



Better understanding and applications of ammonium 12-molybdophosphate-based diffusive gradient in thin film techniques for measuring Cs in waters

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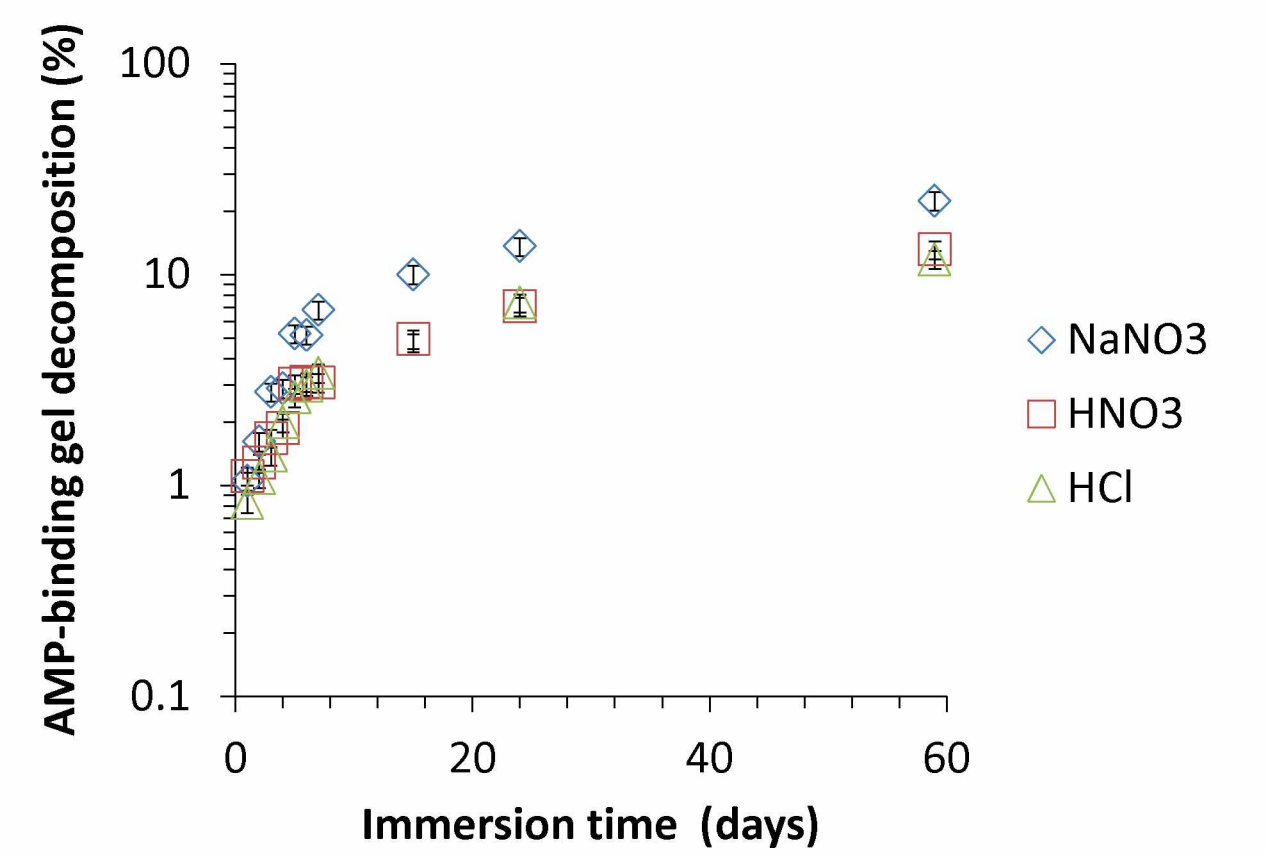
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Context

To improve modeling of Cs migration in the environment, we need to determine the proportion of labile Cs. AMP (ammonium 12-molybdophosphate) DGT is a good candidate to sample and concentrate Cs on field. Nevertheless, chemical conditions in water and soils may disturb the stability of AMP binding gel. Laboratory experiments were designed: (i) to identify factors controlling AMP binding gel degradation during storage and DGT deployment and (ii) to assess the possible impact of AMP degradation over time on the DGT response in waters with various chemical composition. Conclusions on potential limitations of AMP-DGT methods will finally be discussed for a better use of this technique for field applications.

