau_w) \quad (\text{S30})$$

where $\delta = \frac{k^* \tau^*}{k_w \tau_w}$.

The mean travel time ratio between the entire system and the water phase is:

$$\frac{\tau^*}{\tau_w} = \frac{1}{1 - \phi_3} = \frac{\frac{A}{B} + 1 + \frac{E}{F}}{1 + \frac{A}{B}} \quad (\text{S31})$$

Finally, the settled sediment-related modification factor is:

$$\delta = \frac{k^* \tau^*}{k_w \tau} = 1 + \frac{\frac{E}{F}}{\frac{A}{B} \frac{E}{E} \frac{Z_a}{Z_w} + 1} \quad (\text{S32})$$

S3 Possible extensions with other degradation mechanisms

S3.1 Phototransformation

Assume that M_w degrades with k_{photo} in addition to k_w . Then the total system degradation will be:

$$k^* = k_w \frac{M_w}{M_{\text{total}}} + k_{\text{sed}} \frac{M_{\text{sed}}}{M_{\text{total}}} + k_{\text{photo}} \frac{M_w}{M_{\text{total}}} \quad (\text{S33})$$

The ratio normalised by k_w is:

$$\frac{k^*}{k_w} = \frac{M_w}{M_{\text{total}}} + \frac{k_{\text{sed}}}{k_w} \frac{M_{\text{sed}}}{M_{\text{total}}} + \frac{k_{\text{photo}}}{k_w} \frac{M_w}{M_{\text{total}}} \quad (\text{S34})$$

The final modification factor including phototransformation:

$$\delta_{\text{photo+}} = 1 + \frac{\phi_3}{1 - \phi_3} \frac{k_{\text{sed}}}{k_w} + \frac{k_{\text{photo}}}{k_w} = \delta + \frac{k_{\text{photo}}}{k_w} \quad (\text{S35})$$

S3.2 Hydrolysis

Assume that both M_w and M_{sed} degrade with k_{hydr} in addition to k_w . Then the total system degradation will be:

$$k^* = k_w \frac{M_w}{M_{\text{total}}} + k_{\text{sed}} \frac{M_{\text{sed}}}{M_{\text{total}}} + k_{\text{hydr}} \frac{M_w}{M_{\text{total}}} + k_{\text{hydr}} \frac{M_{\text{sed}}}{M_{\text{total}}} \quad (\text{S36})$$

