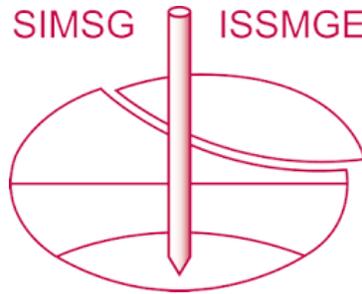


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Field testing of a composite GM – GCL barrier against emission of gaseous mercury from polluted soil

Essais en champ sur une barrière composite GM-GCL contre les émissions de vapeur de mercure provenant du sol pollué

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ABSTRACT During the geoenvironmental assessment of a contaminated site, field measurements of Hg vapours emission from the soil surface and through a composite GM-GCL barrier section were performed over two campaigns, using open dynamic flux chambers (FC). The GM-GCL test section was installed on site, allowing GCL hydration and gas diffusion to reach a steady state. The flux through the barrier was measured with the FC placed directly onto the GM, and compared with emission from soil surface. In both campaigns, the flux measured on the barrier was significantly lower than the flux from soil. The results suggest that composite barriers in caps may contribute in mitigating risks from volatilisation. A reduction in GCL bentonite swelling capacity was observed, likely as a result of cation exchange. Therefore, to preserve the overall efficiency of the barrier, including volatile flux reduction, adequately thick covering layers should be adopted.

RÉSUMÉ Dans l'évaluation géo-environnementale d'un site contaminé, des mesures en champ des émissions de vapeurs de Hg du sol et à travers d'une section expérimentale de barrière composite GM-GCL ont été effectuées sur deux campagnes, à l'aide de chambres ouvertes à flux dynamique (CF). La section GM-GCL a été installée sur le site pour permettre l'hydratation du GCL et l'équilibre de diffusion du vapeur. Le flux à travers la barrière a été mesurés avec la CF placée directement sur la GM et comparés au flux provenant de la surface du sol. Lors des deux campagnes, le flux mesuré sur la barrière était nettement inférieur au flux du sol. Les résultats suggèrent que les barrières composites peuvent contribuer à atténuer les risques posés par la volatilisation. Une réduction de la capacité de gonflement de la bentonite du GCL a été observée, probablement à la suite d'un échange de cations. Par conséquent, pour préserver l'efficacité globale de la barrière, y compris la réduction du flux de volatilisation, il convient d'adopter des couches de couverture suffisamment épaisses.

Keywords : composite barriers, volatilisation, flux, mercury

1 INTRODUCTION

Recent environmental regulations adopted in many countries assigned to site-specific risk assessment of polluted sites a key role in defining the management strategies and the

objectives of the remediation (USEPA, 1996-a; CONCAWE, 2003; ISPRA, 2008). The evaluation of pollutant migration from the source to the targets is a central issue in the risk assessment procedure. The objective is to estimate the concentration at the point of

exposure (C_{POE}) where receptors are assumed to be located. This estimate is usually conducted through mathematical modelling of contaminant migration of different complexity levels (tiered approach) or can be conducted by direct in-situ measurements of pollutant emission (e.g., in case of volatilisation from the surface of polluted soil).

In some cases, achieving the clean-up goals determined by the risk assessment procedure is technically difficult or economically unfeasible. The lack of suitable disposal sites at sustainable costs makes the confinement of the polluted materials, associated to the assessment of residual risks, a frequently adopted solution.

The confinement of polluted soils most often includes a covering (or “capping”) system. The primary functions of caps are to limit infiltration of rainwater into the polluted materials and to prevent direct contact with the pollutants. Polymeric geomembranes (GM) are frequently used in caps, owing to the excellent performances of intact GM against water and gas advection. GM are often coupled with mineral liners (compacted clay or geosynthetic clay lines, GCL), that minimize the influence of holes or defects on the hydraulic performance (Giroud, 1997) of the barrier. The use of GCLs instead of thicker clay liners is preferred when a significant increase in the elevation of the ground level is not suitable, due to technical (e.g., surface drainage) or aesthetic reasons.

