

Supplementary Material

Evaluation of the environmental fate of a semivolatile transformation product of ibuprofen, based on a simple two-media fate model

Cecilia Arsene,^{1,2,3} Iustinian G. Bejan,^{1,2,3} Claudiu Roman,^{1,2,3} Romeo I. Olariu,^{1,2,3*} Marco Minella,⁴ Monica Passananti,^{4,5} Luca Carena,⁴ Davide Vione^{4*}

1 - Department of Chemistry, Faculty of Chemistry, “Alexandru Ioan Cuza” University of Iasi, 11 Carol I, 700506 Iasi, Romania

2 - Integrated Centre of Environmental Science Studies in the North Eastern Region (CERNESIM), “Alexandru Ioan Cuza” University of Iasi, 11 Carol I, 700506 Iasi, Romania

3 - Integrated Centre of Environmental Science Studies in the North Eastern Region (RECENT AIR), “Alexandru Ioan Cuza” University of Iasi, 11 Carol I, 700506 Iasi, Romania

4 - Dipartimento di Chimica, Università degli Studi di Torino, Via Pietro Giuria 5, 10125 Torino, Italy

5 - Institute for Atmospheric and Earth System Research (INAR), University of Helsinki, PL 64 (Gustaf Hällströmin katu 2), 00014 Helsinki, Finland

* Address correspondence to either author. oromeo@uaic.ro (RIO); davide.vione@unito.it (DV)

List of abbreviations

DOC: Dissolved Organic Carbon

IBAP: 4-Isobutylacetophenone

IBP: Ibuprofen

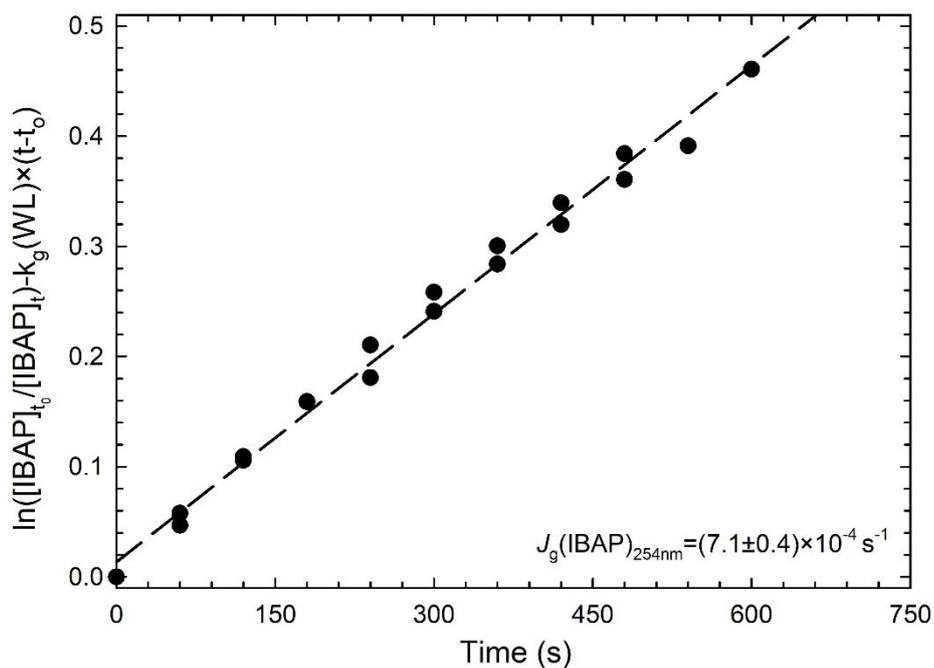


Figure SM1. Plot of 254 nm photolysis of IBAP in the ESC-Q-UAIC reactor, corrected for wall loss.

