Electronic Supplementary Material (ESI) for Green Chemistry.

Mobility and adsorption of liquid organic hydrogen carriers (LOHCs) in soils – environmental hazard perspective

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Electronic Supplementary Information (ESI)

containing text sections S1–S7, six figures (Figure S1–S6), and five tables (Table S1–S5)

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S1. Materials

The LOHC compounds with different degrees of hydrogenation used in the study included quinaldines (2-methyl-quinoline, tetrahydro-2-methyl-quinoline, decahydro-2-methyl-quinoline), indoles (indole and indoline), carbazole derivatives (9-ethyl-9H-carbazole, 9-propyl-9H-carbazole, 9-butyl-9H-carbazole and the respective partially hydrogenated forms), MLH (benzyltoluene and partially hydrogenated forms) and MSH (dibenzyltoluene). The partially hydrogenated LOHC chemicals were technical mixtures (excluding the quinaldine-based system) obtained from the hydrogenation reaction before full conversion was achieved; they contained a mixture of the respective H_2-lean forms at different levels of hydrogenation, including the H_2-lean and H_2-rich compounds as well as intermediate structures.

Citric acid ($C_6H_8O_7 \cdot H_2O$, > 99.5%) was obtained from Acros Organics, New Jersey, USA. Sodium nitrate ($NaNO_3$, 99.5%) was purchased from Riedel-deHaën, Seelze, Germany. Methanol (HPLC grade) was from VWR Chemicals, France. Anhydrous sodium sulfate (Na_2SO_4, 99.9%) was purchased from VWR, Belgium. Tri-sodium citrate dihydrate ($C_6H_5O_7Na_3 \cdot 2H_2O$, 99%) and dichloromethane (DCM, GC grade ≥ 99.8%) were purchased from Merck, Darmstadt, Germany. Atrazine (analytical grade, Table S2), acetone (HPLC grade ≥ 99.8%), quinoline (GC grade = 98%) and naphthalene (GC grade ≥ 99%) were purchased from Sigma-Aldrich (Steinheim, Germany). Unless specifically stated, deionised water filtered through a Carbonit NFP Premium-9 water filter (Heidenheim, Germany) with a pore size of 0.45 µm was used in this study.

The information of the soils was obtained in the product sheet from Fraunhofer IME, Schmallenberg, Germany. Both soils were of the same type but of different batches, which were collected from Schmallenberg, Nordrhein-Westfalen, Germany. No pesticides have been applied to the soils during the previous two years before collection and no fertilisers have been applied one year before collection.

Table S1. Properties of the test soils.

	Sand [%]	**Silt** [%]	**Clay** [%]	**OC** [a] [%]	**Total (N)** [g kg^{-1}]	**pH ($CaCl_2$)**	**CEC** [b] [mmol kg^{-1}]	**WHC** [g kg^{-1}]	**Applied in the test**
Soil I	76.7	17.2	6.1	1.21	0.79	5.41	9.90	291	Batch [c]
Soil II	76.7	17.2	6.1	0.80	0.71	5.33	17.90	291	Leaching [d]

"%" indicates w/w.

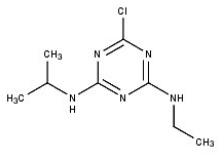
[a] Organic carbon.

[b] Cation exchange capacity.

[c] Adsorption batch equilibrium experiment.

[d] Soil column leaching test.

Table S2. Physicochemical properties of atrazine.

	Formula	**Chemical structure**	**MW** [g mol^{-1}]	**Water solubility** (25 °C) [a] [mg L^{-1}]	**Log K_{ow}** [a]	**Log K_{oc}** [a]
Atrazine	$C_8H_{14}ClN_5$		45.0	214.1	2.82	2.61

[a] Predicted by using Estimation Programs Interface Suite™ (US EPA EPI Suite package v 4.1)[1] (https://www.epa.gov/).