In the presence of volatile contaminants, capping systems may also be required to prevent or reduce gaseous emissions. Even in the absence of holes, some volatile organic compounds (Mc Watters and Rowe, 2009) and elemental Hg vapours (Guo et al., 2012) can migrate through the GM by molecular diffusion. Furthermore, diffusion can be the dominant gas transport mechanism for volatile compounds in soils. Therefore, gas diffusion can represent the governing gas transport mechanism for composite barriers (Xie et al., 2016).

In this study, during the assessment procedure of an actual contaminated site, the emissions of

Hg vapours from the ground surface were measured several times over more than one year to account for seasonal variability, using open dynamic flux chambers (Di Sante et al., 2016; 2017). In parallel, to evaluate the possible application of a capping system, a test section consisting in a composite GM-GCL barrier was installed in the site. The measurements were then repeated with on top of the barrier with the purpose to evaluate the screening effect against emission. The paper briefly describes the study site, the adopted experimental methods and discusses the obtained results in terms of Hg emissions with or without the screening barrier. The implications of the results in terms of risk assessment are discussed.

2 GAS TRANSPORT IN POROUS MATERIALS: BACKGROUND

Gas movement in a partially saturated porous medium occurs via advection (in response to pressure gradient) and diffusion (in response to concentration gradient). The governing parameters for the two mechanisms are the permeability to gas, k_g and the diffusion coefficient D_e . In the case of GCLs, several studies pointed out that gas permeability is strongly affected by the water content and the form of bentonite (granuled or powder) and that the gas flux is strongly reduced if the GCL is sufficiently hydrated (Bouazza, 2002). Conversely, the gas flux can drastically increase in case of desiccation, due to preferential pathways represented by desiccation cracks.

Diffusion of gas through a porous medium can occur according to two scenarios: at low saturation ($S_r < 85-90\%$, where S_r = degree of saturation), diffusion through the continuous air phase in the pore space is predominant: at higher saturation degree (as expected for ideal in-service condition of GCLs) the air phase becomes discontinuous and diffusion occurs both in residual air phase and in the liquid phase through a solubilisation process (Aubertin et al.,

2000). Gas flux by diffusion through a partially saturated porous medium under one-dimensional transport conditions, J_g is described by Fick's law:

$$J_g = -D_e \frac{\partial c}{\partial z} \quad (1)$$

where D_e is the gas diffusion coefficient; c is the gas concentration in pore air; z is the distance in the direction of transport. Experimental results and theoretical prediction based on empirical or semi-empirical models (Aachib et al., 2002; Rouf et al., 2016) show that D_e decreases of several order of magnitude with the increase in the saturation degree. Therefore, it is essential to maintain high level of saturation if gas control is one of the key objective of a single GCL barrier.

Xie et al. (2016) proposed an analytical model able to simulate vapour-phase 1-d diffusion of volatile compounds through composite barriers with a GM. Their simulations showed that composite barriers with GCLs provide a good diffusion barrier for benzene (a representative VOC), being the steady-state flux at the top of the barrier the smallest among five different covers analyzed. With regard to the influence of the saturation of the GCL, the simulations showed that when S_r increases from 0.2 to 0.5, the steady state flux of benzene decreases by a factor of 2.66 and the time required to reach steady-state flux increases by one order of magnitude. Therefore, if the GCL remains with high degrees of saturation, the flux of volatile compounds can be minimized.

3 STUDY SITE AND TESTING METHODS

3.1 Study site

The study was carried out in a brownfield site situated in Central Italy, where a fertilizers production plant was run for more than eighty years. The activity ceased more than 30 years ago. The industrial process required the

production of sulfuric acid, obtained by roasting raw pyrite mineral and resulting in large amounts of residue (pyrite ash). Over the years, large volumes of the residue were buried and are still present within the site, up to a depth of 2.5 m from the ground level (g.l), mixed in variable proportions with the local soil.

