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Modelling the migration of per- and polyfluoroalkyl substances in unsaturated soil into the groundwater

Modélisation de la migration des substances per- et polyfluoroalkyles des sols non saturés vers les eaux souterraines

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ABSTRACT: Per- and polyfluoroalkyl substances (PFAS) were polluted both soil and groundwater for several decays. In this paper, a model is developed to predict the migration of PFHxS (Perfluorohexane sulfonate) from the unsaturated soil media to the groundwater in a location in regional New South Wales, Australia. The initial contaminant level, soil and rock geotechnical parameters, and soil sorption isotherm characteristics were determined through geo-environmental investigation, and laboratory mechanical and chemical analysis. A fully coupled analysis was conducted considering climate interaction at the ground surface for up to 100 years. The model showed that when the contaminated site is covered by a concrete slab, the level of PFHxS in the groundwater will be higher than the guideline value for drinking water after 14 years, with a constant increase in its level up to 100 years. The level of the contaminant in the topsoil reduces over time due to the flow of rainwater through porous media, desorption from soil mass, and decay. When the contaminated site was uncovered due to the potential change in the land use, groundwater was contaminated faster with higher PFHxS concentration.

RÉSUMÉ : Les substances per- et polyfluoroalkyles (PFAS) ont été polluées à la fois dans le sol et les eaux souterraines pendant plusieurs désintégrations. Dans cet article, un modèle est développé pour prédire la migration du PFHxS (Perfluorohexane sulfonate) du sol insaturé vers les eaux souterraines dans un endroit régional de la Nouvelle-Galles du Sud, en Australie. Le niveau de contaminant initial, les paramètres géotechniques du sol et des roches et les caractéristiques isothermes de sorption du sol ont été déterminés au moyen d'une enquête géo-environnementale et d'analyses mécaniques et chimiques en laboratoire. Une analyse entièrement couplée a été menée en tenant compte de l'interaction climatique à la surface du sol pendant jusqu'à 100 ans. Le modèle a montré que lorsque le site contaminé est recouvert d'une dalle de béton, le niveau de PFHxS dans les eaux souterraines sera supérieur à la valeur guide pour l'eau potable après 14 ans, avec une augmentation constante de son niveau jusqu'à 100 ans. Le niveau de contaminant dans la couche arable diminue avec le temps en raison de l'écoulement de l'eau de pluie à travers les milieux poreux, de la désorption de la masse du sol et de la décomposition. Lorsque le site contaminé a été découvert en raison du changement potentiel de l'utilisation des terres, les eaux souterraines ont été contaminées plus rapidement avec une concentration plus élevée de PFHxS.

KEYWORDS: Contaminant transport modelling; Unsaturated soil; Groundwater; PFAS; PFHxS.

1 INTRODUCTION

Rapid urbanisation and industrialisation have led to many new chemicals entering the environment, among them PFAS substances. PFAS are synthetic chemicals with very strong chemical structure, persist in the environment and bio-accumulate in the body of flora and fauna (Bhavsar et al., 2016). They are toxic to the human body, animals, and other environmental elements. They can be washed by rainwater through the unsaturated soil environment towards groundwater. These chemicals are categorised as persistent organic pollutants (POPs) and have been used to build products resistant to heat, oil, stains, grease and water (Kissa, 2001). These compounds are widely used in carpet, fibres, leather, packaging, paper, textile-related industrial products and fire control chemicals (Kissa, 2001). Another widespread use of these chemicals was in aqueous firefighting foam (AFFF) for firefighting activities in fire stations and defence based airports from 1970 tile 2004 (Australian Defence, 2020). There are enormous chemicals in the PFAS category, but the most produced and studied of these chemicals include perfluorooctane sulfonate (PFOS), perfluorooctanoic acid (PFOA), and perfluorohexane sulfonate (PFHxS) (HEPA, 2020).

Various remediation and management strategies have been proposed to eliminate PFAS from the environment (Mahinroosta & Senevirathna, 2020). However, before applying any remediation strategy, it is of paramount importance to predict contamination level in soil and groundwater to direct the remedial actions.

Several studies have been conducted on modelling PFAS fate and transport in the environment. Advection, dispersion, and desorption are the major transport processes (El-Zein, Carter, & W. Airey, 2006) governing the reduction of contaminants concentration in soil and groundwater. The sorption isotherms of PFAS to soil particles are of paramount importance in modelling the adsorption and desorption process (Higgins & Luthy, 2006). Besides, material decay needs to be considered, especially in long-term modelling.