S2. The COSMO-RS model and calculations

COSMO-RS (Conductor like Screening Model for Realistic Solvation)[2] is a statistical thermodynamics model for calculation of the chemical potential of a compound in solution. Thus, it can be used to predict all equilibrium properties that can be derived from the chemical potential, e.g., the octanol–water partition coefficient (K_{ow}) used in this study.

The COSMO-RS model uses the information of an underlying quantum chemical COSMO[3] calculation that minimises the energy of the molecule in the surroundings of a perfect conductor. This artificial state is used as the reference state for the COSMO-RS calculation. The so-called screening charge density, σ, which describes the response of the conductor to the charge distribution of the solute at the solute-solvent boundary, is the most important descriptor used in the statistical thermodynamic procedure of COSMO-RS and contains information about the polarity of the solute. This σ value can also be used to fit quantitative structure-property relationship models for the partitioning between less well-defined phases, such as the soil sorption (K_{oc}) model used in this work[4].

All COSMO-RS calculations were performed with the COSMO*therm* program (Version C3.0 Release 17.01, COSMO*logic* GmbH and Co. KG, Leverkusen, Germany). The BP_TZVP_C30_1701 parameterisation was used for the K_{oc} predictions. All other results were obtained with the BP_TZVPD_FINE_C30_1701 parameter set and the standard conformer treatment. The TURBOMOLE V7.1 program package (TURBOMOLE GmbH, http://www.turbomole.com) was used for the quantum chemical calculations. All structures were optimised with the BP86 functional[5,6,7] and the TZVP basis set[8] using the COSMO model with standard cavity. Single point calculations were performed with the BP functional and the def2-TZVPD[9] basis set with iso-radii COSMO cavity using the optimised structures.

S3. Determination of log K_{oc}

The HPLC instrument (Hewlett Packard system Series 1100, Agilent Technologies, Waldbronn, Germany) was equipped with an autosampler and a UV-vis detector (Agilent Technologies, Waldbronn, Germany) at a wavelength of 210 nm. A normal-phase cyanopropyl column (ZORBAX CN, 5 µm, 4.6 mm ID × 150 mm, Agilent) was used, and the flow rate was 1.0 mL min^{-1}. The mobile phase for HPLC was a mixture of methanol and citrate buffer with a ratio of 55/45% v/v (pH 6.0, 0.01 M consisting of 11.5 mL of a 0.1 M $C_6H_8O_7 \cdot H_2O$ solution plus 88.5 mL of a 0.1 M $C_6H_5O_7Na_3 \cdot 2H_2O$ solution in a total volume of 1 L). Sodium nitrate was used as a non-retained substance to measure the dead-time of the HPLC system. Ten reference compounds were used for calibration which were divided into two groups based on the predicted K_{oc} values to shorten the time of analysis. Group A consisted of acetanilide, acetophenone, 4-chloroaniline, toluene, ethylbenzene, biphenyl, phenanthrene and fluoranthene, and group B contained 4-methoxyphenol and cinnamyl alcohol. The retention time of each compound was measured on three separate days with three injections each day, and the averages of the measurements were calculated. The retention times of the reference substances (t_R) and non-retained substance (t_0) were used to calculate the capacity factor (k) of each reference substance according to Eq. (S1).[10] The calibration was established by linear regression with the literature log K_{oc} values of the reference substances as a function of log k.

$$k = (t_R - t_0)/t_R \quad \text{(S1)}$$

The retention times of the LOHCs under the same HPLC settings were used to calculate their capacity factors, and these in turn were used to estimate the K_{oc} values from the calibration curve. The solutions of the reference substances and LOHC analytical samples were prepared in the mobile phase.

