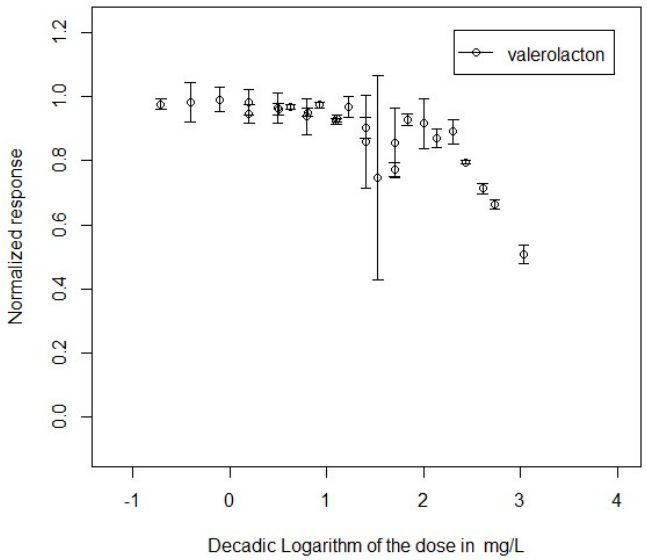
1. Ecotoxicity

Data used in creating (eco)toxicological profile of GVL are presented below in graphical (dose-response curves) and tabular form together with quality criteria.

1.1. Cytotoxicity in IPC-81 cell line

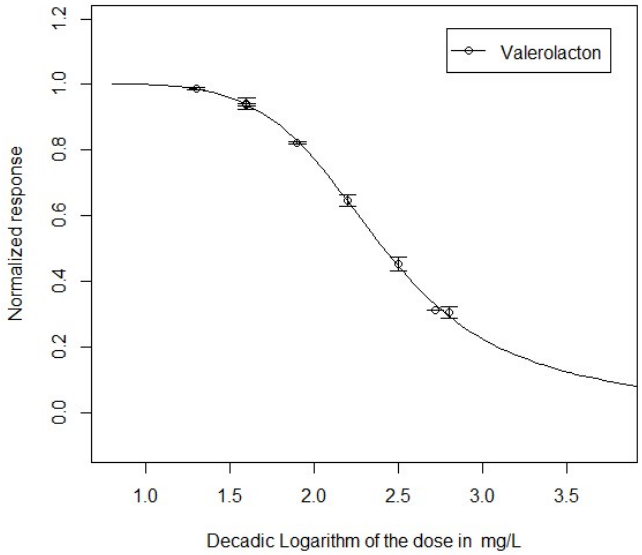


GVL				
dose [mg/L]	response	experiment number	standard deviation in controls	coefficient of variation [%]
50	0.7616	2588	0.02	2.4
25	0.9052	2588		
12.5	0.9297	2588		
6.25	0.9349	2588		
3.125	0.975	2588		
1.563	1.0112	2588		
0.781	1.0254	2588		
0.391	1.0099	2588		
0.195	0.9918	2588		
50	0.7603	2588		
25	0.9362	2588		
12.5	0.9272	2588		
6.25	0.9957	2588		
3.125	1.0035	2588		
1.563	0.9996	2588		
0.781	0.9957	2588		
0.391	1.0241	2588		
0.195	0.9763	2588		
50	0.7991	2588		
25	0.8703	2588		
12.5	0.9129	2588		
6.25	0.8819	2588		
3.125	0.9129	2588		