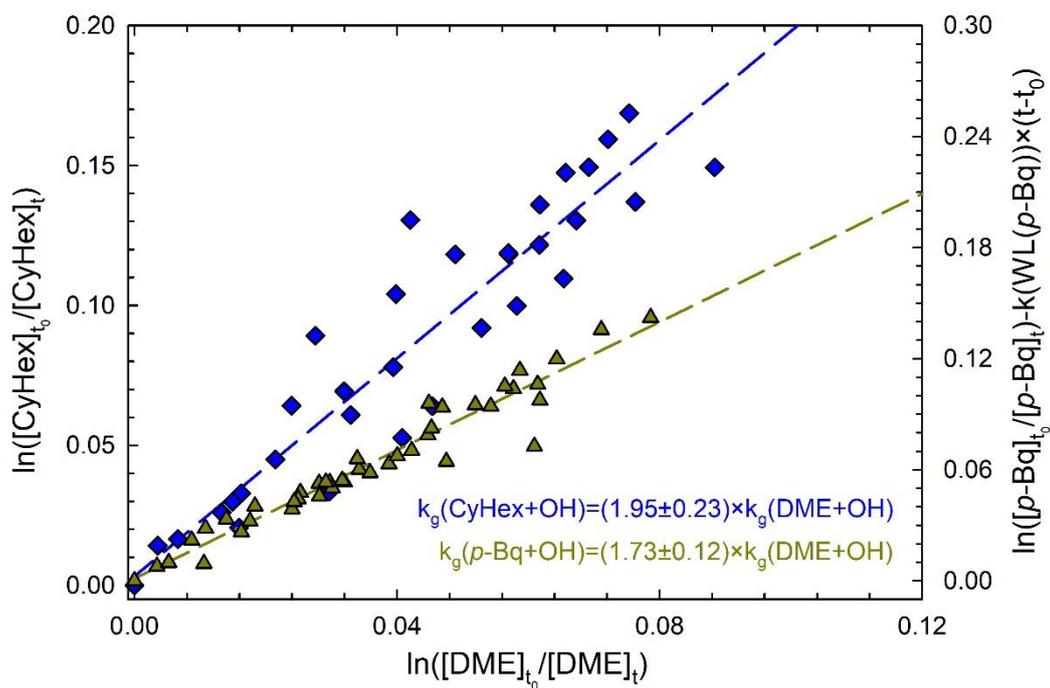


Figure SM2: Relative kinetic control plot, corresponding to the gas-phase reaction of OH radicals with (◆) cyclohexane and (▲) *p*-benzoquinone, versus dimethyl ether in the presence of NO_x.

