

Fate of TiO₂ nanoparticles in carbonate and silicate aquifers

RONCHI, B., JORIS, A., JAMIN, P., BROUYÈRE, S., VESCHKENS, M., FRIPPIAT, C.

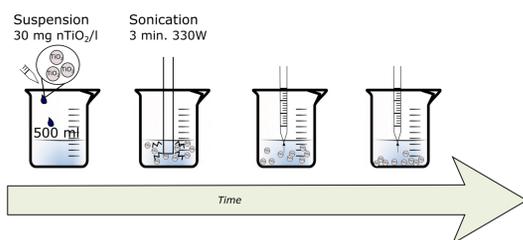
✉ b.ronchi@issep.be

1. Objective

To assess the vulnerability of silicate and carbonate aquifers to the contaminant of emerging concern nano-sized TiO₂ (nTiO₂), its stability is evaluated in different types of water pumped from carbonate and silicate aquifers and in Milli-Q water. In addition, its behaviour in saturated porous media is evaluated using column test with glass beads, carbonate sands and silicate sands.

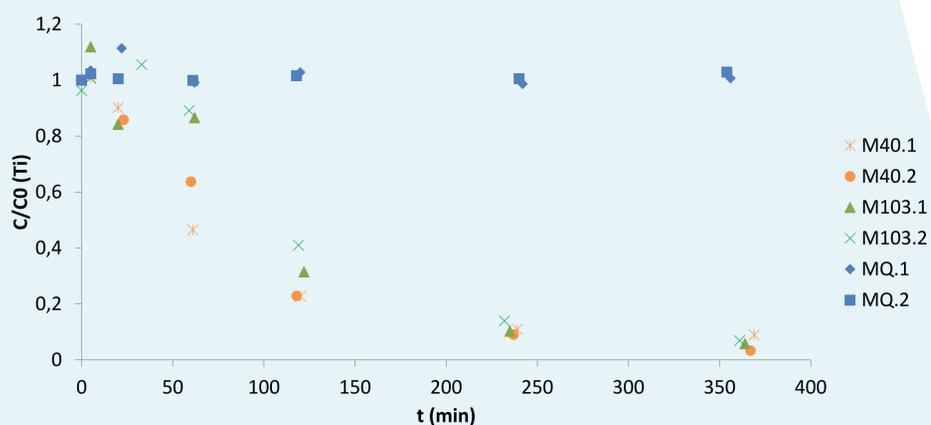
3. Stability test

Two replicates suspensions of nTiO₂ were prepared in 2 types of natural groundwater (filtered at 0.45µm) and Milli-Q water. Concentrations of TiO₂ in the supernatant is analysed over time (ICP-OES; HF/HNO₃/H₃BO₃).



mg/l	Method	M40 Chalk	M103 Sandstone & shale
pH	electrode	7.7	7.2
[F ⁻]	IC	0.087	< 0.047
[Cl ⁻]	IC	58.3	61
[SO ₄ ²⁻]	IC	93.3	32
[NO ₃ ⁻]	IC	51	33
Alkalinity	Titration	175	39
[Ca ²⁺]	ICP-OES	103	24
[Mg ²⁺]	ICP-OES	12.4	7.7
[K ⁺]	ICP-OES	2.9	24
[Na ⁺]	ICP-OES	19.7	19.3
[Ti ⁴⁺]	ICP-OES	<0.3µg/l	<0.3µg/l