1.563	0.9362	2588		
0.781	0.9504	2588		
0.391	0.9116	2588		
0.195	0.9595	2588		
405	0.7174	2593	0.027	4.2
202.5	0.935	2593		
101.25	0.9762	2593		
50.625	0.9727	2593		
25.313	0.9727	2593		
12.656	0.9436	2593		
6.328	0.9625	2593		
3.164	0.9642	2593		
1.582	0.9762	2593		
405	0.7277	2593		
202.5	0.8682	2593		
101.25	0.9419	2593		
50.625	0.762	2593		
25.313	0.6969	2593		
12.656	0.9213	2593		
6.328	0.9539	2593		
3.164	0.9762	2593		
1.582	0.9419	2593		
405	0.6934	2593		
202.5	0.8682	2593		
101.25	0.8288	2593		
50.625	0.8322	2593		
25.313	0.9111	2593		
12.656	0.9316	2593		
6.328	0.9368	2593		
3.164	0.9402	2593		
1.582	0.9196	2593		
1081	0.5059	2636	0.02	3.9
540.5	0.6487	2636		
270.25	0.7914	2636		
135.125	0.882	2636		
67.563	0.9454	2636		
33.781	0.3791	2636		
16.891	0.9726	2636		
8.445	0.984	2636		
4.223	0.9613	2636		
1081	0.5377	2636		
540.5	0.6713	2636		
270.25	0.8005	2636		
135.125	0.8933	2636		
67.563	0.9273	2636		

33.781	0.9386	2636		
16.891	0.9953	2636		
8.445	0.9704	2636		
4.223	0.9749	2636		
1081	0.4788	2636		
540.5	0.6759	2636		
270.25	0.7914	2636		
135.125	0.8367	2636		
67.563	0.9092	2636		
33.781	0.9205	2636		
16.891	0.9318	2636		
8.445	0.9681	2636		
4.223	0.9636	2636		

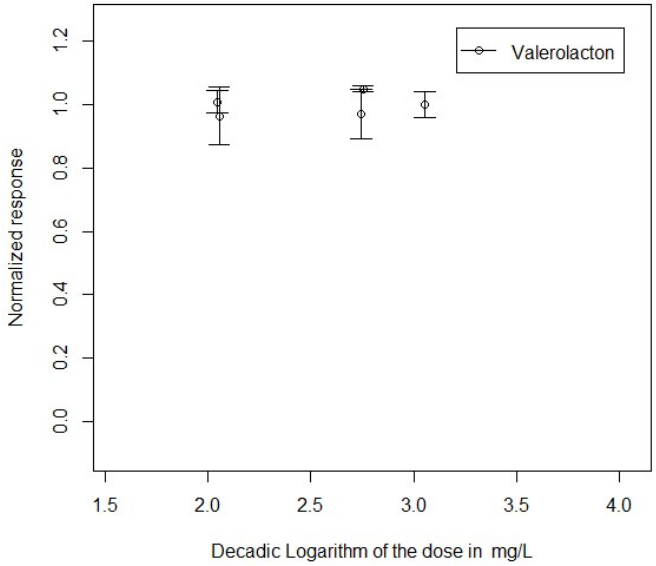
1.2. Luminescence inhibition test with *Aliivibrio fischeri*



dose [mg/L]	response	experiment number	standard deviation in controls	coefficient of variation [%]
525	0.3104	981	290	16.0
525	0.3127	981		
525	0.3127	981		
525	0.3127	981		
635	0.2902	997	76	3.6
635	0.2891	997		
317.5	0.4246	997		
317.5	0.4456	997		
158.75	0.629	997		
158.75	0.6306	997		
79.38	0.82	997		
79.38	0.8256	997		
39.69	0.937	997		

39.69	0.9416	997		
635	0.3183	1025	91	4.6
635	0.3203	1025		
317.5	0.467	1025		
317.5	0.4687	1025		
158.75	0.6544	1025		
158.75	0.6644	1025		
39.688	0.9544	1025		
39.688	0.9296	1025		
19.84	0.9886	1025		
19.84	0.9837	1025		