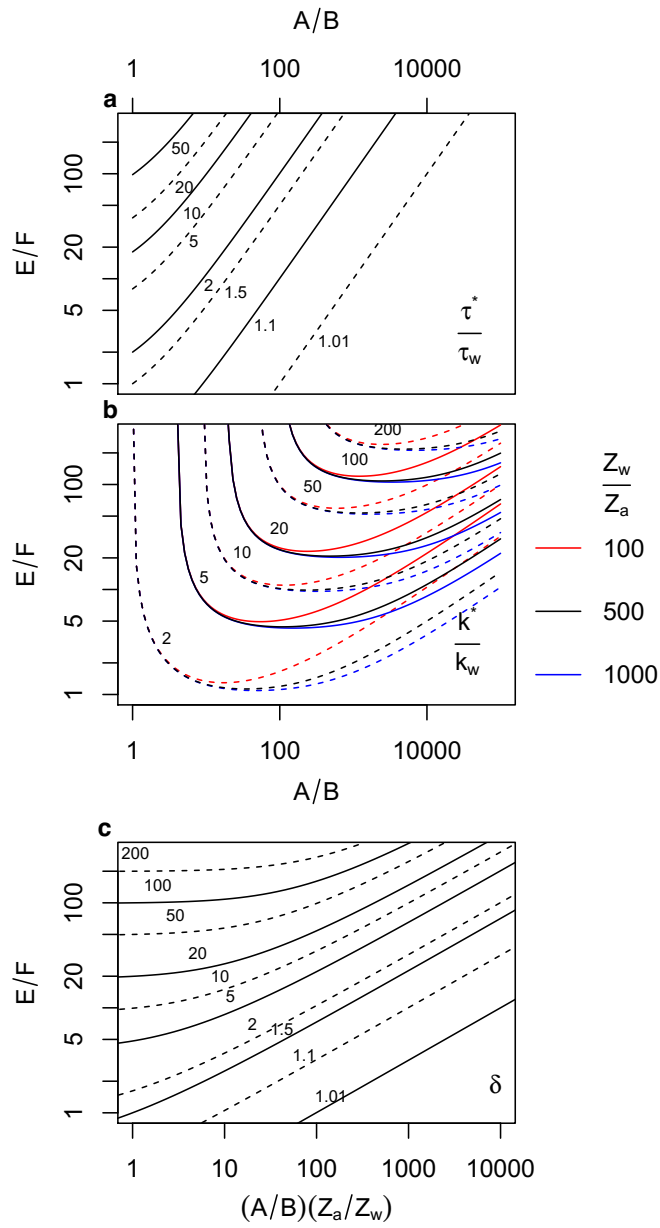


Figure S3. The role of the physical environment (E/F , Z_w/Z_a) and sorption properties (A/B) on dimensionless travel time (panel a), the dimensionless degradation rate constant (panel b), and the settled sediment modification factor (δ , panel c).

The ratio normalised by k_w is:

$$\frac{k^*}{k_w} = \frac{M_w}{M_{\text{total}}} + \frac{k_{\text{sed}}}{k_w} \frac{M_{\text{sed}}}{M_{\text{total}}} + \frac{k_{\text{hydr}}}{k_w} \left(\frac{M_w}{M_{\text{total}}} + \frac{M_{\text{sed}}}{M_{\text{total}}} \right) \quad (\text{S37})$$

The final modification factor including hydrolysis:

$$\delta_{\text{hydr+}} = 1 + \frac{\phi_3}{1 - \phi_3} \frac{k_{\text{sed}}}{k_w} + \frac{1}{1 - \phi_3} \frac{k_{\text{hydr}}}{k_w} = \delta + \frac{1}{1 - \phi_3} \frac{k_{\text{hydr}}}{k_w} \quad (\text{S38})$$

S4 Stream geometry, flow velocity, sediment grainsize distribution, and total suspended solids concentrations

The calculation of API degradation requires the knowledge of Z_w , Z_a , SSC , S , and τ_w in each stream reach. These values are not available on the stream network scale, observations are concentrated in a few points. Therefore, reach-specific values have to be estimated based on the few properties, which are known, namely the drainage area, and the channel slope. Obviously, such estimation is very crude, it just serves finding the approximate order of magnitude for the estimated values.

In a specific catchment discharge of a certain probability is commonly estimated as a power function of drainage area, and depth is estimated with another power function of discharge [????]. Nested power functions form a power function again, so stream depth at mean flow (Z_w [m]) can be estimated a power function of drainage area (A [km²]):

$$Z_w = a \cdot A^b \quad (S39)$$

The parameters a (0.15) and b (0.3) are set to yield a minimal depth of 0.15 m at the drainage area of 1 km², and provide the known 5-6 m along the lower half of the Rhine ($A > 100'000$ km²). Since most natural and channelized streams have high width:depth ratios, the hydraulic radius (R [m]) is approximately equal to Z_w .

We assume that flow extremes determine the long-term grain size distribution of streambeds. Relative flow variability is calculated based on statistics of discharge and drainage area in multiple streams (Fig. S4):

$$\frac{MHQ}{MQ} = 40.928 \cdot A^{-0.217} \quad (S40)$$

where MHQ , and MQ are mean high flow and mean flow, respectively. Similarly,

$$\frac{MHQ}{MLQ} = 298.77 \cdot A^{-0.336} \quad (S41)$$

where MLQ is mean low flow. Mapping from discharge to stage is usually performed by a common power-type rating curve:

