Electronic Supplementary Material (ESI) for Environmental Science: Nano.

Supplementary information

Colloidal silica nanomaterials reduce the toxicity of pesticides to algae, depending on charge and surface area

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	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**
A												Medium
B		K1	C1	K2	C2	K3	C3	K4	C4	K5	C5	
C		K1	C1	K2	C2	K3	C3	K4	C4	K5	C5	
D		K1	C1	K2	C2	K3	C3	K4	C4	K5	C5	
E		K6	C6	K7	C7	K8	C8	K9	C9	K10	C10	
F		K6	C6	K7	C7	K8	C8	K9	C9	K10	C10	
G		K6	C6	K7	C7	K8	C8	K9	C9	K10	C10	
H												

Figure S1. Plate design for single exposures. Concentrations are labelled C1-C10 (yellow background) and negative controls are labelled K1-K10 (green background).

	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**
A												Medium
B		K1	C1+ECX	K2	C2+ECX	K3	C3+ECX	K4	C1	K5	C2	
C		K1	C1+ECX	K2	C2+ECX	K3	C3+ECX	K4	C1	K5	C2	
D		K1	C1+ECX	K2	C2+ECX	K3	C3+ECX	K4	C1	K5	C2	
E		K6	C1+ECX	K7	C2+ECX	K8	C3+ECX	K9	C3	K10	ECX	
F		K6	C1+ECX	K7	C2+ECX	K8	C3+ECX	K9	C3	K10	ECX	
G		K6	C1+ECX	K7	C2+ECX	K8	C3+ECX	K9	C3	K10	ECX	
H												

Figure S2. Plate design for mixture exposures. Mixture concentrations are labelled C1-3+ECx, positive controls are labeled ECx, nanomaterial controls are labelled C1-C3 and negative controls are labelled K1-K10. All wells containing a treatment are marked yellow while negative controls are marked with green colour.