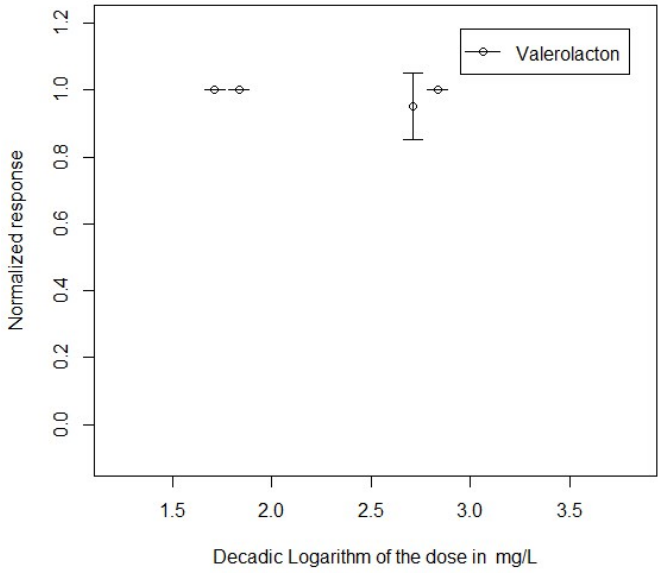
1.3. Growth inhibition test with *Lemna minor*



dose [mg/L]	response	experiment number	standard deviation in controls	coefficient of variation [%]
556	0.9585	1091	5.4	13
111.2	0.9663	1091		
556	0.8987	1091		
111.2	1.0271	1091		
556	1.0514	1091		
111.2	1.0298	1091		
1135	1.0448	1106	4.9	13
567.5	1.0421	1106		
113.5	0.8745	1106		
1135	0.994	1106		
567.5	1.06	1106		
113.5	0.9598	1106		
1135	0.9614	1106		
567.5	1.0452	1106		

113.5	1.0575	1106		

1.4. Acute immobilisation test with *Daphnia magna*



dose [mg/L]	response	experiment number	immobilisation in controls
514	0.8	1263	4%
514	1	1263	
514	1	1263	
514	1	1263	
51.4	1	1263	
51.4	1	1263	
51.4	1	1263	
51.4	1	1263	
683	1	1277	0%
683	1	1277	
683	1	1277	
683	1	1277	
68.3	1	1277	
68.3	1	1277	
68.3	1	1277	
68.3	1	1277	

2. Determination of the HSP of GVL

As stated in the manuscript, the calculation of the HSP of GVL yields the following values:

Table 1. Calculated Hansen solubility parameters of GVL in $MPa^{1/2}$.

δ	δ_d	δ_p	δ_h
23.2	**16.7**	**14.0**	**8.0**

The total Hansen solubility parameter δ is calculated via the cohesive energy density, which can be derived from the enthalpy of vaporization and the molar volume of GVL (H_{vap} = 53.88 ± 0.19 KJ/mol, ρ = 1.0492 ± 0.0004 g/cm^3 at 25 °C)[1,2].

The dispersive contribution δ_d is calculated via the cohesive energy density of the homomorph. The homomorph of a molecule represents the corresponding compound only consisting of carbon and hydrogen atoms. As such a molecule is non-polar, the value of δ_p and δ_h can be assumed to be equal to zero. Thus, the total HSP δ has the same value as δ_d and the latter can be calculated analogously via the cohesive energy density.

The principle is simple, but the choice of the correct homomorph for non-linear molecules is not always evident. In the original publication about the homomorph method by Blanks and Prausnitz, they define the homomorph of non-linear polar molecules as the “non-polar molecule most closely resembling the polar molecule in shape and molar volume when compared at the same reduced temperature”.[3] However, the molecule with the same shape often does not exhibit a very similar molar volume.

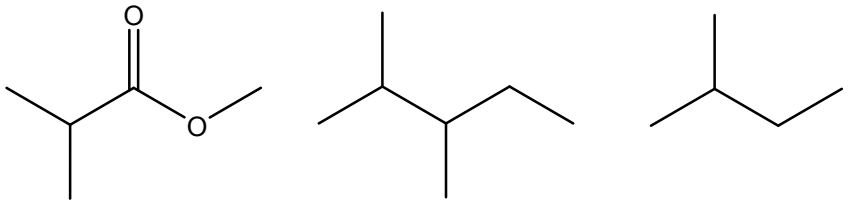


Figure 1. Structure formulae of methyl isobutyrate (a), its corresponding hydrocarbon 2,3-dimethylpentane (b) and its homomorph 2-methylbutane (c).