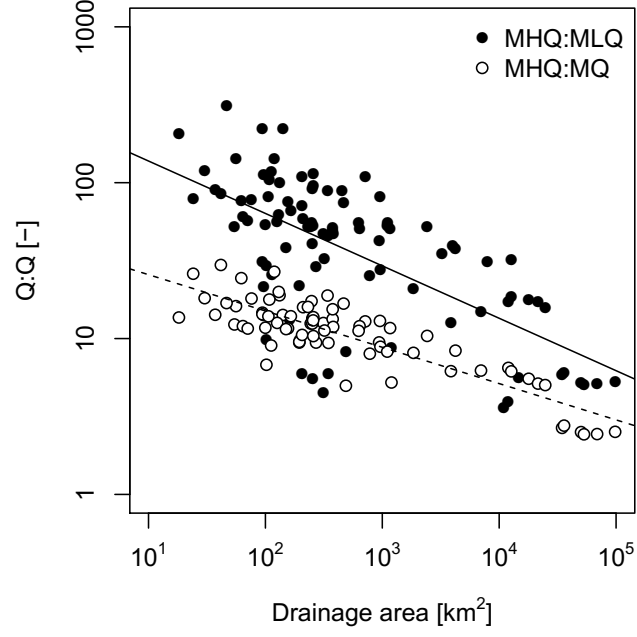


Figure S4. Mean high flow (MHQ) relative to mean flow (MQ) and mean low flow (MLQ) in 100 selected gauges of Bayern and Baden-Württemberg (Rheingebiet I and II).

$$Q \propto Z_w^k \quad (\text{S42})$$

From this

$$Z_w \propto Q^{\frac{1}{k}} \quad (\text{S43})$$

For natural channels where flow depth is small compared to width and bank slopes are gentle, k can be approximated with 2 based on the Manning-Chézy equation. Thus,

$$\frac{MHZ}{MZ} \approx \sqrt{\frac{MHQ}{MQ}} \quad (\text{S44})$$

and

$$\frac{MLZ}{MZ} \approx \sqrt{\frac{MLQ}{MQ}} \quad (\text{S45})$$

where MHZ , MLZ , and MZ are the mean high, low, and mean flow depths, respectively.

The shear velocity [m s^{-1}] for a given flow depth is

$$u^* = \sqrt{gZ_w I} \quad (\text{S46})$$

where I is the channel slope [-]. For the extreme flows

$$u_H^* = \sqrt{gZ_w \frac{MHZ}{MZ} I} \quad (\text{S47})$$

and

$$u_L^* = \sqrt{gZ_w \frac{MLZ}{MZ} I} \quad (\text{S48})$$

because $Z_w = MZ$, as we generally assume mean flow.

These shear velocities allow calculating the extreme values of the grainsize-distribution based on the Rouse numbers ($P = \frac{v_s}{\kappa u^*}$, where v_s is settling velocity [m s^{-1}] and $\kappa = 0.4$ is the von Kármán constant) belonging to full suspension (0.8) and instability (2.5). As the first step, the settling velocity for a particle with D diameter [m] is calculated [?]:

$$v_s = \frac{1.65gD^2}{18 \cdot 10^{-6} + \sqrt{0.75 \cdot 1.65gD^3}} \quad (\text{S49})$$

It is assumed that the largest grainsize is at the limit of stability during high flow, while the smallest is that can be resuspended at low flows. Accordingly, for D_{90} the target settling velocity $2.5\kappa u_H^*$, while for D_{10} it is $0.8\kappa u_L^*$.

From D_{90} the base Manning roughness of the channel is calculated according to a polynomial fit to the USGS channel roughness data for different grain sizes [?]:

$$n = 0.00017 d^3 - 0.00147 d^2 + 0.00547 d + 0.02598 \quad (\text{S50})$$

where $d = \log D_{90}$ and D_{90} has the units of [mm]

Mean flow velocity (U [m s^{-1}]) is calculated by using the Manning and Chézy equations:

$$U = \frac{1}{n} R^{2/3} \sqrt{I} \quad (\text{S51})$$

Knowing D_{10} and D_{90} lets us estimate the entire grainsize-distribution (unimodal, log-normal, with $D_{50} = \sqrt{D_{10}D_{90}}$) and from that the fraction of suspendible material (sand and finer, below 2 mm grainsize):

$$q_{sand} = \frac{1}{2} \left(1 + \operatorname{erf} \left(\frac{\log 0.002 - \log D_{50}}{2.56(\log D_{90} - \log D_{10})\sqrt{2}} \right) \right) \quad (\text{S52})$$

S4.1 Capacity-limited SSC

A significant number of semi-empirical formulas can be found in the literature to quantify suspended sediment loads. The formulas are generally based on hydrological/hydraulic parameters, such as flow depth, flow velocity, bed shear stress, critical bed shear and sediment parameters, e.g. characteristic grain diameter. In this study we use the model of τ_c , which is one of the most tested formulas for the sediment carrying capacity of flow and has been successfully used in a wide variety of riverine applications. Hereby we assume that the suspended sediment is represented by an average sand particle with $D = 0.5$ [mm].