For more details, we invite you to discover our article recently published in *Environmental Science and Pollution Research*.

AMP-binding gel stability over time in storage solution



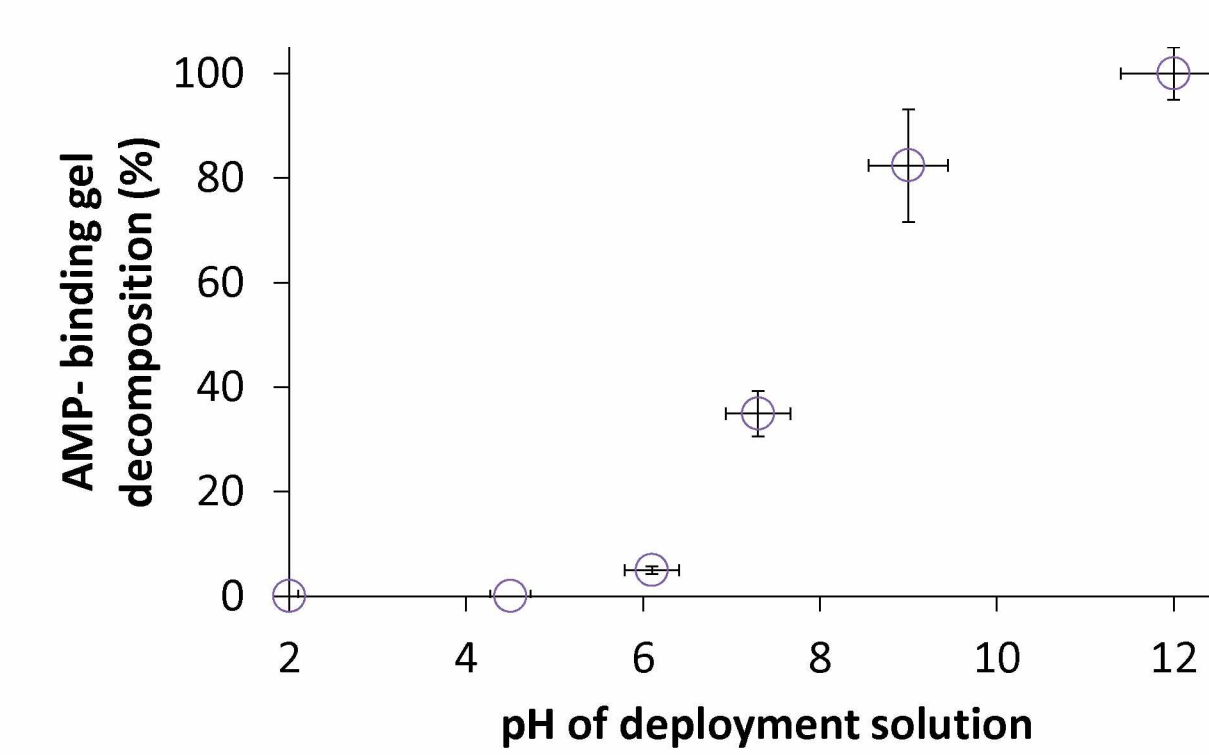
Stability control of AMP-binding gel in 200 mL of storage solution (10^{-2} mol L⁻¹ NaNO₃, HNO₃ or HCl).

The AMP-binding gel is not stable whatever the storage solution.

AMP decomposition at short-term is similar in the three tested solutions.

Acidic conditions improve long storage of AMP-binding gel.

