1 2	Investigations into titanium dioxide nanoparticle and pesticide interactions in aqueous environments
3	Supporting information
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33	suspension in NaCl and $CaCl_2$ solutions of variable IS at pH5 and 8, after 24h, in the
34	absence (NP) and in the presence of AMPA (5 μ g/L) or glyphosate (5 μ g/L). The
35	hydrodynamic diameter of anatase NP (14 nm) is also indicated (red dashed line), the error

- 36 bars correspond to standard deviations of 3 measurements.
- Fig. S7. Average hydrodynamic diameter (size; left) and zeta potential (right) of rutile NP
 suspension in NaCl and CaCl₂ solutions of variable IS at pH5 and 8, after 24h, in the
 absence (NP) and in the presence of AMPA (5µg/L) or glyphosate (5µg/L). The
 hydrodynamic diameter of rutile NP (54 nm) is also indicated (red dashed line), the error
 bars correspond to standard deviations of 3 measurements.
- 42 **Fig. S8.** Average hydrodynamic diameter (size; left) and zeta potential (right) of anatase NP 43 suspension in NaCl and CaCl₂ solutions of variable IS at pH5 and 8, at t₀ (A) and after 24h
- 44 (B), in the absence (NP) and in the presence of 2,4-D ($5\mu g/L$). The hydrodynamic diameter
- 45 of anatase NP (14 nm) is also indicated (red dashed line), the error bars correspond to 46 standard deviations of 3 measurements.
- 47 Fig. S9. Average hydrodynamic diameter (size; left) and zeta potential (right) of rutile NP
 48 suspension in NaCl and CaCl₂ solutions of variable IS at pH5 and 8, at t₀ (A) and after 24h
- 49 (B), in the absence (NP) and in the presence of 2,4-D ($5\mu g/L$). The hydrodynamic diameter
- 50 of rutile NP (54 nm) is also indicated (red dashed line), the error bars correspond to standard 51 deviations of 3 measurements.

53 pH_{IEP} determination

The NPs were injected into the respective aqueous solution, the size and the surface charge were instantly determined by DLS, and the final solution pH was measured just after completion. In this way, pH_{IEP} determination of each sample was independent of those in preceding measurements.

58 Critical coagulation concentration (CCC)

The critical coagulation concentrations (CCC) of anatase and rutile NP suspensions were measured in the presence of NaCl and $CaCl_2$ (Fig. 1-2). In good agreement with theoretical prediction and previous observations from the literature¹⁻³, the CCC values for anatase and rutile NP suspensions were strongly dependent on the NP surface charge, i.e., on the pH.

At pH 5 (<pH_{IEP}), the CCC of the anatase NP suspension (5mg/L) in the presence of NaCl (CCC_{NaCl}) and CaCl₂ (CCC_{CaCl2}) was 10⁻²M and 1.7x10⁻³M, respectively (Fig. 1). That is consistent with Loosli et al.,⁴ who indicated a value of 4x10⁻²M for CCC_{NaCl} of anatase at pH 4.5. The fact that CCC_{CaCl2} < CCC_{NaCl} is also in good agreement with previous studies.^{1, 3-7} Note that under these solution conditions, Cl⁻ plays the role of the counterion.

However, at pH 8 (>pH_{IEP}), Na⁺ and Ca²⁺ play the role of the counterion. The CCC_{NaCl} and 68 CCC_{CaCl2} were <5x10⁻³M and <1.7x10⁻³M, respectively, for the anatase NPs (Fig. 1). Because of the 69 use of the buffer (NaHCO₃ 1mM), it was not possible to work with IS $< 5x10^{-3}$ M, and thereby to 70 accurately measure the low CCC values. Here, the lowest IS studied was higher than the CCC. A 71 rapid aggregation of anatase NPs was observed in all studied solutions. This is in good agreement 72 with DLVO theory and the decrease in the electrostatic NP-NP repulsive forces.⁸⁻¹⁰ For rutile NP 73 suspensions, the CCC_{NaCl} and CCC_{CaCl2} at pH8 (>pH_{PZC}) were 5.10⁻²M and <1.7x10⁻³M, 74 75 respectively (Fig. S5). These values do not contradict the Schulze-Hardy rule that says that the $CCC_{NaCl}/CCC_{CaCl2} = 1/2^6 = 1/64$.^{11-14,} Indeed, following this relation, the CCC_{CaCl2} value for rutile 76 NPs should be 7.8×10^{-4} M (i.e $< 1.7 \times 10^{-3}$ M as found above). 77

78 At pH 5 (near pH_{IEP} of 4.0-4.2), the CCC_{NaCl} and CCC_{CaCl2} for the rutile NPs (5 mg/L) were low:

 79 <10⁻⁴M and <3.3x10⁻⁵M, respectively (Fig. S5). The CCC_{NaCl} at pH 5 was much lower than at pH 8 80 (5x10⁻²M) confirming that pH conditions closer to the pH_{IEP} result in lower CCC values.¹¹ Any 81 slight modifications of the solution physical-chemistry when pH is close to pH_{IEP} may therefore 82 strongly affect NP homoaggregation.