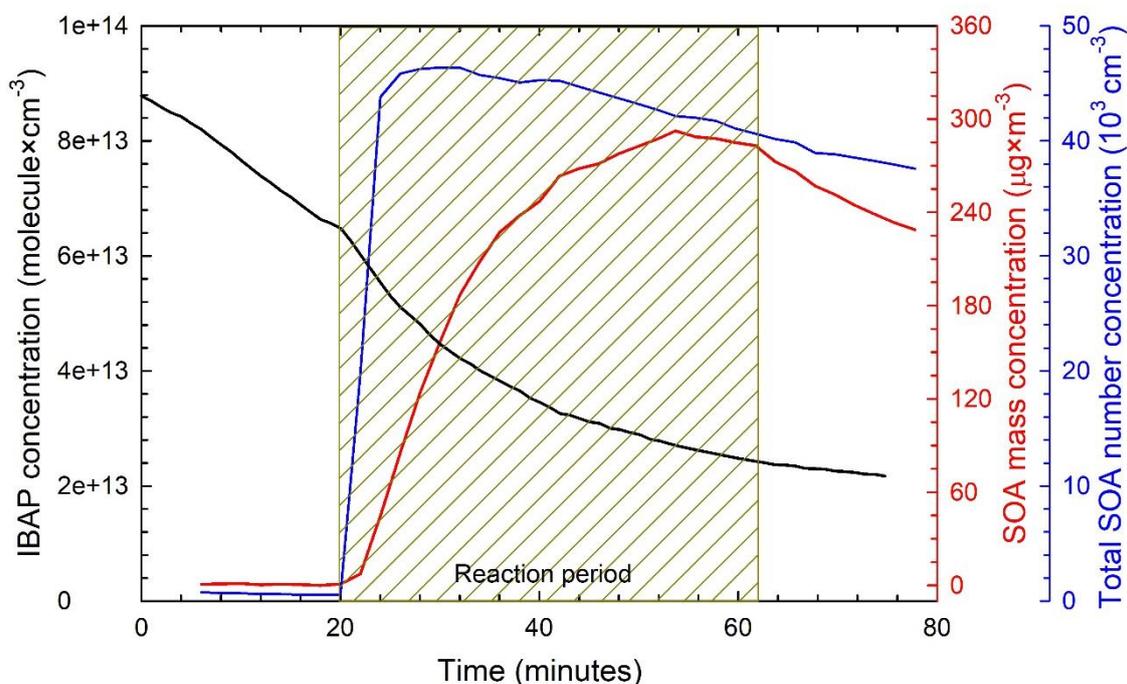


Figure SM3: Time profile of IBAP with OH/NO_x, and the evolution of the total number and mass concentration of Secondary Organic Aerosol (SOA) in the ESC-Q-UAIC chamber.

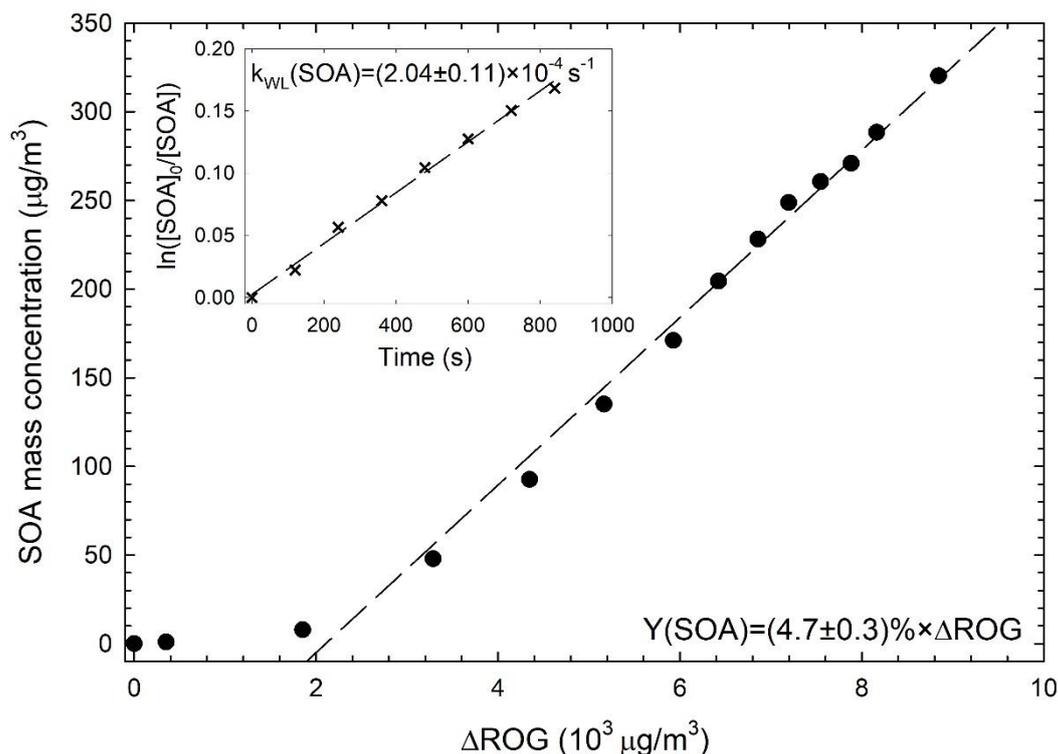


Figure SM4: Distribution of the mass concentration of secondary organic aerosols (SOAs) formed in the ESC-Q-UAIC chamber, during the OH radicals-initiated oxidation of IBAP in the presence No_x, as a function of IBAP consumption (ΔROG – mass concentration of the reactive organic (IBAP) consumed during the photooxidation process). The intercept with the x axes indicates that SOAs formation occurs only when a critical amount of the reactive organic is consumed (DROG), and transformed into initial aerosol precursor materials occurring in the gas phase.