In addition to the adsorption of PFAS onto the soil, other adsorption features have been studied by researchers in the field. The retention of PFAS during transport through unsaturated subsurface systems considering the air-water interface was modelled by Lyu et al. (2018). Brusseau (2020) developed a transport model considering various retention processes such as adsorption at air-water and oil-water interfaces, adsorption by the solid phase, and diffusive mass transfer between advective and non-advective domains. Although these new features made PFAS transport modelling so accurate, they need advanced equipment to conduct chemical analysis and develop the model's new parameters.

In this study, a fully coupled transport model was developed to predict PFHxS level in soil and groundwater due to precipitation and evapotranspiration for up to 100 years. The contaminated site is a localised area in Bathurst regional airport in central west New South Wales, Australia. The soil physicochemical parameters were determined through extensive in-situ and lab tests and compared with relevant literature. The contaminant model includes the main functions of contaminant transport modelling: advection, dispersion, adsorption, and decay.

2 SITE SPECIFICATION AND GEO-ENVIRONMENTAL INVESTIGATION

Extensive geo-environmental investigations of a fire truck shed in the airport showed that contamination levels of PFOS and PFHxS were high due to past firefighting activities. Contamination levels in the soil, surface water, groundwater, sediment and biota (EPA NSW, 2017) were thoroughly investigated, and it was found that the concentrations of PFAS in some soil samples were above the commercial/industrial guidelines.

The area is located on a granite rock formation. The weathering process historically changed the granite formation to low permeable material such as clay, silty clay, and fine sand at the ground level. The depth of the bedrock in the area is between 7.5 m and 8.5 m. The groundwater level is present at about 26 m below the surface.

From the results of the chemical analysis on soil samples from 13 boreholes around the site (Sullivan, 2018), the contours of initial PFAS concentration in the soil under the fire truck shed was developed. Figure 1 shows the initial concentration of PFHxS in the site. The maximum PFOS and PFHxS reported in the area were 17.8, and 4.01 mg/kg, respectively. The sum of PFOS and PFHxS concentrations in the soil exceeded the guideline value for a commercial land (20mg/kg) (HEPA, 2018).

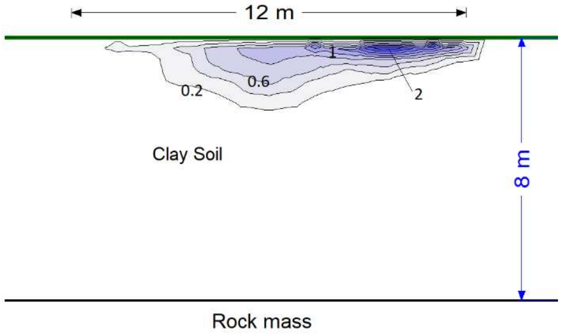

Figure 1. Initial PFHxS levels (mg/kg) in the contaminated site

2.1 *Laboratory tests*

The laboratory tests were conducted to determine the soil characteristics and soil sorption isotherm. Soil samples (disturbed and undisturbed) were collected from different locations up to 60 cm in depth. The soil moisture content, particle size distribution, hydraulic conductivity, and the density of the soil samples were determined at the Charles Sturt Geotechnical Engineering laboratory. The soil samples were classified as sandy soils (SC in unified classification; sand 63%, silt and clay 27%) with an average moisture content of 22%. The average dry density of the soil samples from the nuclear density test was 1670 kg/m^3.

For the soil sorption isotherm characteristics, both kinetic and sorption tests were conducted based on the standard procedure in National Life Sciences Hub at Charles Sturt University. A dosage of 1.0 ± 0.1 g of natural soil was suspended in 100 mL of prepared PFHxS with the initial concentrations of 5 µg/l, 50 µg/l, 100 µg/l, 200 µg/l, 300 µg/l, 400 µg/l, 500 µg/l, 700 µg/l, and 900 µg/l. The methodology of the test was described thoroughly in another study by Mahinroosta and Senevirathna (2021). Results of the sorption isotherm tests are shown in Figure 2. In this figure, S is the concentration in the solid phase, and C is the equilibrium concentration of solute in solution. The sorption isotherms of the contaminants onto the soil is of paramount importance in contaminant transport modelling in terms of sorption and desorption of contaminants from soil particles, especially in PFAS chemicals.