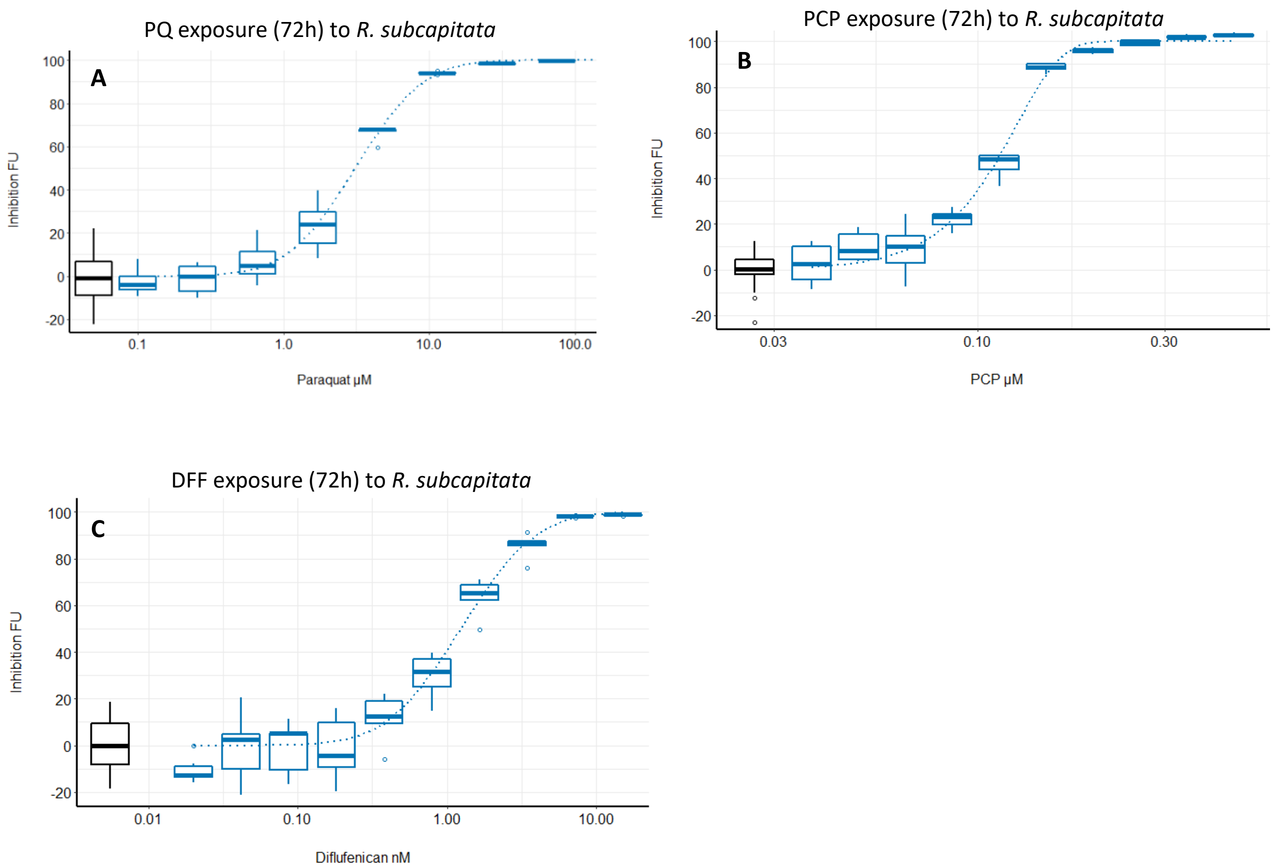

Figure S3: Concentration-response curve for R. subcapitata after 72h exposure to PQ (A), PCP (B) and DFF (C). The boxes show the inhibition (median, lower/upper quartile, and lower/upper extreme) at the tested concentration and the dotted line shows the fitted curve calculated from a two-parametric concentration-response model. The box shown in black colour (first box from the left) represents the unexposed control.

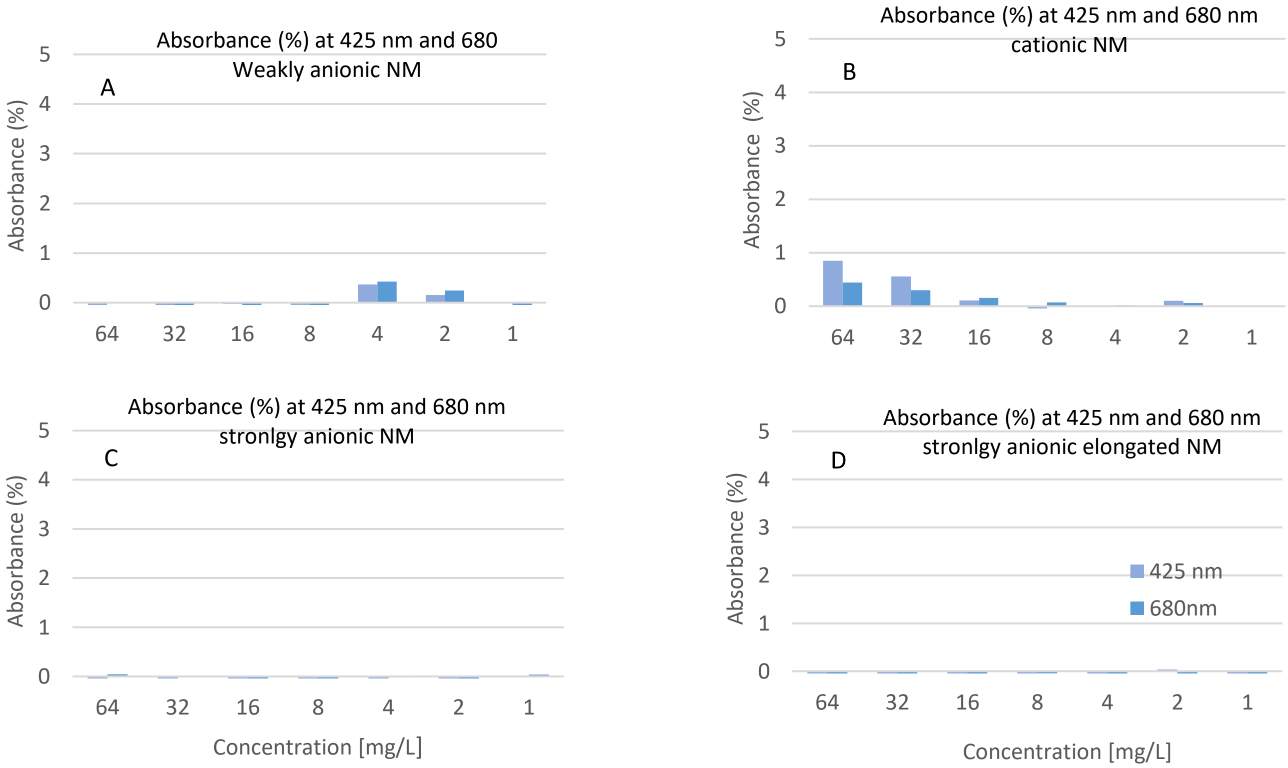

Figure S4: Absorbed light (%) at excitation/emission wavelengths 425/680 for the different silica nanoparticles, weakly anionic (A), cationic (B), strongly anionic (C) and anionic strongly elongated (D).