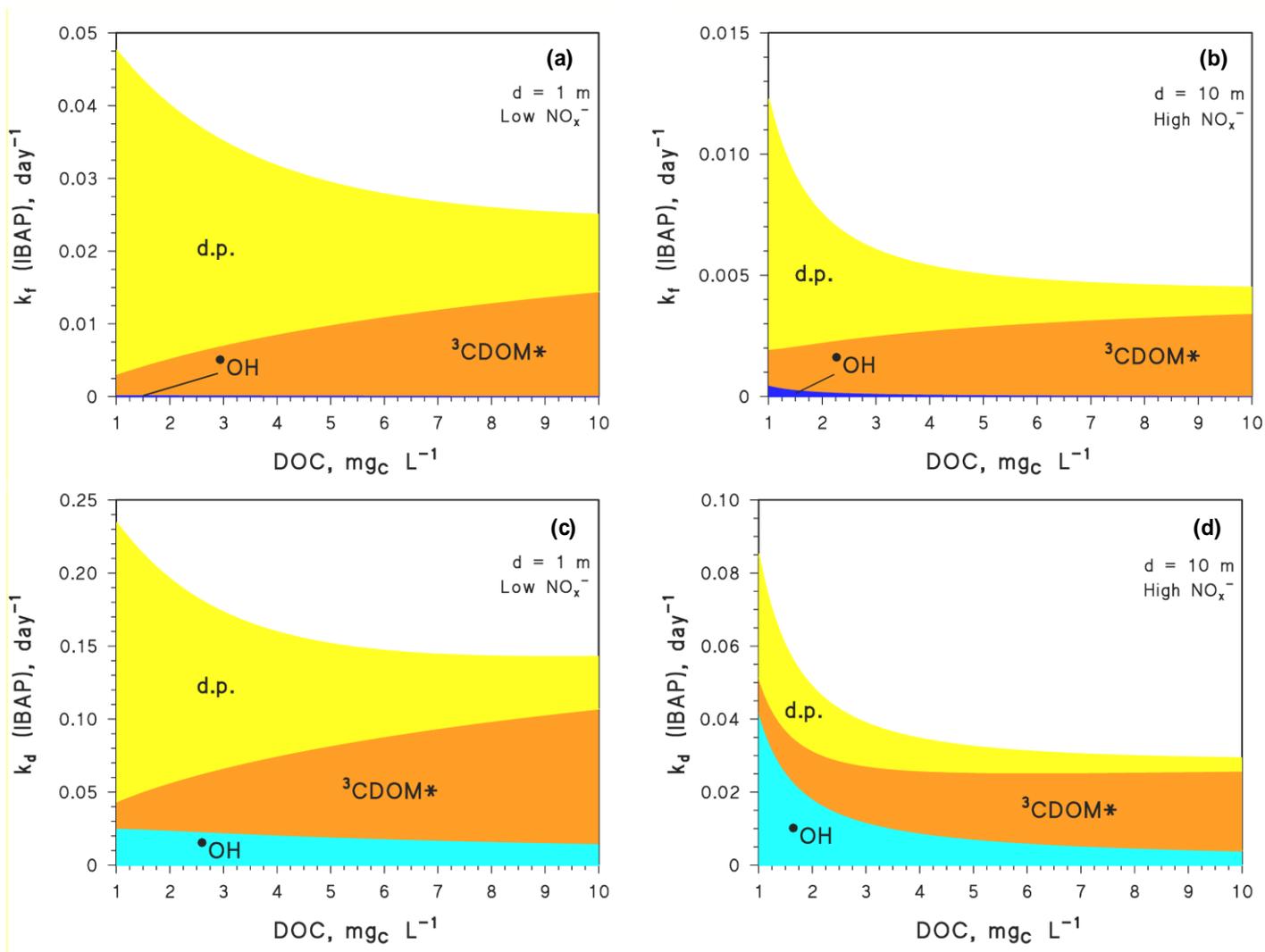


Figure SM5. (a,b) Modeled formation rate constants of IBAP from IBP, as a function of water DOC. Other conditions: 10^{-3} M HCO_3^- ; 10^{-5} M CO_3^{2-} ; water depth d (a) 1 m, (b) 10 m; inorganic nitrogen (a) $[\text{NO}_3^-] = 10^{-6}$ M & $[\text{NO}_2^-] = 10^{-8}$ M (low NO_x^-), (b) $[\text{NO}_3^-] = 10^{-4}$ M & $[\text{NO}_2^-] = 10^{-6}$ M (high NO_x^-). (c,d) Modelled photodegradation rate constants of IBAP, as a function of water DOC. Other conditions: 10^{-3} M HCO_3^- ; 10^{-5} M CO_3^{2-} ; water depth d (c) 1 m, (d) 10 m; inorganic nitrogen (c) $[\text{NO}_3^-] = 10^{-6}$ M & $[\text{NO}_2^-] = 10^{-8}$ M (low NO_x^-), (d) $[\text{NO}_3^-] = 10^{-4}$ M & $[\text{NO}_2^-] = 10^{-6}$ M (high NO_x^-). In all the cases, photochemical modelling was carried out with the APEX software.