For example, the homomorph of methyl isobutyrate is 2-methylbutane, according to Blanks and Prausnitz, although the corresponding hydrocarbon with the same shape is 2,3-dimethylpentane (cf. Fig. 1). This circumstance gets evident after taking a look at the molar volumes of the respective molecules.

Table 2. Molar volumes of the compounds shown in Fig. 1. The required data were taken from www.nist.gov.

compound	*v* [ml/mol]
methyl isobutyrate	114.6
2-methylbutane	116.4
2,3-dimethylpentane	144.2

Hence, 2,3-dimethylpentane is the molecule with the same shape, but 2-methylbutane is the correct homomorph, as the molar volume is much closer to the one of methyl isobutyrate.

Accordingly, cyclopentane was chosen as the homomorph of GVL, as its molar volume is the closest to the one of GVL (cf. Table 3).

Table 3. Molar volumes of GVL and its possible homomorphs with 1,3-dimethylcyclopentane being the corresponding compound with the same shape as GVL. *The molar volume was calculated from literature data.[4,5]

compound	v [mL/mol]
GVL	95.42
cyclopentane	94.70*
methylcyclopentane	114.78
1,3-dimethylcyclopentane	128.18

The dispersive contribution δ_d of GVL is equal to 16.67 MPa$^{1/2}$ when taking cyclopentane as the homomorph (H_{vap} = 28.8 ± 0.6 KJ/mol at 298.15 K)[5].

As stated in the manuscript, the polar contribution δ_p was calculated via the Böttcher equation.

$$\delta_p = \frac{12108}{\nu^2}\frac{\varepsilon - 1}{2\varepsilon + n_D^2}\left(n_D^2 + 2\right)\mu^2 \quad \left[\frac{cal}{cm^3}\right] \qquad \textbf{(1)}$$

The required values for the refractive index (n_D = 1.4316 ± 0.0005), the dielectric constant (ε = 36.46) and the dipole moment (μ = 4.30 D) at T = 298.15 K were taken from literature and ultimately yield δ_p= 14.04 MPa$^{1/2}$.[1,6,7]

3. HSP values of GVL and common solvents

Table 4. Hansen solubility parameters (HSP) of the solvents shown in Fig. 2 of the manuscript. The respective contributions δ(d), δ(p) and δ(h) as well as the total HSP (Hildebrand parameter) are given in MPa$^{1/2}$, R_a represents the distance of the respective compound to GVL in Hansen space.

group	compound	*δ(d)*	*δ(p)*	*δ(h)*	*δ(H)*	R_a
lactones	GVL	*16.7*	*14.0*	*8.0*	*23.2*	*0.0*
water	water	*15.5*	*16*	*42.3*	*47.8*	*34.5*
alcohols	methanol	*15.1*	*12.3*	*22.3*	*29.6*	*14.8*
	ethanol	*15.8*	*8.8*	*19.4*	*26.5*	*12.7*
	isopropanol	*15.8*	*6.1*	*16.4*	*23.6*	*11.7*
	butanol	*16*	*5.7*	*15.8*	*23.2*	*11.5*
	tert-butanol	*15.2*	*5.1*	*14.7*	*21.8*	*11.6*
	benzyl alcohol	*18.4*	*6.3*	*13.7*	*23.8*	*10.2*
	ethylene glycol	*17*	*11*	*26*	*33.0*	*18.3*
ketones	acetone	*15.5*	*10.4*	*7*	*19.9*	*4.4*
	MEK	*16*	*9*	*5.1*	*19.1*	*6.0*
	MIBK	*15.3*	*6.1*	*4.1*	*17.0*	*9.2*
	cyclohexanone	*17.8*	*6.3*	*5.1*	*19.6*	*8.6*
esters	methyl acetate	*15.5*	*7.2*	*7.6*	*18.7*	*7.2*
	ethyl acetate	*15.8*	*5.3*	*7.2*	*18.2*	*8.9*
	n-butyl acetate	*15.8*	*3.7*	*6.3*	*17.4*	*10.6*
	isopropyl acetate	*14.9*	*4.5*	*8.2*	*17.6*	*10.2*
ethers	diethyl ether	*14.5*	*2.9*	*5.1*	*15.6*	*12.3*
	isopropyl ether	*13.7*	*3.9*	*2.3*	*14.4*	*13.0*
	MTBE	*14.8*	*4.3*	*5*	*16.2*	*10.8*