Table S1. Size and ZP of silica nanomaterials individually and in mixture with PQ, PCP and DFF in MBL medium at the start and end (t0-t72h). Nanomaterial size was derived from the particle size distributions from the DLS measurements. The size corresponds to the nanomaterial population with the largest volume in percent (% volume), i.e. the largest peak (peak 1) in the size distribution by volume. Samples not measurable, i.e. the DLS could not detect any nanomaterial (due to sedimentation) are presented with N.M.

			Start 0h				End 72h			
Nanomaterial	T [°C]	Concentration (mg/L)	Peak 1, 2 size (d.nm) ± SD	% volume	ZP Peak 1 ,2 [mV]	ZP Peak 1, 2 (% volume)	Peak 1, 2 size (d.nm) ± SD	% volume	Zeta Potential [mV]	ZP Peak 1, 2 (% volume)
Cationic	22	5000 in MQW	47 ± 22	100	42 ± 12	100				
	22	500	2043 ± 30, 4633 ± 819	74, 25	2 ± 3	100	1784 ± 542, 4568 ± 922	68, 32	8 ± 3	100
	22	150	2198 ± 356	100	4 ± 3	100	4952 ± 789	98	-3 ± 3	100
	22	50	2395 ± 583	97	-1 ± 3	100	693 ± 119, 24 ± 4, 1 ± 0	100	-3 ± 3	100
	22	20	1612 ± 345	100	-2 ± 5	100	5335 ± 661, 686 ± 163	69, 31	-8 ± 3	100
	22	10	1514 ± 308	100	-1 ± 3	99	1983 ± 353, 5407 ± 649	68, 32	-8 ± 3	100
Strongly anionic	22	5000 in MQW	19 ± 5	100	-36 ± 5	94				
	22	500	20 ± 7	100	-23 ± 5	100	20 ± 7	96	-27 ± 8	100
	22	150	21 ± 7	100	-12 ± 5	100	20 ± 7	100	-26 ± 6	100
	22	50	21 ± 7	100	-4 ± 5, -37 ± 6	58, 34	21 ± 7	100	-11 ± 4	100
	22	20	27 ± 11	99	-16 ± 4, 90 ± 2	92, 8	28 ± 9	99	-27 ± 5, 72 ± 2	85, 15
	22	10	19 ± 8	100	-23 ± 5, 90 ± 2	81, 19	24 ± 9	99	-14 ± 4	96
Strongly anionic elongated	22	5000 in MQW	38 ± 35	100	-49 ± 5	100				
	22	150	29 ± 23	100	45 ± 2, -71 ± 48	52, 48	24 ± 20	100	-39 ± 7, 76 ± 2	76, 23
	22	50	37 ± 33	71, 29	-31 ± 6, 84 ± 2	54, 25	34 ± 38	99	-31 ± 10, 86 ± 2	76, 21
	22	20	40 ± 40	98	N.A	N.A	41 ± 50	100	-53 ± 6, 57 ± 2	51, 49
	22	10	36 ± 49	100	-35 ± 11, 78 ± 3	36, 14	40 ± 48	99	41 ± 2, -74 ± 4	63, 37
Weakly anionic	22	5000 in MQW	16 ± 6	100	-27 ± 9,-55 ± 8	64, 20				
	22	500	14 ± 6	100	-22 ± 6	93	15 ± 6	100	-33 ± 6	100
	22	150	20 ± 9	100	-16 ± 9	94	16 ± 5	100	-36 ± 4	99
	22	50	20 ± 9	99	-15 ± 3	99	17 ± 4	100	-40 ± 4, 7 ± 2	66, 34
	22	20	20 ± 8	100	-19 ± 4	100	17 ± 8	100	-25 ± 4, 82 ± 26	91, 9
	22	10	27 ± 9	100	-10 ± 6	95	24 ± 9	99	-13 ± 4	95
Mixture with PQ										
Cationic + PQ	22	50	1580 ± 279	100	-3 ± 3	100	N.M	N.M	N.M	N.M
	22	10	1670 ± 317	100	-3 ± 1	100	N.M	N.M	N.M	N.M
Strongly anionic + PQ	22	50	21 ± 8	100	-35 ± 3, 97 ± 2	75,24	22 ± 8	100	-14 ± 5, -2 ± 3	67,32
	22	20	21 ± 7	100	-20 ± 4, 100 ± 2	82, 18	19 ± 8	100	13 ± 2	100