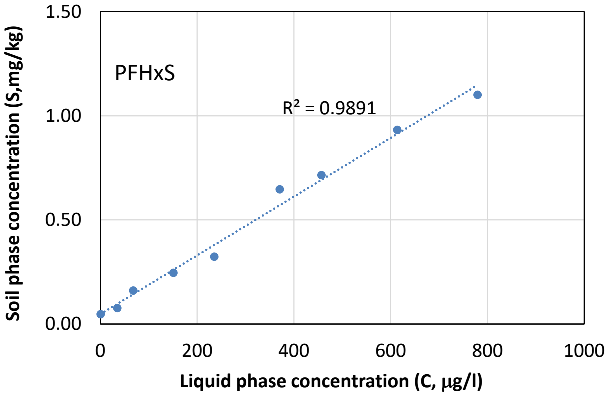

Figure 2. Sorption isotherms of PFHxS onto the soil (the solid line was used for modelling)

3 GEOMETRY OF THE MODEL, BOUNDARY CONDITIONS AND INPUT PARAMETERS

For contaminant transport, four primary functions of advection, dispersion, adsorption, and decay were applied using GeoStudio (2019) software. The fully coupled modelling was used with the water transfer model (SEEP/W) and contaminant transfer model (CTRAN/W), considering both saturated and unsaturated media.

The geometry of the model and finite element mesh is depicted in Figure 3. The model is in a plane strain condition using both triangular and quadrilateral finite elements. The 12 m by 12 m fire truck shed is founded on a 5 cm thick concrete slab. The boundaries of the model extended 50 m to both sides to reduce the effect of boundaries on the results.

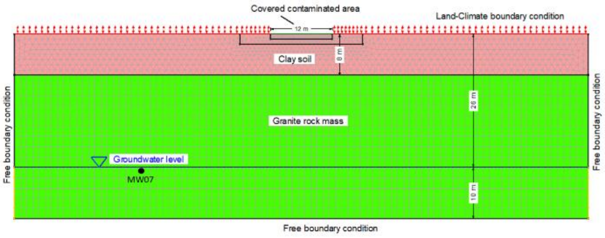

Figure 3. Finite element mesh and boundary conditions

The hydraulic boundary conditions are the land-climate interactions at the ground surface and groundwater level, 26 m below the ground. Complete precipitation and evapotranspiration using the Penman-Monteith method (Monteith, 1981; Penman, 1948) was used at the top of the model. For instance, the time history of climate data, including air temperature, precipitation, relative humidity, wind speed, and net radiation flux derived from the Australian Bureau of Meteorology (2020), were used from 1/1/2009 to 31/12/2019, and the same climate trend was extended to 100 years. In terms of contamination boundaries, the free boundary conditions were used in the left, right and bottom of the model so that contaminant does not accumulate in the boundaries.

For the initial conditions, the initial PFHxS values depicted in Figure 1 was used in the software. The initial condition for pore water pressure is the same as the water level.

The mechanical parameters of the model are shown in Table 1. The soil parameters were determined from laboratory and in-situ tests, whereas the granite rock mass, whose parameters were derived by comparison with similar rock masses (de Marsily, 1986; Domenico & Schwartz, 1998).

Table 1. Mechanical parameters used in different zones of the model

Zone	Dry density (g/cm^3)	Saturated volume water content (θ_{sat})	Compressibility (1/Pa)	Hydraulic conductivity (m/s)
Clay soil	1.67	0.35	10^{-7}	10^{-8}
Granite Rock mass	2.4	0.05	10^{-9}	10^{-5}

In addition to the above parameters, the parameters related to adsorption, dispersion, and decay should be determined. In terms of adsorption, the sorption isotherm characteristics from Figure 2 were used in the soil environment. No adsorption capacity was considered for the rock mass because of the large particle sizes of fractured rocks. However, this should be investigated in future.

For the dispersion contribution on contaminant transport modelling, an approximate value of 0.1 times the scale of the system (2.6 m longitudinal and 1.3 m transverse) was used for the dispersivity parameter (the ratio of the hydrodynamic dispersion coefficient to the pore water velocity) based on Fetter (1993) suggestion.