83

85 Table S1. Pesticide properties.

Product	Molar Mass, g/mol	Formula	IUPAC Name	рКа	solubility, mg/L	density, g/cm³	log K _{ow}	Max conc. in surface waters, µg/L
2,4-D	221.03	$C_8H_6Cl_2O_3$	2-(2,4- dichlorophenoxy)ac etic acid	2.73	677	1.42	2.81	700
AMPA	111.03	CH ₆ NO₃P	methylaminophosp honic acid	pKa1 = 1.8; pKa2 = 5.4; pKa3 = 10.0	>20000*			1-5
Glyphosate	169.07	C₃H ₈ NO₅P	2- (phosphonomethyla mino)acetic acid	pKa1 = 0.8; pKa2 = 2.3; pKa3 = 6.0; pKa4 = 11.0	12000	1.7	-3.4	42

pH 8, CaCl₂			
Ionic Strength, Mol	[Ca ²⁺], Mol	[Cl ⁻], Mol	Notes
1x10 ⁻⁴	3.33x10 ⁻⁵	6.67x10 ⁻⁵	*no NaHCO ₃
1x10 ⁻³	3.33x10 ⁻⁴	6.67x10 ⁻⁴	*no NaHCO₃
5x10 ⁻³	1.33x10 ⁻³	2.67x10 ⁻³	**with 10 ⁻³ M NaHCO ₃
1x10 ⁻²	3.33x10 ⁻³	6.67x10 ⁻³	** no 10⁻³M NaHCO₃
1.1x10 ⁻²	3.33x10 ⁻³	6.67x10 ⁻³	** with 10 ⁻³ M NaHCO ₃
1x10 ⁻¹	3.33x10 ⁻²	6.67x10 ⁻²	** no 10⁻³M NaHCO₃
1.01x10 ⁻¹	3.33x10 ⁻²	6.67x10 ⁻²	** with 10 ⁻³ M NaHCO ₃
pH 8, NaCl			
Ionic Strength, Mol	[Na⁺], Mol	[Cl ⁻], Mol	
1x10 ⁻⁴	1x10 ⁻⁴	1x10 ⁻⁴	*no NaHCO₃
1x10 ⁻³	1x10 ⁻³	1x10 ⁻³	*no NaHCO₃
5x10 ⁻³	5x10 ⁻³	4x10 ⁻³	**with 10 ⁻³ M NaHCO ₃
1x10 ⁻²	1x10 ⁻²	1x10 ⁻²	** no 10⁻³M NaHCO₃
1.1x10 ⁻²	1.1x10 ⁻²	1x10 ⁻²	** with 10 ⁻³ M NaHCO ₃
1x10 ⁻¹	1x10 ⁻¹	1x10 ⁻¹	** no 10⁻³M NaHCO₃
1.01x10 ⁻¹	1.01x10 ⁻¹	1x10 ⁻¹	** with 10 ⁻³ M NaHCO ₃
pH 5, CaCl₂			
Ionic Strength, Mol	[Ca ²⁺], Mol	[Cl ⁻], Mol	
1x10 ⁻⁴	3.33x10⁻⁵	6.67x10 ⁻⁵	
1x10 ⁻³	3.33x10 ⁻⁴	6.67x10 ⁻⁴	
1x10 ⁻²	3.33x10 ⁻³	6.67x10 ⁻³	
1x10 ⁻¹	3.33x10 ⁻²	6.67x10 ⁻²	
pH 5, NaCl			
Ionic Strength, Mol	[Na⁺], Mol	[Cl ⁻], Mol	
1x10 ⁻⁴	1x10 ⁻⁴	1x10 ⁻⁴	
1x10 ⁻³	1x10 ⁻³	1x10 ⁻³	
1x10 ⁻²	1x10 ⁻²	1x10 ⁻²	
1x10 ⁻¹	1x10 ⁻¹	1x10 ⁻¹	

Table S2. Corresponding Ionic Strength – electrolyte concentration in the modeled solutions.

- 89 Table S3. Results of Mann-Whitney test comparing rutile NP hydrodynamic diameter
- 90 measurements at pH5 in presence or absence of glyphosate.