Pyrite ash is composed mainly of iron oxides (Domenech et al, 2017) but typically contains trace concentrations of heavy metals (Pb, Zn, Cu) and other potentially toxic elements (As, Hg). During a geo-environmental characterization aimed at the remediation and redevelopment of the site (14 hectares in size), more than 150 soil samples collected from 55 boreholes were analyzed for the relevant substances, as required by the national environmental regulation. In particular, the analytical results pointed out that the screening levels for Hg were exceeded at 18 out of the 55 investigated locations. Since some forms of Hg are considered volatile, in order to assess the risks connected to vapours inhalation, a speciation analysis of the Hg forms actually present in the site would be necessary (e.g. Saponaro et al., 2005). In alternative, the actual emission due to volatilisation from soil can be measured. In particular, flux chambers (USEPA, 1986) allow measuring the mass flux of a volatile substance from the ground surface. In this study, following the soil characterization, open dynamic flux chambers were used to measure outdoor emissions of Hg from the ground surface.

3.2 Flux measurements

The open dynamic flux chamber (FC) used in this study is made of Teflon™ and consists of a rigid ring (50 cm internal diameter and 20 cm in height) and of airtight top cap. To measure the flux from the ground, the top soil and grass were removed to obtain a flat root-free surface where the chamber was placed. The measuring chamber was isolated from external air by a moistened sand seal around the base.

Sampling was preceded by a purging stage, performed by pushing nitrogen for one hour at flow rate of 4 l/min into the chamber and letting air flow out. During sampling, which lasted 5 or 8 hours, inflow of nitrogen continued and the gas acted as a carrier fluid. Nitrogen was induced to flow through a vial by aspirating it with a pump at a flow rate equal to 0.2 l/min. The ratio between the outflow and the inflow rates was equal to 0.05. The vial contains a material capable of accumulating Hg (carulite®). Although static closed chambers are more commonly used to measure gas emission from engineered covers (e.g., Tassi et al., 2011), in this study, open dynamic flux chambers were used to measure the flux of Hg through a GM-GCL test section. To carry out the measurement, the FC was placed directly onto the GM layer (see 3.4) and the same procedure as described above was followed.

3.3 *Geosynthetic materials and composite barrier configuration*

The test section consisted by a square sample (0.6 m × 0.6 m) of GCL, overlain by a square sample (0.7 m × 0.7 m) of a polymeric GM. The GCL consisted of a polypropylene carrier nonwoven geotextiles (640 g/m²) and of PE woven cover geotextile (150 g/m²), held together by needlepunching and enclosing a layer of powder sodium bentonite (4,750 g/m²). The GM sample was 2 mm-thick HDPE commercial product, complying with the national recommendations for use in landfills (CTD, 1997).

The geosynthetic materials were put in contact with the in-situ soil, mainly to allow the GCL to hydrate with soil moisture and the bentonite to reach or approach equilibrium with the geochemical conditions (compatibly with the time scale of test duration) of the site. The surface soil (0.0-1.0 m from g.l.) at the selected location consisted of 78.7 % sand (2.00-0.06 mm), 12.8% silt (0.06-0.002 mm), 8.5% clay (<0.002 mm); chemical characterization showed

relatively high Hg concentration in the soil (~70 times the screening level) at shallow depth (0-0.40 cm from g.l.)

The geosynthetic materials were placed in an approximately square and shallow pit manually dug to the depth at which the soil was practically root-free (about 0.25 m from the ground level). The GCL was placed directly onto the soil (nonwoven geotextile facing downwards), and overlain by the GM (Figure 1a), with the aim of simulating the in-service hydration conditions. The GM was then covered with clean sand (20 cm) and with a plastic sheet, larger in size than the GM sample, to prevent direct infiltration of rainwater. The adopted thickness of covering soil is lower than the minimum required by building codes to protect mineral barriers in landfill covers from seasonal temperature excursion (≥ 1 m). However, as a barrier thickness ≥ 1 m would not be possible in the redevelopment project without excavating part of the in situ materials, the thickness of the covering layer (0.25 m) was selected to ensure a minimum confinement and simulate a shallow barrier.

3.4 *Monitoring and testing program*

The GCL and GM samples were installed on site as depicted in Figure 1a on July 11 2014. Subsequently, to monitor GCL hydration, the GM was periodically uncovered and partially lifted to cut a small piece of GCL from the edge of the larger sample, for water content measurement.