S4. Determination of K_d and adsorption isotherm

An optimum soil/liquid ratio of 1:10 and equilibration time of 6 days were determined from preliminary experiments. The adsorption isotherms were investigated for five concentrations. One gram dry weight (dw) of soil was equilibrated in 9 mL 0.01 M $CaCl_2$ (in 40-mL glass vials with polytetrafluoroethylene (PTFE)-lined screw caps) by agitation on a horizontal shaker (240 rpm, compact flat orbital shaker, IKA® HS 260 control, IKA®-Werke GmbH and Co. KG, Staufen, Germany) at room temperature for 24 h. A 1-mL aliquot of the quinaldine stock solution (in 0.01 M $CaCl_2$) was added to obtain a soil/liquid ratio of 1:10, and the mixture was shaken for 6 days. The liquid phase was then transferred to a 15-mL centrifuge tube (VWR, Germany) and centrifuged at 3,000 g for 15 min at 20 °C (Labofuge 400R, Thermo Scientific Heraeus, Schnackenberg, Germany). Any soil residues in the supernatant were further removed by filtration through a Pasteur pipette packed with glass wool (2.5 cm). One quality control containing only the test substance in 10 mL of 0.01 M $CaCl_2$ and no soil was prepared for each concentration to account for possible losses (e.g., sorption on the test vessels). One blank run (1 g dw of soil and 10 mL of 0.01 M $CaCl_2$ solution without a test substance) was prepared in parallel for each test.

S5. Leaching in soil columns

Columns made of carbon steel (3.8 cm inner diameter and 35 cm in length) were sealed at both ends with polyvinylchloride caps (each approx. 1.15 cm long). A steel capillary was inserted through each cap to provide an inlet and an outlet. Air-dried soil was uniformly packed in the columns in small portions with a spoon and pressed with a plunger to obtain uniform packing, to a height of approximately 28 cm (until the top of the soil was levelled) followed by a pre-wetting procedure from bottom to top with 0.01 M $CaCl_2$ and then allowed to drain. Quinaldine was then spiked into the top of the soil columns using a small amount of soil as a vector as follows. The quinaldine was first dissolved in 10 mL of acetone and then spiked into 20 g (dw) of soil. The acetone was allowed to evaporate over 24 h, after which atrazine, which served as the reference compound, was added to the spiked soil and thoroughly mixed. The soil matrix was then added carefully and evenly to the top of the soil column and covered with a round piece of filter paper.

The K_d values of the quinaldines from the column leaching tests were calculated using the relationship $K_d = [(R_f - 1) \times n]/\rho_b$.[11] The R_f (retardation factor) is the ratio of V_p (assumed to be the pore water velocity) to V_c (the contaminant velocity). The parameters n and ρ_b indicate the total porosity and bulk density, respectively, of soil II and were calculated for each test column. To obtain V_p, the PV (in mL) of the packed soil in each column was first calculated by subtracting the volume of the soil particles (calculated from the particle density and soil weight) from the total volume of soil that was packed into the column. The time that the artificial rain passed the pores in the soil column (t_0) was thus calculated as PV/0.108 (0.108 mL min^{-1} was the flow rate). V_p (cm h^{-1}) was presumed to be the velocity of the artificial rain passing through the column and thus was the quotient of the height of soil packed in each column (L_s, cm) divided by t_0. V_c was the division of L_s by the time in which the first portion of each quinaldine was collected and detected (t_q).

S6. Liquid-liquid extraction

A 10-mL aliquot of the quinaldine samples was subjected to extraction. Quinoline, which served as a surrogate standard, was prepared in water, and a 10 µL aliquot of this solution was spiked into the aqueous sample to give a final concentration of 1.0 mg L^{-1}. Then, 2 mL of dichloromethane was added, and the sample was vortexed for 45 s. The organic phase was subsequently transferred to a new vial, and approximately 0.3 g of anhydrous sodium sulfate (Na_2SO_4) was added to remove the remaining water. A 1-mL portion of the extract was transferred to a GC vial, and 10 µL of naphthalene in dichloromethane (internal standard, 2.0 g L^{-1}) was spiked into the final sample. The concentrations were measured by GC/MS.