The critical depth-averaged velocity for initiation of motion [m s^{-1}] is:

$$U_{cr} = 8.5D_{50}^{0.6} \log \left(12 \frac{Z_w}{Z_a} \right) \quad (\text{S53})$$

where Z_a is the thickness of the active sediment layer ([m] $Z_a = 3D_{50}$).

The mobility parameter [-]:

$$M_e = \frac{U - U_{cr}}{\sqrt{1.65gD}} \quad (\text{S54})$$

where U is the mean flow velocity [m s^{-1}].

The dimensionless particle size [-]:

$$D^* = D \left(\frac{1.65g}{\nu^2} \right)^{1/3} \quad (\text{S55})$$

where ν is the kinematic viscosity of water [$10^{-6} \text{ m}^2 \text{ s}^{-1}$]

Specific suspended sediment discharge or sediment transport rate [$\text{kg m}^{-1} \text{ s}^{-1}$]:

$$q_{s,cap} = 0.012 \cdot \rho \cdot UDM_e^{2.4} D^{*-0.6} \quad (\text{S56})$$

where $\rho = 2650$ [kg m^{-3}] is the sediment density (for quartz).

SSC assuming capacity limitation [kg m^{-3}]:

$$SSC_{cap} = \frac{q_{s,cap}}{q_w} = \frac{q_{s,cap}}{UZ_w} \quad (\text{S57})$$

where $q_w = U \cdot Z_w$ is the specific flow discharge [$\text{m}^2 \text{s}^{-1}$].

S4.2 Supply-limited SSC

Assume that SSC is determined by sediment supply, and source of the suspended material is the streambed (by mean flow land supply should be negligible due to the lack of current surface runoff). For the supply-limited transport it is again assumed that the resuspended particle is an average sand with $D = 0.5$ [mm].

The settled (suspendible) sediment stock calculates from the active sediment depth ($Z_a = 3D$), the sediment porosity (θ), and the sand content:

$$S = Z_a \cdot (1 - \theta) \cdot \rho \cdot q_{sand} \quad (\text{S58})$$

The resuspension rate constant [m s^{-1}] is expressed as function of the excess shear velocity:

$$k_s = \alpha \left(\frac{u^*}{v_s} - 1 \right) \exp \left(-\frac{D_{50}}{D} \right) \quad (\text{S59})$$

where $\alpha = 0.52$ [m s^{-1}] is a calibrated constant, $\frac{D_{50}}{D}$ is a grain-diameter ratio between the “average” sand particle and D_{50} , because high grain diversity hinders resuspension of finer particles due to streambed armouring.

The suspended sediment transport rate under supply-limitation [$\text{kg m}^{-1} \text{s}^{-1}$]:

$$q_{s,sup} = k_s S \quad (\text{S60})$$

SSC assuming supply limitation [kg m^{-3}]:

$$SSC_{sup} = \frac{q_{s,sup}}{q_w} = \frac{q_{s,sup}}{UZ_w} \quad (\text{S61})$$

S4.3 Actual SSC

The actual SSC is the smaller value from the capacity- and supply-limited pair:

$$SSC = \min(SSC_{sup}, SSC_{cap}) \quad (\text{S62})$$

In the Rhine basin SSC_{sup} was almost exclusively determining SSC , so most channels are possibly supply-limited.

Modelled $SSCs$ were typically between 30 and 100 [mg L^{-1}] (Fig. S5) in major rivers. For the Rhine channel mean annual $SSCs$ are reported to be 27 [mg L^{-1}] at Maxau [?], and 20-50 [mg L^{-1}] along the entire German section [?]. The modelled values fell into the same range. Smaller tributaries had typically higher $SSCs$, with channel slope as a secondary selection factor. Among the major inflows, the Main had the lowest and the Aare had the highest modelled $SSCs$. Mean measured SSC in the lower Aare varies between 80-200 [mg L^{-1}] [?].

