

USE OF DGT PASSIVE SAMPLERS FOR URANIUM MONITORING IN MINING SITES AND ACTIVE NUCLEAR SITES: WHAT DO WE MEASURE WITH DGT?

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This project is the result of a long standing collaboration between Orano Mining and the Vrije Universiteit Brussel (VUB) on the use of Diffusive Gradient in Thin-Films (DGT) passive samplers in environmental R&D studies in post-mining environments, and the Environmental Monitoring Laboratory at the Orano site in Tricastin. The main objective is the transfer of an innovative technique and its adaptation to routine monitoring of uranium in the waters of the Tricastin nuclear site.

The DGT technique consists of a specifically designed piston that houses a binding gel, a diffusive gel and a filter membrane. Under perfect sink condition, compounds passing through the filter membrane and diffusive layer are rapidly and irreversibly trapped on the binding gel layer, resulting in a controlled diffusion rate following Fick's diffusion law. The analysed mass of analyte on the binding layer can be converted to the time weighted average (TWA) concentration in solution by the simple DGT formula.

The Orano Tricastin site is an industrial platform that offers uranium processing services including conversion and enrichment preceding the final stage of manufacturing the fuel needed for nuclear power plant reactors. The potential influence of industrial activities on the environment is monitored very regularly by the Orano Tricastin site. This monitoring is based on measurement stations in air, water, soil as well as sampling of fauna and flora over a perimeter of several kilometers around the Tricastin site. The results of the 28,000 measurements carried out per year around the Tricastin site are regularly communicated to the authorities and stakeholders (local residents, associations, information commissions, elected officials, etc.). Besides the surface water, the groundwater at the Tricastin site is particularly studied and monitored because of its shallow depth and its connection with surface watercourses. As a result, several hundred piezometers are installed on the site and nearby outside the site in order to sample groundwater environment. The regulatory supervision of the Orano Tricastin site requires weekly to monthly monitoring of certain watercourses. These samplings are made on an ad hoc basis and not following the composition of an aliquot. Therefore, it was interesting to investigate whether the DGT technique could be used to give representative time weighted average (TWA) concentrations in the surface waters and the groundwater of the Orano Tricastin site. The two main research questions were 1) can DGT be used as a long term (up to 1 month) monitoring tool at the site and 2) How will the DGT device react to changes in the water composition in case of an accidental spill in the uranium processing activities.

On order to develop and validate the uranium DGT technique for the specific site, a preliminary expedition was performed in March 2018, in which DGTs containing Chelex® resin were deployed in eight piezometers for 24h and in the Gaffiere river, flowing through the site, DGT units with Chelex resin were deployed for 24h up to one month. Point samples were taken at the start and end of each deployment for comparison and water samples were taken to characterize the water composition. A comparison was also made with DGT containing Iontosorb® resin, containing 8-hydroxyquinoline functional groups. The preliminary expedition revealed the need to determine the diffusion boundary layer thickness for quantification of uranium concentrations in piezometers and river water and showed a non-perfect sink behavior of uranium in the calcium bicarbonate rich waters for a deployment time of longer than two days.

To further develop the technique for its application in uranium monitoring for longer time periods, laboratory tests were performed using different resins (such as Diphonix, Dow Piwba, Chelex-100, Iontosorb and mixed resins and later Lewatit-FO 36), different diffusion gel thicknesses, single and double resin gel layers, using the river water as deployment solution as well as carbonate rich tap water. Uptake kinetics and competitive uptake of Ca and Mg on the resin gels were evaluated. Diffusion coefficients were determined in carbonate rich waters using by both the diffusion cell as DGT experiments. A second field expedition on the Orano Tricastin site was held in May 2019, comparing Diphonix, Dow-Piwba and Chelex resin on both the Gaffiere River and a piezometer for sampling periods from one day to up to one month, using double layer resin gels and evaluating the diffusion boundary layer. The results confirmed the linear accumulation on the first resin gel layer for Diphonix up to one month, a significant accumulation of U on the second resin layer for Dow-Piwba after one month, but linear accumulation of U on the sum of both layers and for Chelex a non-linear accumulation is found after two day and after one week the concentration is both resin layers is equal and no further accumulation is observed. The calculated CDGT U-concentrations for Dow-Piwba were in good agreement with the TWA concentrations obtained by grab sampling at the different time intervals, but due to a calibration problem with the eluent for Diphonix, accurate concentrations could not be performed and a confirmation expedition is planned.

In the next phase, laboratory experiments were performed where concentration changes in the deployment solutions were made. DGT units were transferred from solution from low to high U concentrations and vice versa, or from low to high and back to low, simulating a temporal increase. Deployment solutions were either 1M NaNO₃ solutions, diluted tap water with the same carbonate content as the Tricastin waters and solutions containing the composition of a simulated accidental spill (such as low pH, high U, high F, high NO₃) at a dilution of 1:100. Both Lewatit FO-36 and Diphonix were used as resins in these experiments. Control experiments were always performed in which the DGT units stayed in the same solution. When the spike was added to diluted tap water CDGT U-concentrations were in good agreement with the TWA calculated concentrations whereas this was not the case for solutions spiked in 1M NaNO₃. Speciation calculations showed the predominance of carbonated U species in the spiked tap water whereas the spike composition dominates in the simple solution.

As U-DGT measurements in natural waters will be influenced by U complexation with humic acids (HA), fulvic acids (FA), carbonates and the competition between these species, experiments were carried out in which U was spiked in different concentrations of FA and HA. Chelex-100, Lewatit FO-36 and Diphonix were used as resins in the DGT units which were deployed for 24h and 72h. The results show a drop in the DGT labile fraction in the function of the concentration of HA to 20% at 10 mg/L for all resins, largely due to the colloidal nature of the complexes, whereas for the FA solutions, the DGT labile fraction decreases to 60% for Lewatit-FO 36 and Diphonix and to 20% for Chelex. Addition of different concentrations of carbonates to solutions of 5mg/L HA and FA (different dilutions of tapwater) resulted in an increase in the DGT labile fraction to around 100% when using Lewatit and Diphonix, at carbonate concentrations higher than 200mg/L, whereas for Chelex, a maximum DGT labile fraction was observed at 200mg/L carbonates, followed by a further decrease at higher carbonate levels, which is also more pronounced for the longer deployment times. Speciation modelling confirmed the speciation changes towards carbonate complexes in the model



solution and analysis of the particles in solution confirm the solubilization of U from the HA. The use of different resins thus allows us to gain insight in the lability and mobility of U complexes and possibly increase our understanding on the bioaccumulation of U.