In terms of decay (the loss of mass due to the decay of ions in the pore water and decay of ions attached to the soil particles), the decay half-life of PFHxS in the pore water and groundwater needs to be addressed due to the prediction for a long time (for up to 100 years). The half-life of PFHxS depends on the environment and species. Unfortunately, no study was found in the literature on the half-life of PFHxS in "water". The half-life of PFHxS in the human body is the highest reported for any PFAS and varies between 5.3 and 35 years (Persistent Organic Pollutants Review Committee, 2018); in another study in the same reference, the half-life of PFHxS in the human body was approximately 1.5 times longer than for PFOS. Knowing that the half-life of PFOS in aqueous solutions or water is more than 41 years (OECD, 2002), the half-life of PFHxS in pore water and groundwater was assumed 50 years in this study to be on the conservative side.

4 RESULTS OF CONTAMINANT TRANSPORT MODELING

In order to predict PFHxS migration through the soil and rock mass to the groundwater, two scenarios were considered as follows:

Scenario 1 – covered contaminated site; in this scenario, the concrete slab and the fire truck shed were kept in place, and no changes were proposed to the site for up to 100 years. It was assumed that the concrete slab was not cracked, and no activity would change the status of the concrete slab and the soil environment. The topsoil is under the land-climate boundary condition, except above the area with the concrete slab, which is impermeable.

Scenario 2 – uncovered contaminated site due to complete removal of the current protective systems; in this scenario, it was assumed that the concrete slab and the fire truck shed were completely removed due to a change in land use. Therefore, the boundary of the topsoil is exposed to climate interaction in all areas.

In these scenarios, the analyses were conducted with a time increment of one day to simulate continuous contaminant migration day by day for up to 100 years. All the steps of the analysis converged smoothly with this time increment.

4.1 *Migration of PFHxS -covered contaminated site*

In the current situation, due to the fire truck shed, there is no direct exposure of the top of the covered area to precipitation and evapotranspiration. The PFHxS contours in the topsoil after 25, 50, and 100 years are shown in Figure 4. This figure shows that the PFHxS level decreases gradually from the initial value of more than 2 mg/kg in Figure 1 to 0.8, 0.6, and 0.2 mg/kg in 25, 50, and 100 years, respectively. The results are all less than the guideline values for soil, based on human health criterion (20 mg/kg) in industrial/commercial land use (HEPA, 2020). Also, the extension of PFHxS concentration is found to reduce. For example, reductions in the area with a minimum level of 0.2 mg/kg after 50 years and 100 years are about 50% and 60%, respectively. The area with the maximum concentration remains almost at the same level (1 m below the ground surface). The flow of rainwater (convection) has little influence on the PFHxS level in the covered section of the soil. The PFHxS level in the covered contaminated area is reduced mainly because of decay. In general, with a half-life of 50 years, the initial concentration of 2 mg/kg will decrease to 0.5 mg/kg only because of decay. The difference between this value and 0.2 mg/kg after 100 years is the effect of the other three functions (advection, adsorption, and dispersion).

Figure 5 shows the concentration of PFHxS in the pore water and groundwater at different times. The minimum and maximum contour levels are set to the guideline values for drinking water, and recreational water which are 0.07 µg/l and 0.7 µg/l (HEPA, 2020), respectively.

It was assumed the concentration of PFHxS in groundwater at the beginning of the modelling was zero. The maximum levels of PFHxS in groundwater after 25, 50 and 100 years are 0.42 µg/l, 1 µg/l and 1.04 µg/l, respectively, which are more than the guideline value for drinking water (0.07µg/l). The PFHxS values increase in the groundwater over time and become even higher than the guideline value for recreational water after 50 years. In general, the level of PFHxS in groundwater is increasing, and the domain of polluted groundwater is extending to six times the contaminated area after 50 years.

The results show that the groundwater might be polluted by PFHxS and will not be suitable for drinking. Therefore, no boreholes or wells should be dug for drinking water near the contaminated site (less than 500 distance from the site).