^{S1} Average sunlight irradiance & day unit corresponding to fair-weather 15 July at 45°N latitude. The color code highlights the different photochemical reaction pathways (d.p. = direct photolysis).

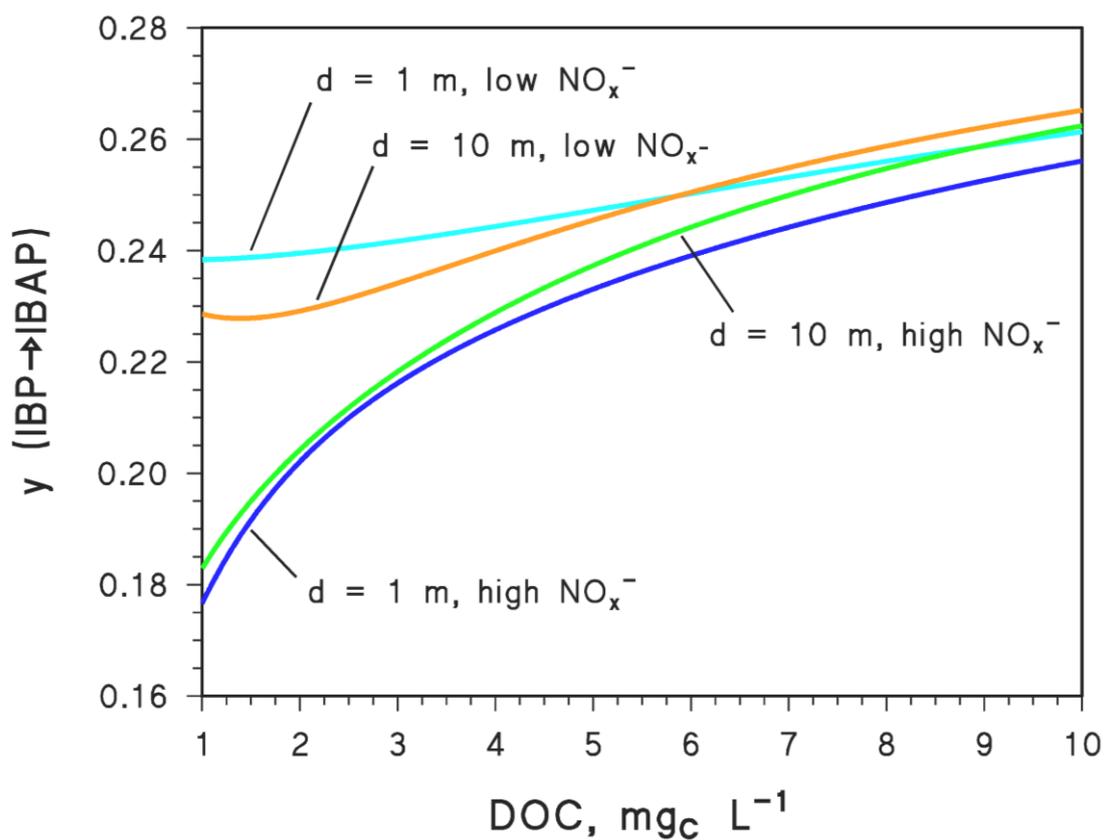


Figure SM6. Modeled formation yields of IBAP from IBP, as a function of water DOC. Water conditions: 10^{-3} M HCO_3^- ; 10^{-5} M CO_3^{2-} ; water depth $d = 1$ m or 10 m. High NO_x^- : $[\text{NO}_3^-] = 10^{-4}$ M & $[\text{NO}_2^-] = 10^{-6}$ M; low NO_x^- : $[\text{NO}_3^-] = 10^{-6}$ M & $[\text{NO}_2^-] = 10^{-8}$ M. Sunlight irradiation conditions correspond to fair-weather 15 July at 45°N latitude.