S7. GC/MS analysis

The samples (2 µL) were injected in pressure-pulsed splitless mode with the aid of an autosampler. The capillary column (CS, FS-Supreme-5ms column, 0.25 mm ID × 30 m, 0.25 µm film thickness) was operated at a pressure of 2.01 atm with a flow rate of 3.0 mL min^{-1} using helium as the carrier gas. The GC method parameters were as follows: inlet temperature: 250 °C; oven program: 100 °C, hold 0.6 min, ramp to 150 °C at 20 °C min^{-1}, ramp to 300 °C at 35 °C min^{-1}, hold 1 min. The MS source and the temperature of the quadrupole were set to 230 °C and 150 °C, respectively. The MS detector was operated in positive ion mode using an electron ionisation energy of 70 eV. Spectra were recorded in full scan mode with a scan rate of 3.0 scans s^{-1}. The results were evaluated with Chemstation software (Agilent Technologies, Waldbronn, Germany). The concentrations of each component in the extract were determined using the peak area normalised by the internal standard (naphthalene) and an eleven-point calibration series (containing naphthalene, quinoline, atrazine, Quin-2Me, Quin-2Me-ph and Quin-2Me-H10, with the latter five at concentrations ranging from 0.5 to 100 mg L^{-1} in dichloromethane).

Table S3. Log K_{oc} values (n = 3, ± SD) determined by HPLC screening for the components in each mixture.

LOHC	**Car-2-ph**		**Car-3-ph**		**Car-4-ph**		**MLH**	
Log K_{oc}	4.27 ± 0.01	4.35 ± 0.01	4.59 ± 0.01	4.67 ± 0.01	4.96 ± 0.01	5.06 ± 0.01	3.78 ± 0.01	3.85 ± 0.01
LOHC	**MLH**	**MLH-ph**						**MSH**
Log K_{oc}	3.92 ± 0.01	5.10 ± 0.03	5.28 ± 0.03	5.34 ± 0.03	5.43 ± 0.03	5.53 ± 0.03	5.76 ± 0.03	5.11 ± 0.03
LOHC	**MSH**							
Log K_{oc}	5.20 ± 0.03	5.28 ± 0.03	5.35 ± 0.03	5.44 ± 0.03	5.54 ± 0.03	5.76 ± 0.04		

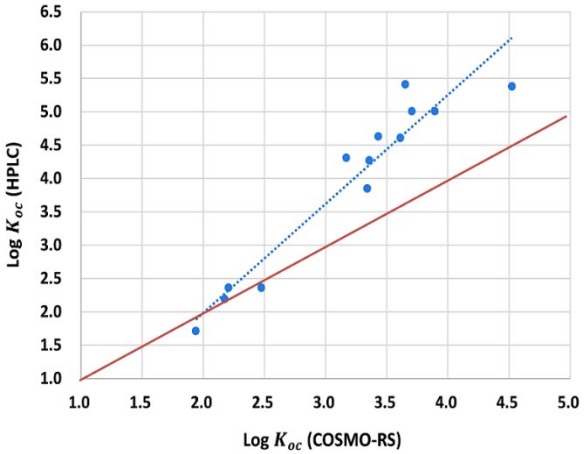


Figure S1. Relationship (R^2 = 0.92) between log K_{oc} (n = 13, HPLC) and COSMO-RS-predicted log K_{oc}. A one-to-one line (red solid) is added indicating ideal agreement between both parameters.