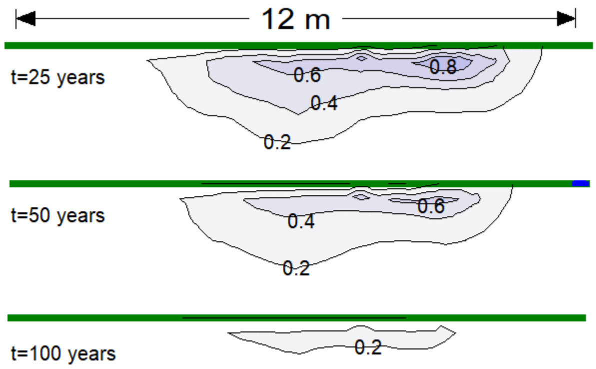

Figure 4. PFHxS concentration (mg/Kg) in soil at different times-covered contaminated site

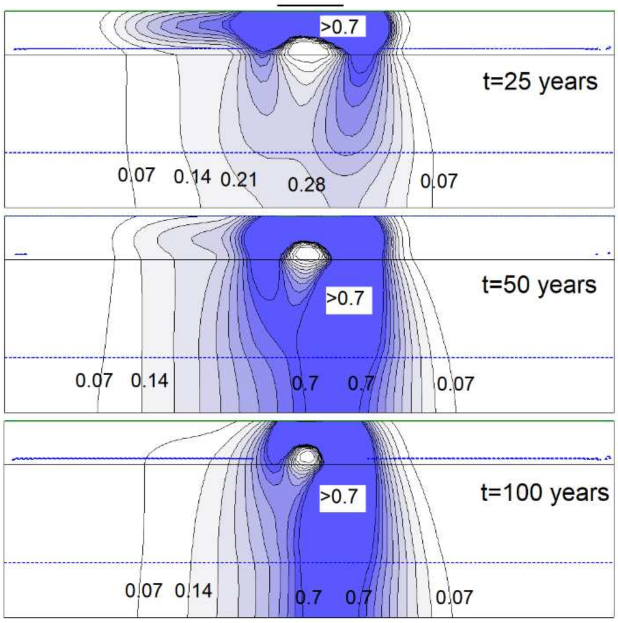

Figure 5. Contours of PFHxS level (μg/l) in pore water and groundwater at different times-covered contaminated sit

4.2 *PFHxS migration-uncovered contaminated area*

In this condition, it was assumed that the concrete slab and the fire truck shed were removed due to a change in land use. The contour of PFHxS in pore water and groundwater are shown in Figure 6 for different timeframes. It can be seen that the extent of the affected area and the intensity of PFHxS in groundwater are much greater than in the previous section. The maximum level of PFHxS in groundwater after 25, 50 and 100 years reaches 3.5, 9.5 and 6.5 μg/l, respectively, which is higher than the guideline values. The maximum concentration is almost 130 and thirteen folds the guideline values for drinking water and recreational water, respectively. Therefore, exposing the contaminated area for another land use without any remediation is not recommended.

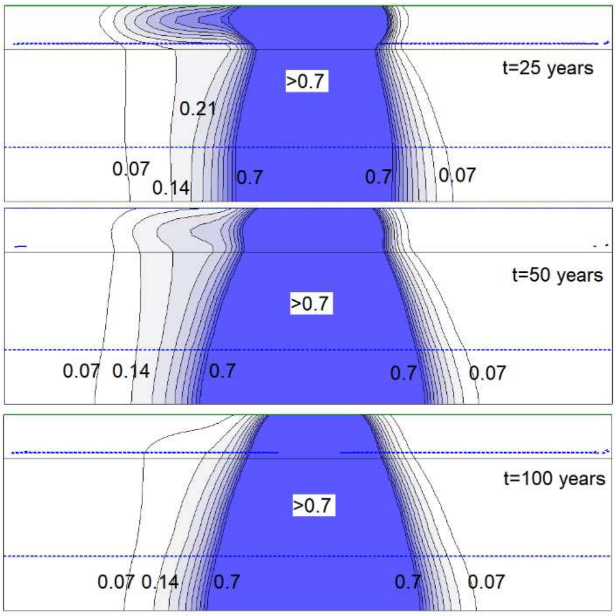

Figure 6. Contours of PFHxS level (μg/l) in pore water and groundwater at different times-uncovered contaminated site

4.3 *PFHxS changes with time*

The changes of PFHxS with time in groundwater right below the centre of the contaminated site for the above two scenarios are shown in Figure 7. It can be seen that when the contaminants are covered, the level of PFHxS reaches the guideline values for drinking water and recreational water after 14 years and 40 years, respectively. In the uncovered scenario, these timeframes become shorter at 7 years and 17 years, respectively. Also, the contaminant level in the uncovered scenario reduces gradually after 60 years, while the concentration value is still above the guideline values.