	22	10	22 ± 9	99	3 ± 2	100	22 ± 7	100	3 ± 2	100
Strongly anionic elongated + PQ	22	20	32 ± 28	99	47 ± 2, -66 ± 5	54, 46	38 ± 47	98	29 ± 2	95.5
	22	10	56 ± 19	93	-1 ± 2	100	39 ± 24	96	-23 ± 5, -69 ± 2	52, 46
	22	0.4	803 ± 367, 51 ± 16	36, 36	-18 ± 13, 77 ± 3	73,12	53 ± 13, 324 ± 91	76,14	-26 ± 7, -8 ± 5	51,23
Weakly anionic + PQ	22	50	19 ± 7	99	-18± 7	94	25 ± 8	99	-31 ± 5, 65 ± 2	62, 38
	22	10	20 ± 9	100	15 ± 2, -80 ± 4	85, 13	16 ± 5	100	1 ± 2	100
Mixture with PCP										
Cationic + PCP 6mg/L (x100 stock)	22	5000	46 ± 22	100	40 ± 10	100	50 ± 23	100	28 ± 5	100
	22	1000	47 ± 24	100	30 ± 11	99	49 ± 21	100	-13 ± 3	100
Cationic + PCP (from x100 stock)	22	50	1659 ± 412	98	-2 ± 3	100	N.M	N.M	N.M	N.M
	22	10	1551 ± 379	100	2 ± 5	100	N.M	N.M	-5 ± 3	100
Cationic + PCP	22	50	2113 ± 590, 5093 ± 713	90, 10	-3 ± 3	100	N.M	N.M	N.M	N.M
	22	10	1475 ± 601, 4037 ± 989	64, 36	-5 ± 3	100	N.M	N.M	N.M	N.M
Strongly anionic + PCP	22	50	21 ± 10	100	69 ± 2,-36 ± 3	52, 48	21 ± 7	100	-10 ± 9	100
	22	10	26 ± 12	99	-22 ± 7, 86 ± 2	69, 21	32 ± 13	97	-13 ± 8, 90 ± 2	79, 21
Weakly anionic + PCP	22	50	18 ± 7	100	-25 ± 9, -85 ± 8	40, 6	22 ± 8	100	-17 ± 5	99
	22	10	20 ± 8	100	-16 ± 7, 90 ± 2	78, 21	24 ± 9	100	-7 ± 4	99
Mixture with DFF										
Cationic + DFF	22	50	1503 ± 222	100	-3 ± 3	100	240 ± 31	100	-7 ± 6	95
	22	10	1694 ± 382	100	-3 ± 3	100	N.M	N.M	-19 ± 5, 68 ± 2	77, 23
Strongly anionic + DFF	22	50	21 ± 6	100	-14 ± 6	97	28 ± 9	98	-11 ± 4	100
	22	10	28 ± 9	98	46 ± 2, -62 ± 2	54, 46	28 ± 9	98	-26 ± 4, 91 ± 2	80, 21
Weakly anionic + DFF	22	50	16 ± 5	100	-25 ± 11, 1 ± 5	53, 27	17 ± 7	100	-6 ± 6	99
	22	10	17 ± 5	100	-29 ± 6, 83 ± 2	68, 31	18 ± 6	100	49 ± 2, -60 ± 6	54, 46