AMP-binding gel stability as a function of pH



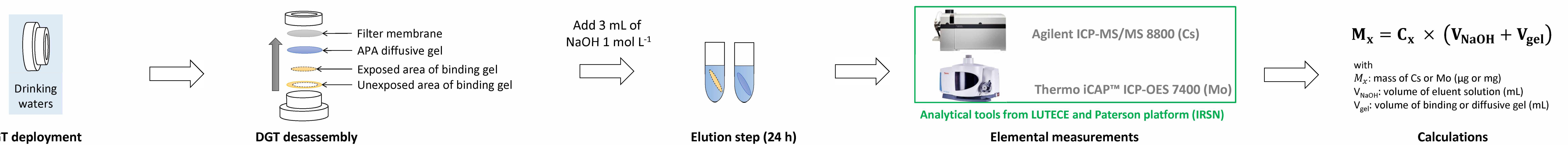
Stability investigation of AMP-binding gel during 21 h of deployment time in 20 mL of 10^{-2} mol L⁻¹ NaNO₃ solution at various pH (2–12).

The AMP-binding gel is not stable for pH > 6.

Total elution of Cs from AMP-binding gel is consequently possible using a basic eluent solution.

Comparison of AMP-DGT response in soft and hard drinking waters

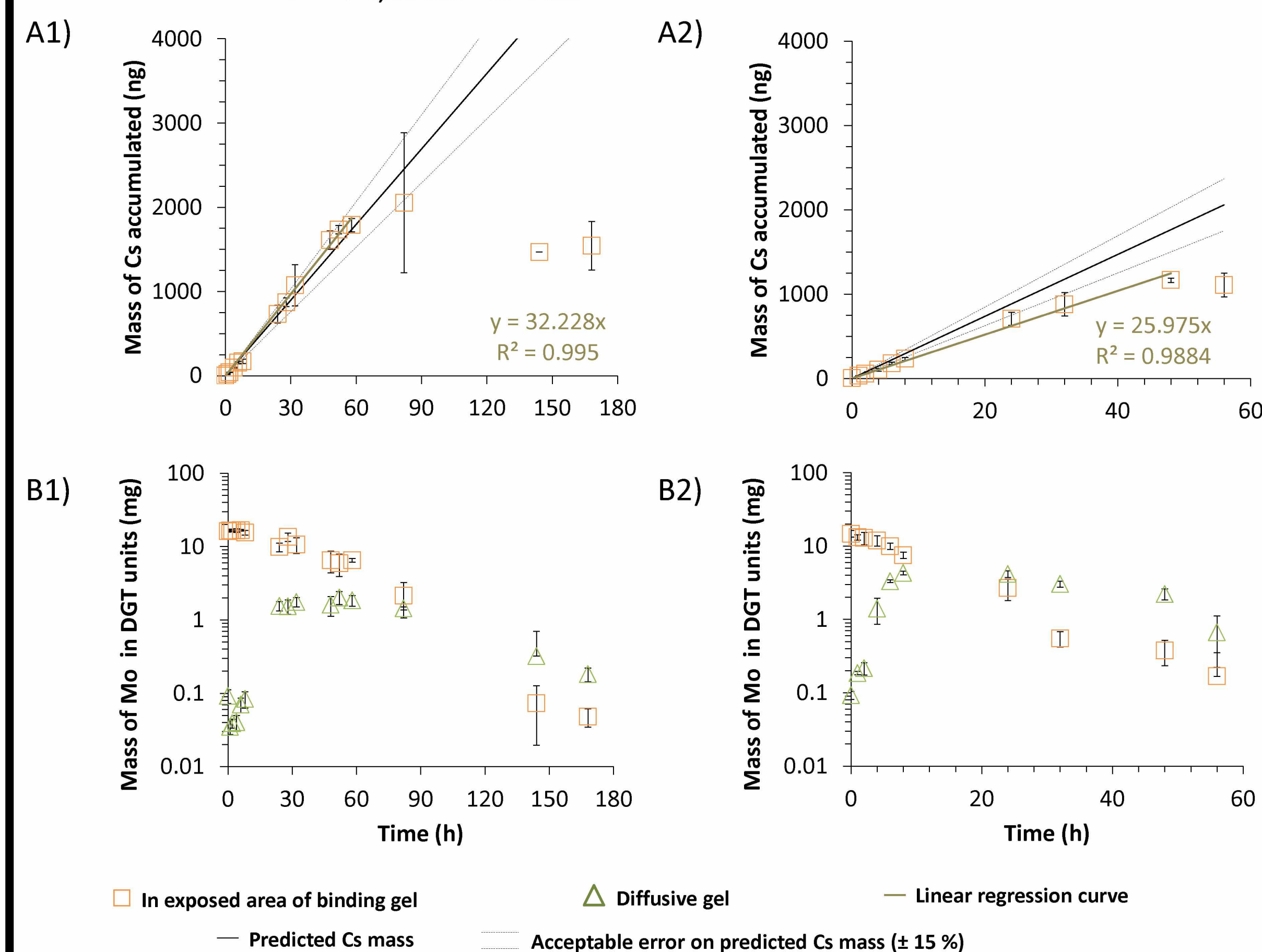
Experimental setup and calculation



Results and discussion

Soft water (Volvic®):
pH 7.85 ± 0.45 , [Cs] = 22.2 ± 1.8 µg L⁻¹,
T = 22.9 ± 1.5 °C, 39 AMP-DGT units

Hard water (Hepar®):
pH 7.90 ± 0.45 , [Cs] = 27.3 ± 0.7 µg L⁻¹,
T = 23.9 ± 0.3 °C, 30 AMP-DGT units



Results of time-series experiments performed with APA diffusive gel in soft and hard waters: A) evolution of the mass of Cs accumulated in the exposed area of AMP binding gel and B) Mo mass evolution in the diffusive gel and the exposed area of AMP-binding gel.

Linear accumulation of Cs by AMP-DGT samplers is observed over 58 and 48 h (Fig. A1 and A2), respectively, for soft and hard water ($R^2 > 0.98$). The amount of total Cs determined by AMP-DGT samplers was $77 \pm 10\%$ (mean \pm standard deviation) and $94 \pm 16\%$ of the total Cs concentration in hard and soft waters, respectively. **Lower linear accumulation of Cs in hard water is linked to the presence of interference cationic species, notably Ca²⁺ and Mg²⁺.**