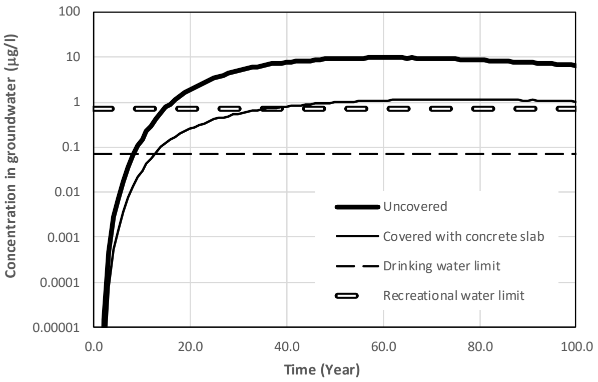

Figure 7. Changes in PFHxS level in groundwater over 100 years

The changes of the contaminant's concentration in the soil environment at the point with maximum PFHxS concentration in both scenarios are shown in Figure 8. This figure shows that the concentration of PFHxS at this point in the soil is decreasing with time, with a higher rate in the uncovered scenario. The rate of reduction in uncovered case during the first ten years is very high, which shows that the contaminant will be washed very rapidly due to the precipitation and infiltration. It should be mentioned that this trend will not necessarily happen in other locations in the soil mass. Some areas may experience rise and fall or even rise in PFHxS level due to contaminant migration, although in all cases, the PFHxS levels are lower than the human health investigation levels in soil (20mg/kg). (HEPA, 2020).

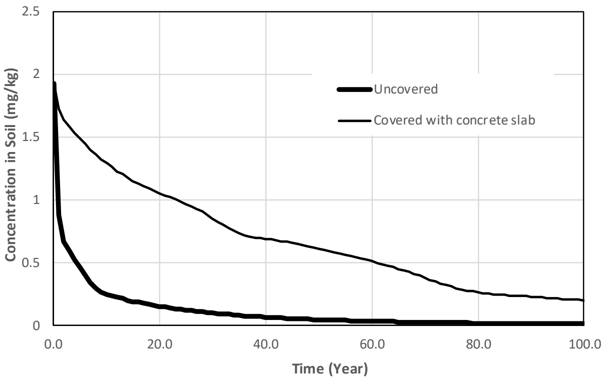

Figure 8. Changes in PFHxS level in soil over 100 years

It has to be mentioned that this study had some limitations, which need further studies to improve the contaminant transport model. Some of the issues are as follows:

- In terms of retardation factor, only solid-phase adsorption was considered in this study. Other factors such as vapour, adsorption at the air-water interface, etc need to be considered with applying more advanced numerical models (Brusseau, 2020).

- The effect of other PFAS in PFHxS migration (co-transport) should be studied, which was beyond the scope of this study.
- Develop 3D contaminate transport model considering potential deviations of the input parameters.

5 CONCLUSIONS

In this study, the profile of PFHxS in the ground and groundwater was predicted in a regional area, which was used previously for firefighting activities and the deposit of PFAS chemicals. In-situ and laboratory experiments were conducted to acquire the soil specifications and sorption isotherm characteristics for the model inputs. A fully integrated PFHxS transport model addressing advection, dispersion, adsorption, and decay was developed to investigate contaminant transport due to precipitation, evapotranspiration, and infiltration for up to 100 years. The model showed that the PFHxS level in the contaminated soil is reduced mainly due to washing with rainwater and decay. The level of PFHxS in the soil was very low when the current barriers were removed.

The model shows that the level of PFHxS in groundwater increases continuously and will reach the threshold for drinking water in less than 14 years when the contaminated site is covered. When the contaminated area is exposed to the climate interactions (uncovered scenario), the level of PFHxS in groundwater will be even higher than the guideline values for recreational activities after 17 years. However, as the studied area is an industrial/commercial area, no boreholes will be used for drinking water from the groundwater. So the recommendation at this stage would be a do-nothing approach unless an appropriate remediation strategy is applied.

6 ACKNOWLEDGEMENTS

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