Results

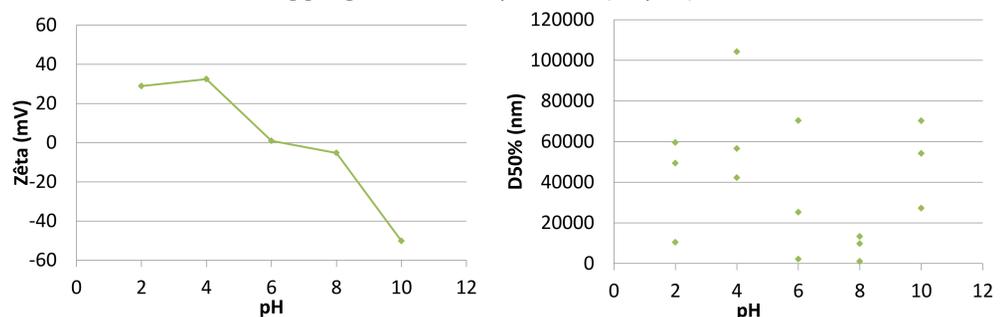


Sedimentation rates $k_{sed} = -\frac{\ln \frac{C}{C_0}}{t}$

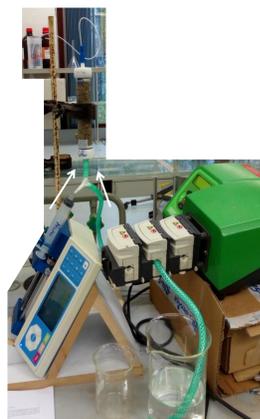
1-2.10⁻⁴ s⁻¹ in groundwater (pH>7)
10⁻⁶-10⁻⁷ s⁻¹ in MQ (pH 3.9)

2. nTiO₂ characterisation

The nTiO₂ are produced at the NCE lab of ULiège. Diameters and zeta potentials are analysed with DLS. The isoelectric point is measured at pH 6. Diameters of nTiO₂ aggregates are important (>1µm) and variable.



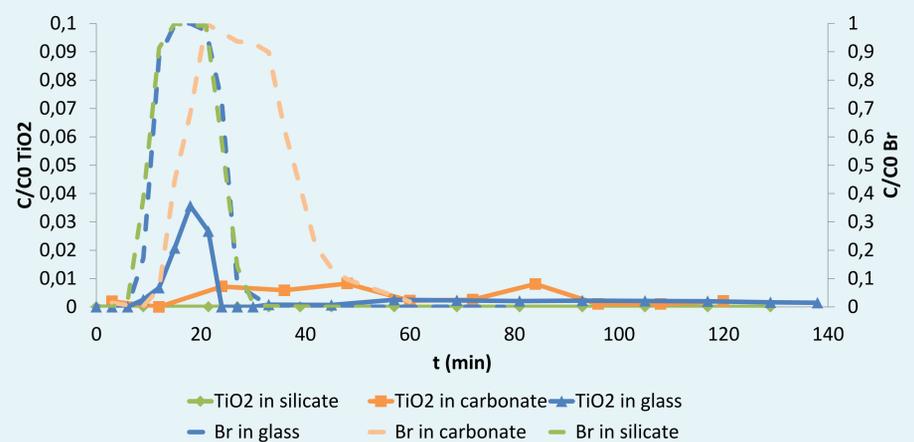
4. Column test



12 cm long-columns are filled with carbonate sands, silicate sands or glass beads. Air was first flushed with CO₂, then with water.

1. First a conservative tracer is injected at a flow rate of 4ml/min.
2. Then, a suspension of 150mg/l of nTiO₂ in Milli-Q water at pH 3.1 is injected at the same rate.
3. The outflow is analysed by ICP-OES after a triacid digestion (HF/HNO₃/H₃BO₃) procedure.

Results



	Silicate	Carbonate	Glass
Recovery TiO ₂ (%)	0	0.01	0.25

Filtration is considered as an active process when the ratio between diameters of nanoparticles and collectors (N_R) varies between 0.002 and 0.15 (Rahman et al., 2013; Xu et al., 2006).

pH	matrice	d _p (µm)	d _c (µm)	N _R
3	carbonate	50	813	0.0615
3	glass	50	1750	0.0286
3	silicate	50	880	0.0568

5. Conclusion

- nTiO₂ sedimentation is 2-3 orders of magnitude faster in neutral natural groundwater than in acid Milli-Q water.
- The transport of these nTiO₂ is limited in sandy media by filtration, as nTiO₂ aggregates have large diameters.
- The mix of natural minerals in silicate and carbonate sands attenuates naturally nTiO₂ transport.
- **Questions for future research:** study accumulation of nanoparticles in top soils and the evolution of its pollution front.