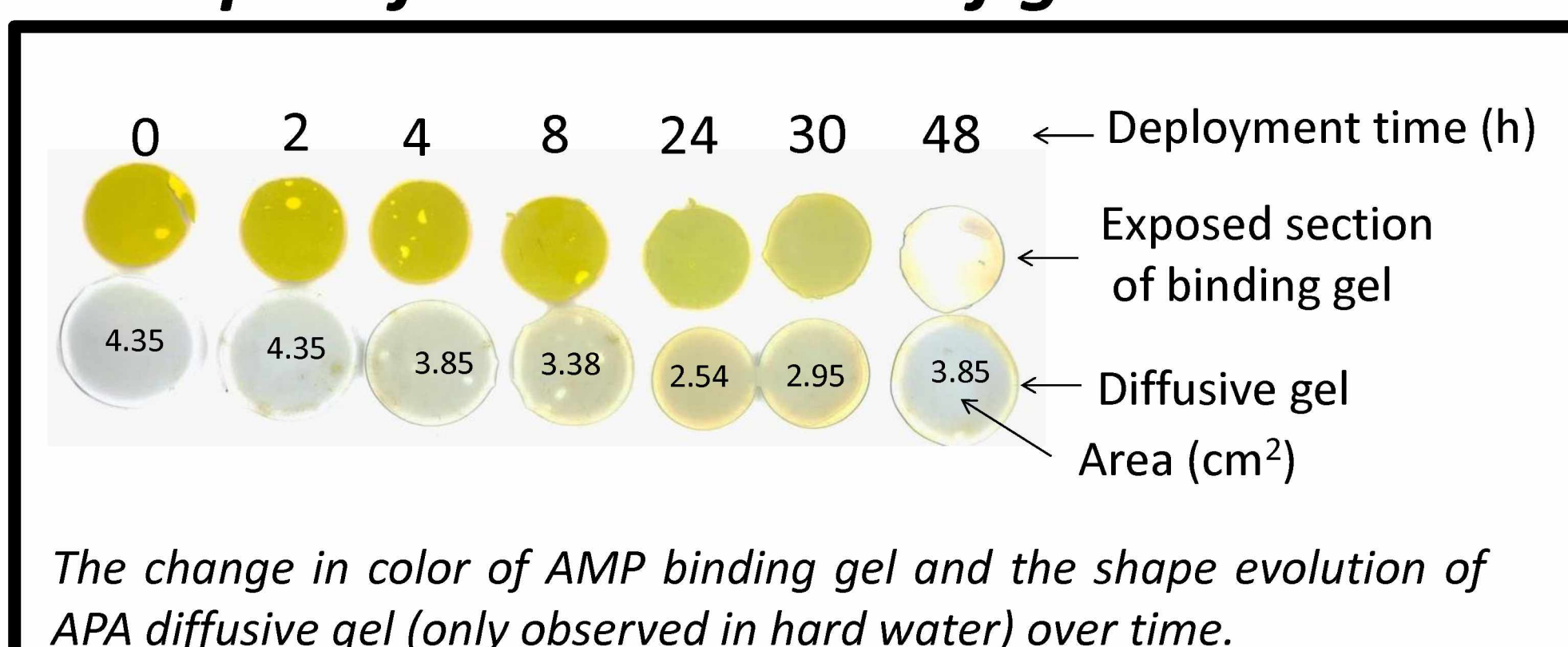
Short deployment time (less 24 h) should be used for a robust quantitative determination of Cs in hard water with AMP-DGT method.

Stability of AMP in DGT unit was evaluated over time by measuring the Mo mass in binding gel (Fig. B1 and B2), which could potentially reveal impacts on DGT measurements. The mass of Mo decreased in the binding gel with time and significantly increased in the diffusive gel in the first 24 h whatever the deployment solution. **This confirms that AMP-binding gel was not stable during deployment in moderately basic environmental waters.**

The AMP decomposition rate is around 2.4 times higher in hard water (2.06 ± 0.10 day⁻¹) than in soft water (0.86 ± 0.03 day⁻¹), whereas the pH values of these drinking waters are very similar and close to 7.9. **The ionic strength, which is around 35 times higher in hard water, must impact the AMP degradation level.**