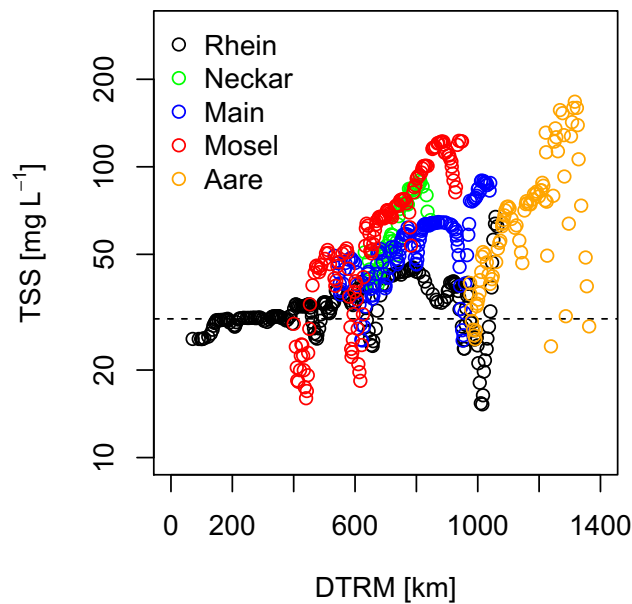


Figure S5. Modelled $SSCs$ in major rivers. DTRM: distance to Rhine mouth. Dashed line: mean measured concentrations for the Rhine channel (see text). High amplitude fluctuations in SSC are due to the coarse resolution of channel slope data and the lack of longitudinal coherence in the presented simple SSC approximation.

S5 Role of input uncertainty

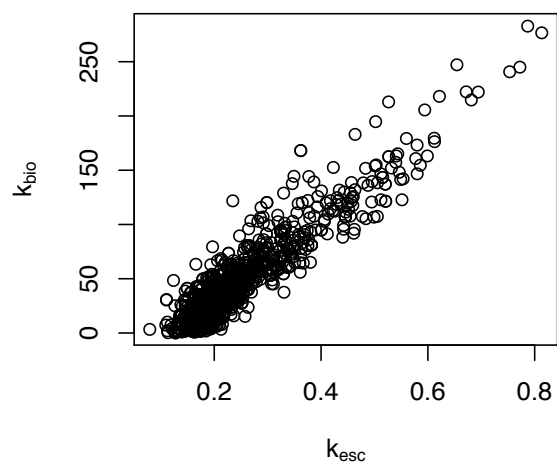


Figure S6. Dependence between k'_{esc} [-] and k'_{bio} [$\text{d}^{-1} (\text{kg OC m}^{-3})^{-1}$]. Posterior sample for API8 with vague (wide uniform) priors. True value for k'_{esc} is 0.09 (Singer et al. 2016).