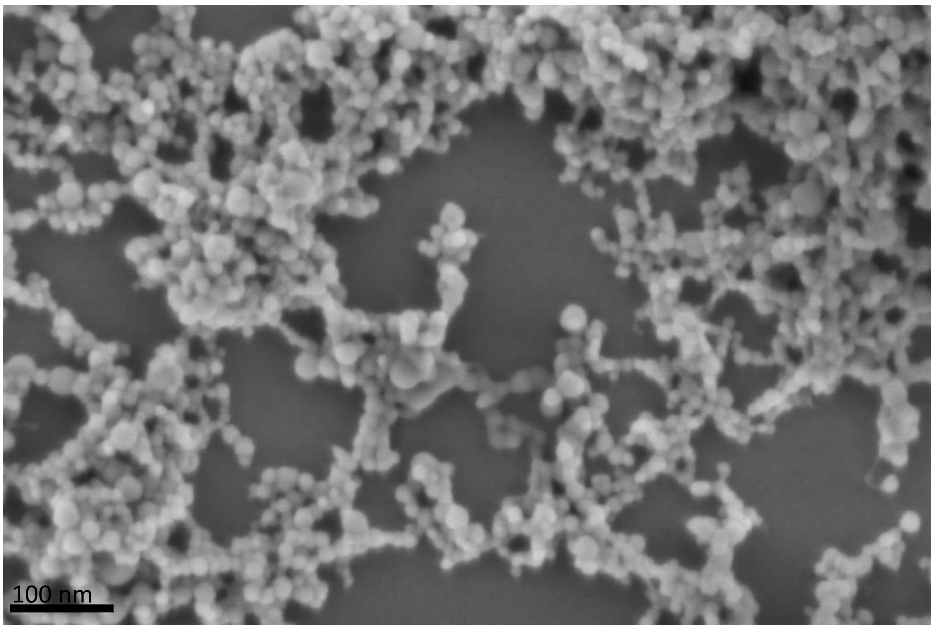

Figure S5. SEM image of the cationic silica nanomaterial.

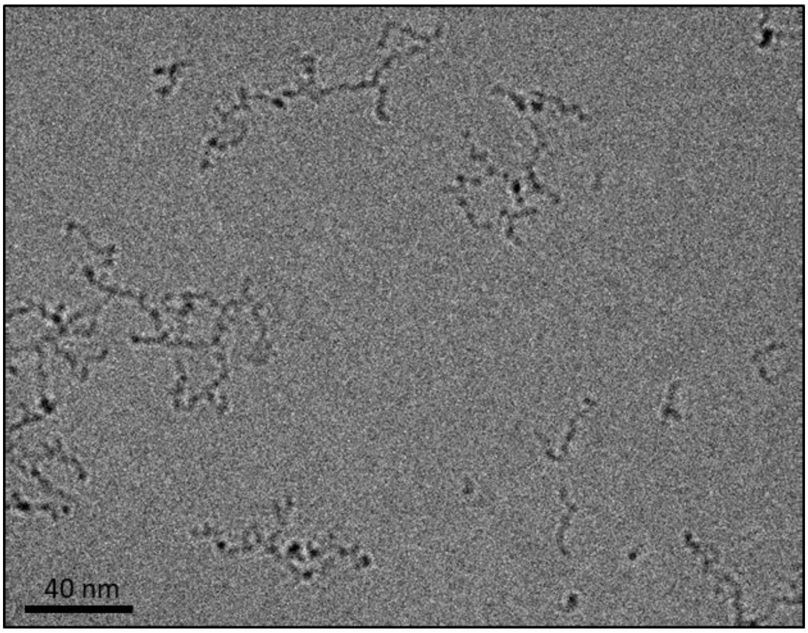

Figure S6. SEM image of elongated silica nanomaterial

Table S2. Pesticide concentration after ultracentrifugation expressed in µM. The values are presented as the average of three replicates with the standard deviation in brackets.

Pesticide concentration (µM) after ultracentrifugation (%)

		Weakly anionic		**Cationic**		**Strongly anionic**		**Strongly anionic elongated**		
Pesticide	**Only pesticide**	10 mg/L	50 mg/L	10 mg/L	50 mg/L	10 mg/L	50 mg/L	0.4 mg/L	16 mg/L	50 mg/L

PQ	6.4 (± 0.4) 6.3 (± 0.4)[b]	5.3 (± 0.5)	2.2 (± 0.2)	2.5 (± 0.5)	0.65 (± 0.10)	0.03 (± 0.01)	0.03 (± 0.01)	0.44 (±0.22)	0.00 (± 0.00)	0.00 (± 0.00)
PCP	0.22 (± 0.00) 0.22 (± 0.00)[b]	0.22 (± 0.83)	0.22 (± 0.83)	0.22 (± 0.8) 0.22 (± 0.82)[a]	0.17 (± 0.66) 0.22 (± 0.81)[a]	0.23 (± 0.86)	0.23 (± 0.88)			
DFF	0.0020 (± 0.0001) 0.0020 (± 0.0001)[b]	0.0021 (± 0.00)	0.0024 (± 0.0000)	0.0018 (± 0.0000)	0.0019 (± 0.0002)	0.0018 (± 0.0001)	0.0017 (± 0.0000)			

[a]No pre-mixture
[b]Pesticide-recovery control