Text SM1. Mapping the parameter ν for IBAP volatilization.

As described in the main manuscript, IBAP can undergo both photodegradation in, and volatilization from, surface waters. The fraction of IBAP that volatilizes is defined as $\nu = k_{vol} (k_{vol} + k'_d)^{-1}$, where k_{vol} is the volatilization rate constant of IBAP from an aqueous environment to the gas phase, and k'_d is the overall photodegradation rate constant of IBAP in water.

We calculated the value of ν for some European rivers, and mapped it over the region included between 40 and 50°N during the month of June, in the decade 1990 - 2000. The values are averaged over that period. Photochemical computation of k'_d was mainly based on the values of DOC (Dissolved Organic Carbon, $\text{mg}_C \text{L}^{-1}$) of the considered rivers.^{S2} This means that the photolysis rate constant k'_d was assessed, without considering the photochemistry of nitrate and nitrite. For a complete description of data sources and treatment, the reader is referred to ref. **S3**. Briefly, the overall rate coefficient of IBAP photodegradation is mainly accounted for by reactions with OH radicals and $^3\text{CDOM}^*$, as well as by direct photolysis. Therefore, for a given river, one has that $k'_d = k_{IBAP,^3\text{CDOM}^*} [^3\text{CDOM}^*] + k_{IBAP,OH} [\text{OH}] + \Phi \times P'_a(\text{IBAP})$, where the values of $k_{IBAP,^3\text{CDOM}^*}$, $k_{IBAP,OH}$, and Φ are reported in Table 1 of the main manuscript. $P'_a(\text{IBAP})$ is the rate coefficient of solar-light absorption by IBAP in the considered river, and it was assessed as

$$P'_a(\text{IBAP}) = \sum_{\lambda} p^{\circ}(\lambda) \varepsilon_{\text{IBAP}}(\lambda) [1 - 10^{-A_1(\lambda) l^{\text{DOC}}}] (A_1(\lambda) \text{DOC})^{-1} \Delta\lambda.$$

In particular, $p^{\circ}(\lambda)$ is the spectral solar photon flux ($\text{Ein L}^{-1} \text{s}^{-1} \text{nm}^{-1}$) reaching the water body in mid-June, $\varepsilon_{\text{IBAP}}(\lambda)$ is the molar absorption coefficient of IBAP ($\text{L mol}^{-1} \text{cm}^{-1}$), $A_1(\lambda) = 0.45 \exp(-0.015 \lambda)$ ^{S1} is the specific absorbance of CDOM along an optical path length of 1 cm (units of $\text{L mg}_C^{-1} \text{cm}^{-1}$), and l (cm) is the river optical path length (which is a function of the water depth^{S1}). $[^3\text{CDOM}^*]$ and $[\text{OH}]$ were calculated with APEX,^{S1} from the DOC values of the considered rivers.

With the values of k'_d thus calculated (units of s^{-1}), as well as $k_{vol} = 0.052 \text{ day}^{-1} = 6.02 \cdot 10^{-7} \text{ s}^{-1}$, the parameter ν was computed and mapped over the European region, by means of the QGIS software, version 3.2.2 'Bonn' (QGIS Developmental Team, 2020. QGIS Geographic Information System. Open Source Geospatial Foundation Project; 2018). **Figure SM7** shows the calculated values of ν for water depths of 1 and 3 m. The intermediate case (2 m) is shown in the main manuscript.