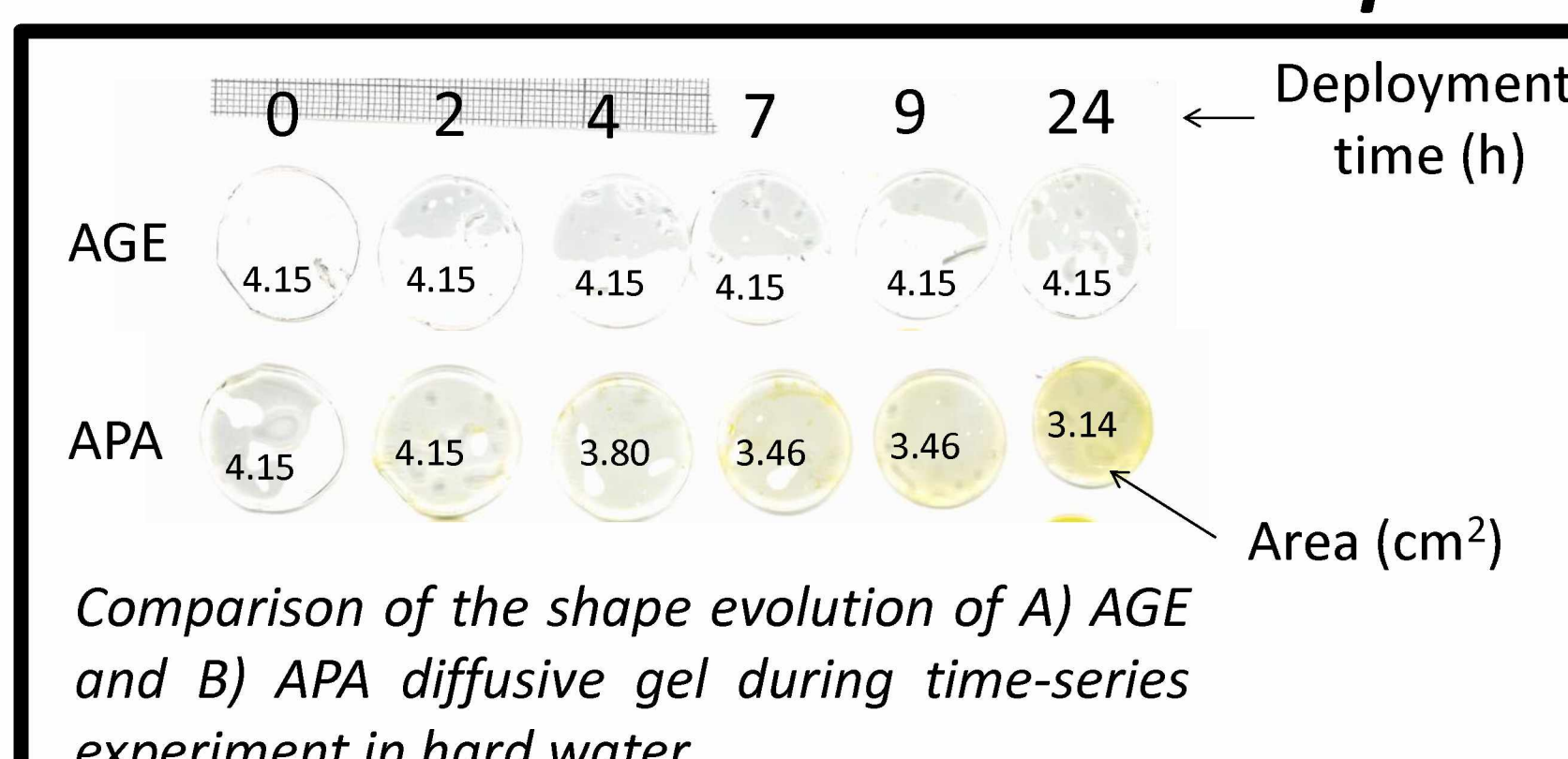
The shrinkage of the APA diffusive gel was experimentally observed in times-series experiment in hard water (see below), but did not affect the measurements as the exposure area of the binding gel remained completely covered by the diffusive gel.

Example of the evolution of gels over time



The change in color of AMP binding gel and the shape evolution of APA diffusive gel (only observed in hard water) over time.

Comparing different types of diffusive gels



Comparison of the shape evolution of A) AGE and B) APA diffusive gel during time-series experiment in hard water.

Although the DGT response was the same whatever the nature of diffusive gel, it is advised to commonly use the AGE hydrogel as standard diffusive gel for AMP-DGT method, since its physical properties are not impacted by the diffusion AMP degradation products.

Conclusion and perspectives

To perform a robust quantitative measurement of Cs with AMP-DGT samplers, laboratory investigations should be systematically performed to control the AMP-binding gel stability and evaluate the maximal deployment time under similar environmental waters. It is also recommended to use AGE hydrogel as reference diffusive gel.

The need for a new binding gel for Cs, which properties are not impacted by the deployment conditions is still open.

Our research team is open to collaboration on many topics:

- Impact of radioactive waste storage and uranium mining activities;
- Pre-concentration/purification technique (Cs, I, Pb, Ra, Th, U, etc.);
- Speciation measurement (passive samplers, IC-ICP-MS, etc.).

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