S6 Longitudinal profiles of APIs in the Rhine

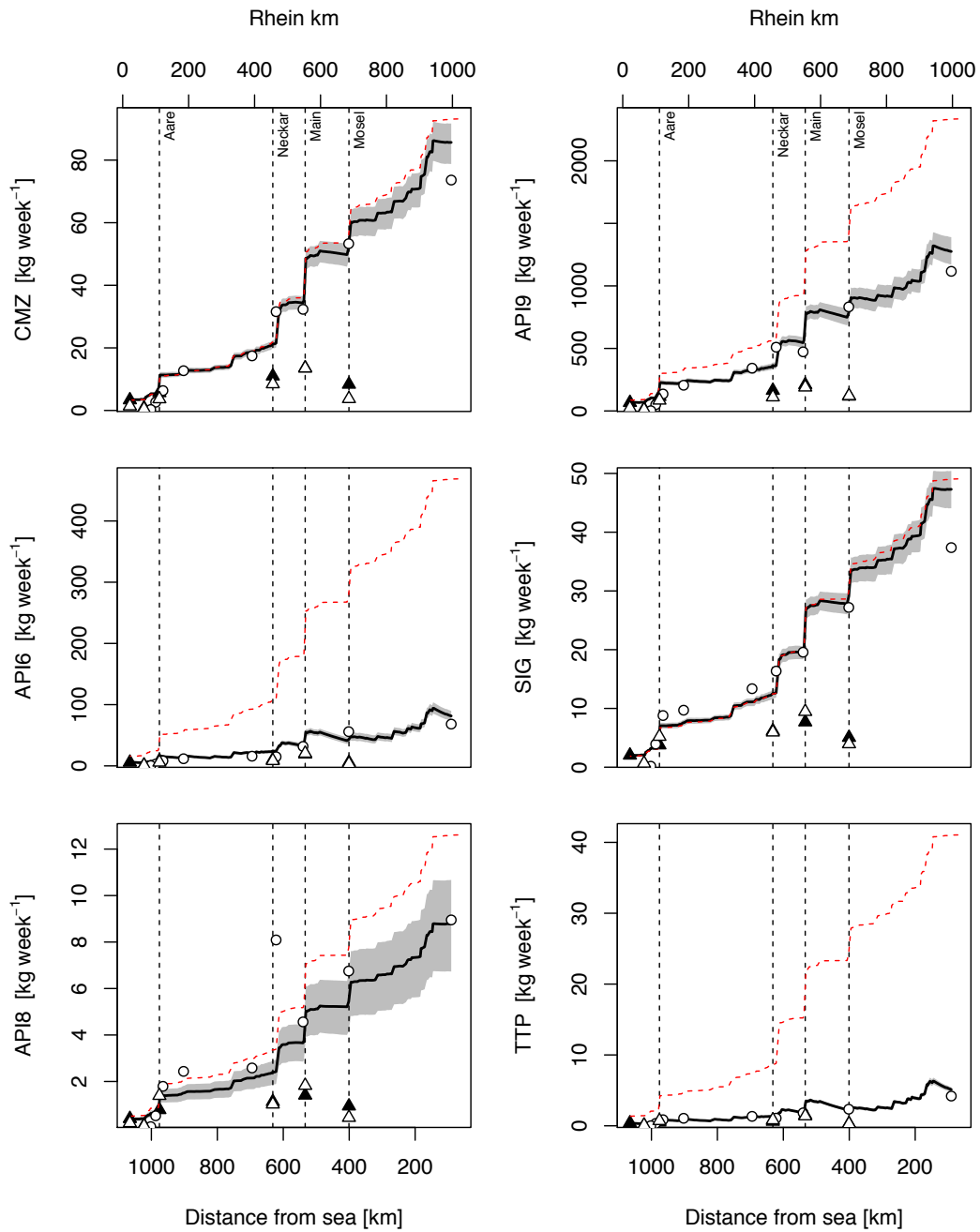


Figure S7. Degradation profiles of APIs along the Rhine (1). Open symbols: measurements (circles: Rhine, triangles: tributaries), closed symbols: modelled values for tributary inflows. Dashed red line: conservative assumption (accumulated load). Black line: best model fit. Grey band: 95% uncertainty interval.

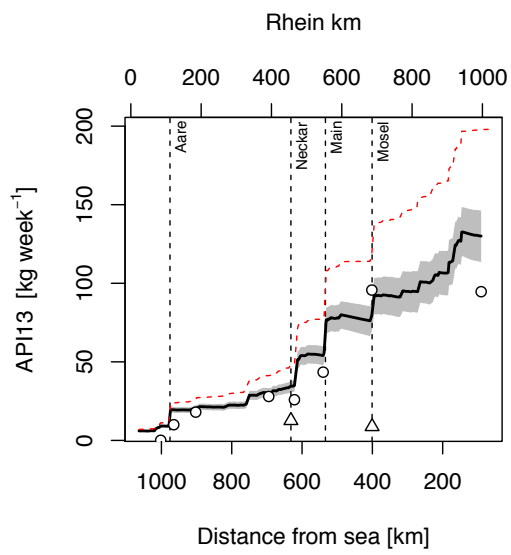


Figure S8. Degradation profiles of APIs along the Rhine (2). Open symbols: measurements (circles: Rhine, triangles: tributaries), closed symbols: modelled values for tributary inflows. Dashed line: conservative assumption (accumulated load). Black line: best model fit. Grey band: 95% uncertainty interval.