	THF	*16.8*	*5.7*	*8*	*19.5*	*8.3*
	1,4-dioxane	*19*	*1.8*	*7.4*	*20.5*	*13.1*
	anisole	*17.8*	*4.1*	*6.7*	*19.5*	*10.3*
alkanes	hexane	*14.9*	*0*	*0*	*14.9*	*16.5*
	toluene	*18*	*1.4*	*2*	*18.2*	*14.2*
	cyclohexane	*16.8*	*0*	*0.2*	*16.8*	*16.0*
	benzene	*18.4*	*0*	*2*	*18.5*	*15.6*
	xylene	*17.6*	*1*	*3.1*	*17.9*	*14.0*
halogenated	methylene chloride	*18.2*	*6.3*	*6.1*	*20.2*	*8.5*
	chlorobenzene	*19*	*4.3*	*2*	*19.6*	*12.3*
	chloroform	*17.8*	*3.1*	*5.7*	*18.9*	*11.4*
aprotic polar	acetonitrile	*15.3*	*18*	*6.1*	*24.4*	*5.2*
	N-methyl-2-pyrrolidone	*18*	*12.3*	*7.2*	*23.0*	*3.3*
	DMSO	*18.4*	*16.4*	*10.2*	*26.7*	*4.7*
	sulfolane	*20.3*	*18.2*	*10.9*	*29.4*	*8.9*
	DMPU	*17.4*	*10.2*	*8.5*	*21.9*	*4.1*
	DMAc	*16.8*	*11.5*	*10.2*	*22.8*	*3.4*
	DMF	*17.4*	*13.7*	*11.3*	*24.9*	*3.7*
	HMPA	*18.5*	*8.6*	*11.3*	*23.3*	*7.4*
	nitromethane	*15.8*	*18.8*	*5.1*	*25.1*	*5.8*
amines	pyridine	*19*	*8.8*	*5.9*	*21.8*	*7.3*
	triethanolamine	*17.3*	*22.4*	*23.2*	*36.6*	*17.4*
Acids	formic acid	*14.3*	*11.9*	*16.6*	*24.9*	*10.1*
	acetic acid	*14.5*	*8*	*13.5*	*21.4*	*9.3*
miscellaneous	methoxy-ethanol	*16.2*	*9.2*	*16.4*	*24.8*	*9.8*
	carbon disulfide	*20.5*	*0*	*0.6*	*20.5*	*17.6*

The HSP values were taken from Hansen's book[8], aside from the HSP of DMPU, which were found in a different publication and calculated via the HSPiP software.[9] The distance R_a of two solvents in Hansen space was calculated according to the equation:

$$R_a = \sqrt{4\left(\delta(d)_1 - \delta(d)_2\right)^2 + \left(\delta(p)_1 - \delta(p)_2\right)^2 + \left(\delta(h)_1 - \delta(h)_2\right)^2} \qquad \textbf{(2)}$$

Hence, the distance R_a of two solvents in Hansen space can be calculated from the difference in dispersive, polar and hydrogen bonding HSP of solvent 1 and 2 and is a measure of how alike two molecules are.[8]

Literature

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