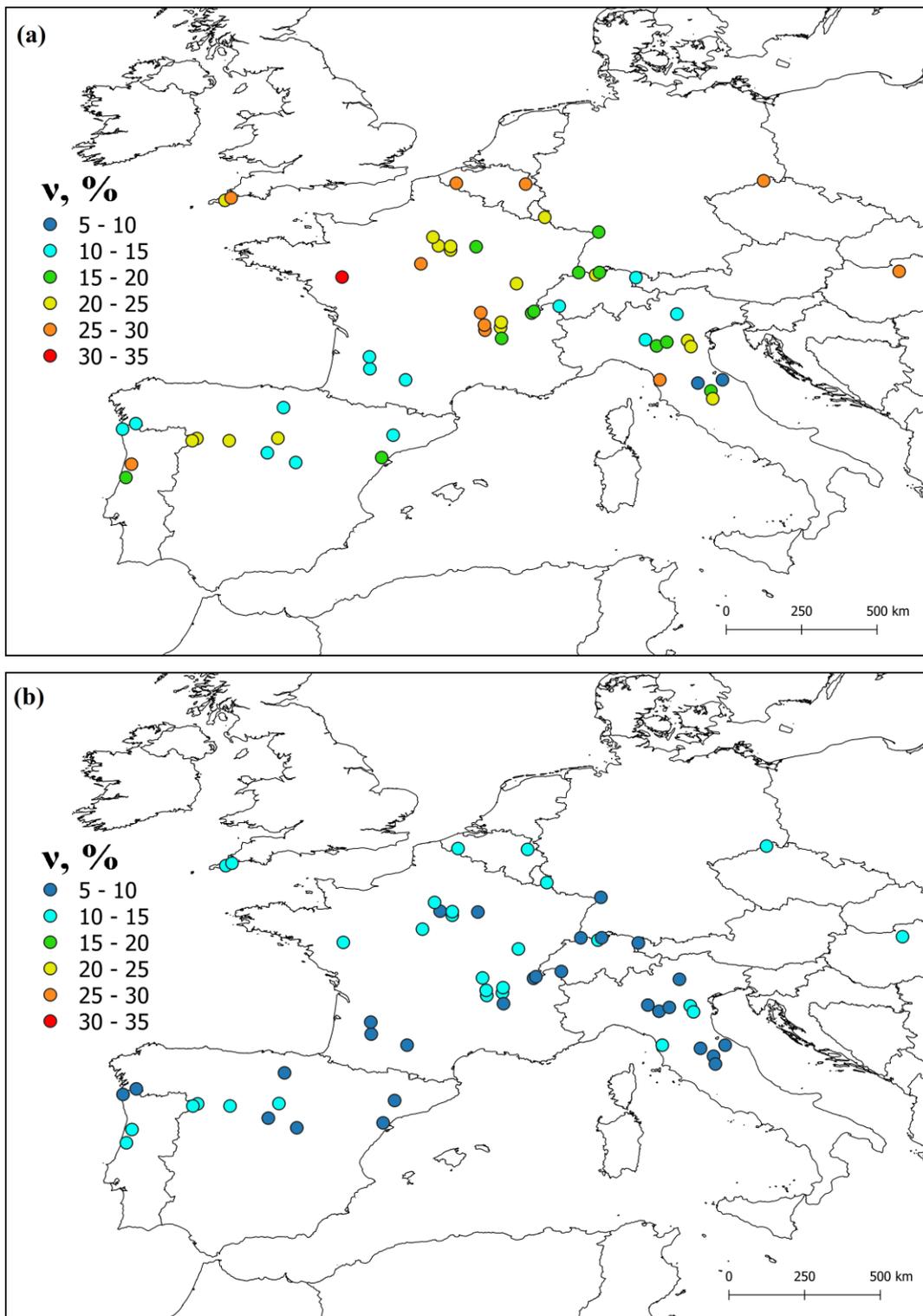


Figure SM7. European maps of the parameter v (%) for IBAP, as obtained from the adopted photochemical model, for water depth = 3 m (a) and 1 m (b).

References

- S1) Bodrato, M.; Vione, D. APEX (Aqueous Photochemistry of Environmentally occurring Xenobiotics): A free software tool to predict the kinetics of photochemical processes in surface waters. *Environ. Sci.-Proc. Imp.* **2014**, *16*, 732-740.
- S2) GEMSTAT, <http://www.GEMStat.org>.
- S3) Carena, L.; Vione, D. Mapping the photochemistry of European mid-Latitudes rivers: An assessment of their ability to photodegrade contaminants. *Molecules* **2020**, *25*.