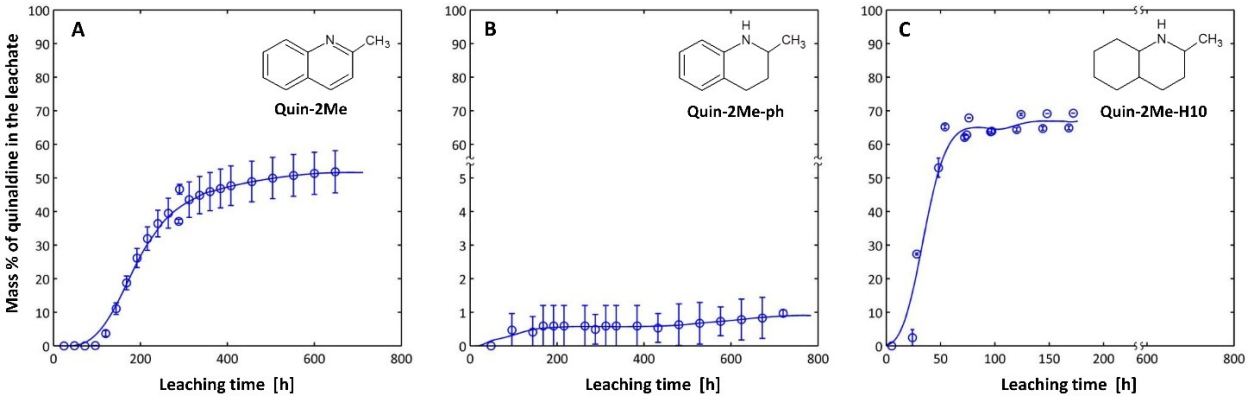


Figure S2. Breakthrough curves (mass% in the leachate, n = 4, ± SD) of Quin-2Me (**A**), Quin-2Me-ph (**B**) and Quin-2Me-H10 (**C**) in soil columns (soil II) over 648, 720, and 172 h, respectively.

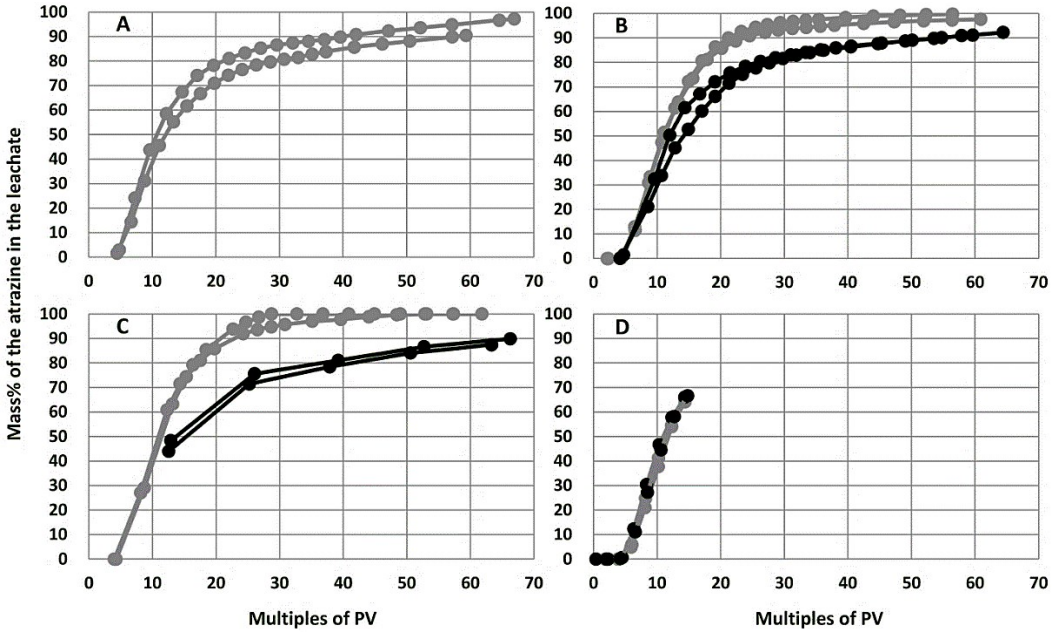


Figure S3. Breakthrough curves (mass% in the leachate) for the column leaching of pure atrazine independently in two columns (**A**) or together with Quin-2Me (**B**), Quin-2Me-ph (**C**) and Quin-2Me-H10 (**D**) in two independent experiments (grey and black), each with two columns of soil II. PV: pore volume.