	IS, Mol	p-values
NaCl	1x10 ⁻⁴	2.9x10 ⁻³
	1x10 ⁻³	2.2x10 ⁻³
	1x10 ⁻²	2.9x10 ⁻³
	1x10 ⁻¹	0.12
CaCl ₂	1x10 ⁻⁴	2.3x10 ⁻³
	1x10 ⁻³	4.0x10 ⁻³
	1x10 ⁻²	0.11
	1x10 ⁻¹	7.3 x10 ⁻³

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93 Table S4. Molal ratio between surface site and pesticide.

Ratio area NP/pesticide for [NP]=5mg/L and [pesticide]=0.5µg/L, [NP]/[pesticides]= 10000 (in mg/L)

Ratio	NP/Glyphosate	NP/AMPA	NP/2,4-D
Anatase	7018.8	4609.3	9175.9
Rutile	350.9	230.5	458.8

Ratio area NP/pesticide for [NP]=5mg/L and [pesticide]=5µg/L, [NP]/[pesticides]= 1000 (in mg/L)

Ratio	NP/Glyphosate	NP/AMPA	NP/2,4-D
Anatase	701.9	460.9	917.6
Rutile	35.1	23.0	45.9

Ratio area NP/pesticide for [NP]=5mg/L and [pesticide]=50µg/L, [NP]/[pesticides]= 100 (in mg/L)

	U /		
Ratio	NP/Glyphosate	NP/AMPA	NP/2,4-D
Anatase	70.2	46.1	91.8
Rutile	3.5	2.3	4.6

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99 Figure S1. Schematic presentation of anatase (A) and rutile (R) NP surface charge, and glyphosate, AMPA and 2,4-D dominant forms at pH 5 and 8.



 IO1
 Record 1815: NPsR5mg/LpH5NaClis1e-4Glyphosate5µg/L 1
 Record 3188: NPsR5mg/LpH5NaClis1e-4 2

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 Figure S2. The size distribution of rutile NP aggregates at pH5, in NaCl, in the presence (red line)

 103
 and absence (green line) of glyphosate.



109 Figure S3. Zeta potential and hydrodynamic diameter (size) of anatase (left) and rutile (right) NPs as a function of pH (in 1mM NaCl solution).
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- 113 electrolyte concentrations (NaCl and CaCl₂) at pH 5 and 8. The error bars correspond to standard
- 114 deviations of 3 measurements.



- 117 Figure S5. Hydrodynamic diameter (size) of rutile NP suspension (5mg/L) as a function of
- 118 electrolyte concentrations (NaCl and CaCl₂) at pH 5 and 8. The error bars correspond to standard
- 119 deviations of 3 measurements.



124 125 Figure S6. Average hydrodynamic diameter (size; left) and zeta potential (right) of anatase NP suspension in NaCl and CaCl₂ solutions of variable IS at pH5 and 8, after 24h, in the absence (NP) 126 and in the presence of AMPA (5µg/L) or glyphosate (5µg/L). The hydrodynamic diameter of 127 128 anatase NP (14 nm) is also indicated (red dashed line), the error bars correspond to standard 129 deviations of 3 measurements.



131 132 Figure S7. Average hydrodynamic diameter (size; left) and zeta potential (right) of rutile NP suspension in NaCl and CaCl₂ solutions of variable IS at pH5 and 8, after 24h, in the absence (NP) 133 and in the presence of AMPA (5µg/L) or glyphosate (5µg/L). The hydrodynamic diameter of rutile 134 135 NP (54 nm) is also indicated (red dashed line), the error bars correspond to standard deviations of 3 136 measurements.





140 Figure S8. Average hydrodynamic diameter (size; left) and zeta potential (right) of anatase NP

suspension in NaCl and CaCl₂ solutions of variable IS at pH5 and 8, at t₀ (A) and after 24h (B), in 141

the absence (NP) and in the presence of 2,4-D (5µg/L). The hydrodynamic diameter of anatase NP 142

143 (14 nm) is also indicated (red dashed line), the error bars correspond to standard deviations of 3

144 measurements.





Figure S9. Average hydrodynamic diameter (size; left) and zeta potential (right) of rutile NP 147 148 suspension in NaCl and CaCl₂ solutions of variable IS at pH5 and 8, at t₀ (A) and after 24h (B), in 149 the absence (NP) and in the presence of 2,4-D (5µg/L). The hydrodynamic diameter of rutile NP

150 (54 nm) is also indicated (red dashed line), the error bars correspond to standard deviations of 3

151 measurements.

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