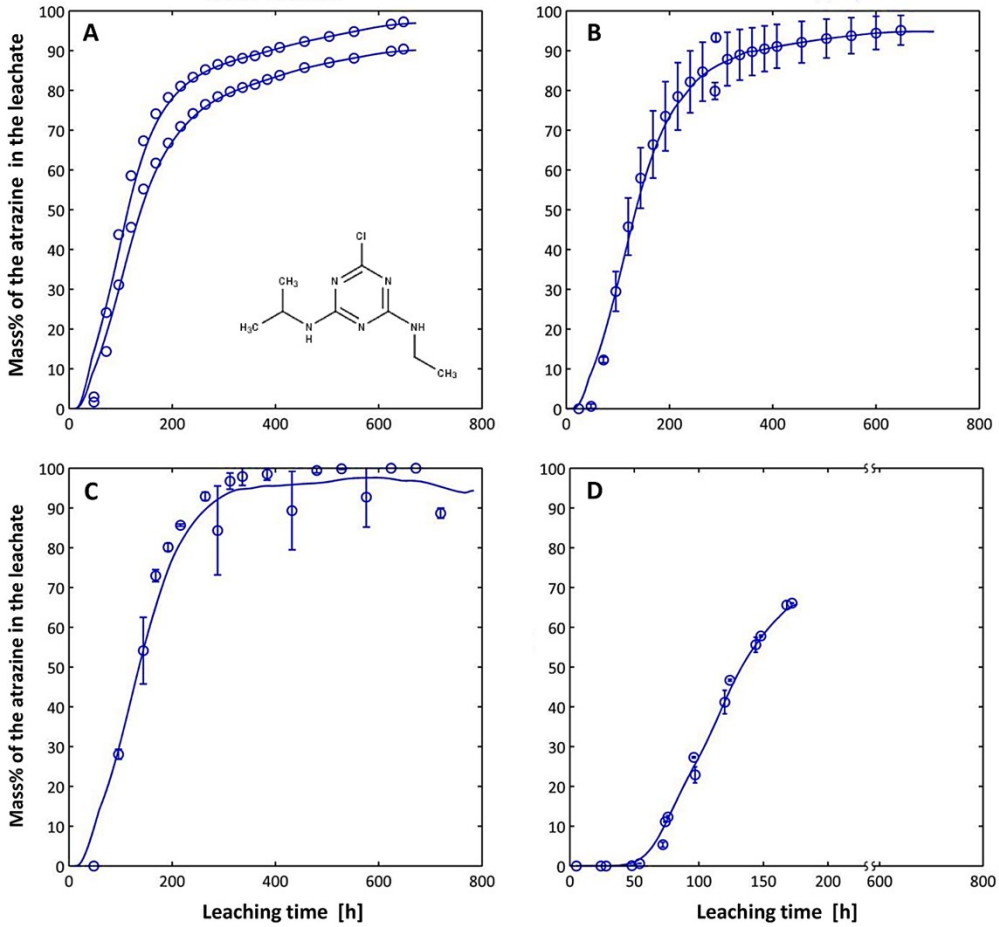


Figure S4. Breakthrough curves (mass% in the leachate) of pure atrazine alone (**A**) or in the presence of Quin-2Me (**B**), Quin-2Me-ph (**C**) and Quin-2Me-H10 (**D**) (n = 4, ± SD) in soil columns (soil II) over 648, 648, 720, and 172 h, respectively.

Table S4. K_d values of atrazine extrapolated from the column leaching test in soil II.

	Column-K_d [mL g^{-1}]	**Log $K_{oc,column}$**
Atrazine (with Quin-2Me)	0.46	1.76
Atrazine (with Quin-2Me-ph)	1.39	2.24
Atrazine (with Quin-2Me-H10)	0.82	2.01
Atrazine (pure)	0.61	1.88
Average	**0.82**	**2.01**

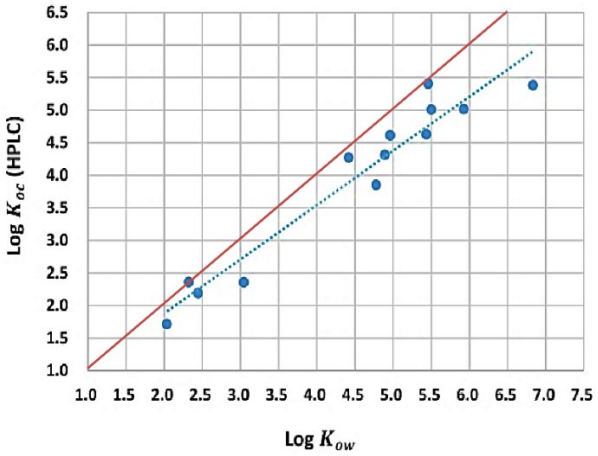


Figure S5. Relationship between HPLC-measured log K_{oc} and the COSMO-RS-predicted log K_{ow} values of the LOHC chemicals (dotted line, log K_{oc} = 0.8339 log K_{ow} + 0.2061, R^2 = 0.94). A one-to-one line indicating ideal agreement between both parameters is shown in addition (red solid).

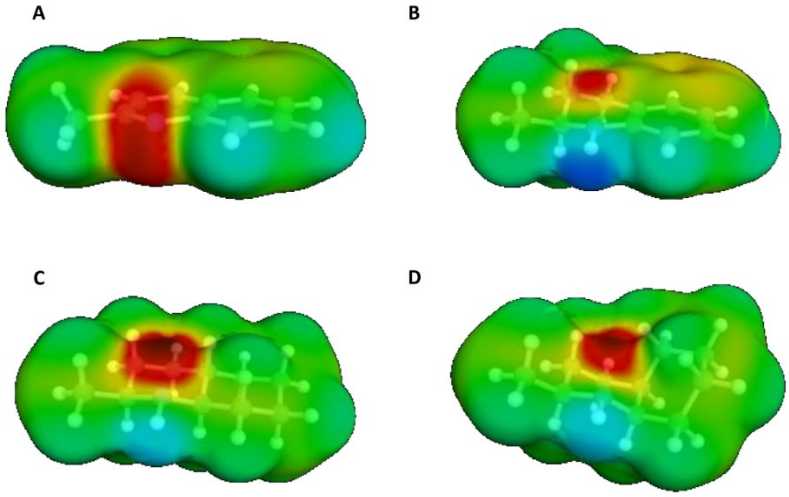


Figure S6. COSMO screening charge density (σ) on the surfaces of Quin-2Me (**A**), Quin-2Me-ph (**B**), *trans*-Quin-2Me-H10 (**C**), and *cis*-Quin-2Me-H10 (**D**).

Table S5. Acute EC_{50} values of alkylcarbazole derivatives as well as MLH- and MSH-based LOHC towards green algae, daphnids and fish predicted using EPA ECOSAR package[1] (Ecological Structure Activity Relationships). Whenever more than one value was predicted (e.g., by different group specific models) the lowest value was chosen. The particular EC_{50} values as well as compounds themselves are assigned to toxicity classes according to GHS (Globally Harmonised System).

Substance	EC_{50} (algae) mg/L	EC_{50} (daphnids) mg/L	EC_{50} (fish) mg/L
Indoline	37.7	49.5	86.8
Car-2	1.823	1.029	1.470
Car-2-ph (ethyl-octahydrocarbazole)	0.013	0.048	0.0019
Car-2-H12	0.376	0.635	4.502
Car-3	0.890*	0.418*	0.571*
Car-3-ph (propyl-octahydrocarbazole)	0.006	0.019	0.00074
Car-3-H12	0.181	0.341	2.287
Car-4	0.396	0.150	0.195
Car-4-ph (butyl-octahydrocarbazole)	0.003	0.008	0.00029
Car-4-H12	0.086	0.183	1.288
MLH	1.066	0.538	0.748
MLH-ph	0.142	0.044	0.054
MSH	0.063	0.015	0.017
Colour code	**Acute 1 (EC_{50} < 1mg/L)**	**Acute 2 (EC_{50} 1 – 10 mg/L)**	**Acute 3 (EC_{50} 10 – 100 mg/L)**

* The compound might not be soluble enough to cause that effect, no effects might be observed at the water solubility limit.

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