On May 20th 2015, the GM-GCL test section was carefully exhumed and reinstalled at very close distance onto the measurement spot that had previously tested positive for Hg emission. The layout shown in Figure 1a was restored, with the aim of reaching or approaching steady-state 1-d diffusion of vapours across the barrier. On June 12, 2015, in accordance with the schedule of the survey campaign, the measurement of Hg emission was repeated with the FC placed directly on top of the GM barrier,

centred with respect to the test section, as schematically illustrated in Figure 1 b. After the test, the GM was again covered as illustrated in Fig 1a. The measurement with the FC placed onto the GM were repeated on September 07, 2015; after that, the GM-GCL test section was removed and the flux from the base soil was again repeated on the same spot on September 09, 2015. The GCL was brought to laboratory and stored in an airtight plastic bag; after about one month, circular 101 mm diameter specimens were cut from the centre and the edge of sample and tested for permeability in flexible wall permeameter. Bentonite was sampled and tested for swell index as per ASTM D 5890.

4 RESULTS

4.1 GCL hydration

The results of water content, w , are illustrated in Figure 2. The w of the base in-situ soil was measured upon the first installation and was equal to 32 %. The w of the GCL (determined by oven drying) refers to the total solids (bentonite and geotextiles). The measured w of the GCL increased from initially unhydrated conditions ($w=12\%$) to $w=100\%$ (January 2015) during the humid season; in the subsequent

warm season, the w decreased to 45-40 % (May –June 2015) and then slightly increased to 54 % (September 2015). Possible reasons for the large variation in w of the GCL are: 1) the thin cover layer; 2) the specimens for w measurement were taken from the edge of the sample, more likely affected by changes in w of the surrounding soil. 3) the progressive exchange of sodium in bentonite for multivalent cations from soil, with concurrent decrease in water retention capacity.

A significant difference in w between the edge (35.5 %) and the center (60 %) of the GCL was observed on the specimens taken for permeability testing. Therefore, the in-situ w of the central part of the sample, presumably affecting the most the measured flux, could be underestimated.

4.2 Flux of vapors

The results of the measurements with FC are shown in Figure 3. With reference to the campaign of May-June 2015, the measured flux of Hg from soil was equal to $0.165 \mu\text{g}/\text{m}^2/\text{h}$. The flux measured with the barrier interposed between the soil and the chamber was $0.029 \mu\text{g}/\text{m}^2/\text{h}$. With reference to the September 2015 campaign, the flux measured with the barrier

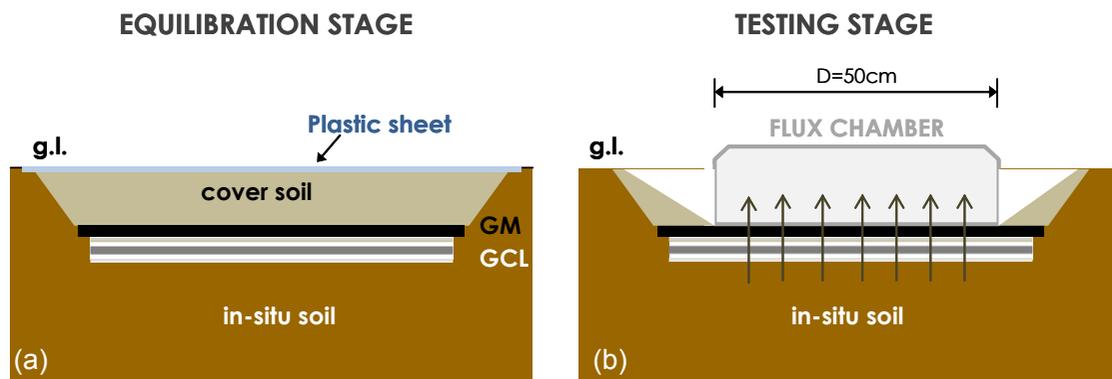


Figure 1. (a) GM-GCL barrier set up (a) for the hydration-equilibration stage, (b) during the measurement with the flux chamber (not to scale)

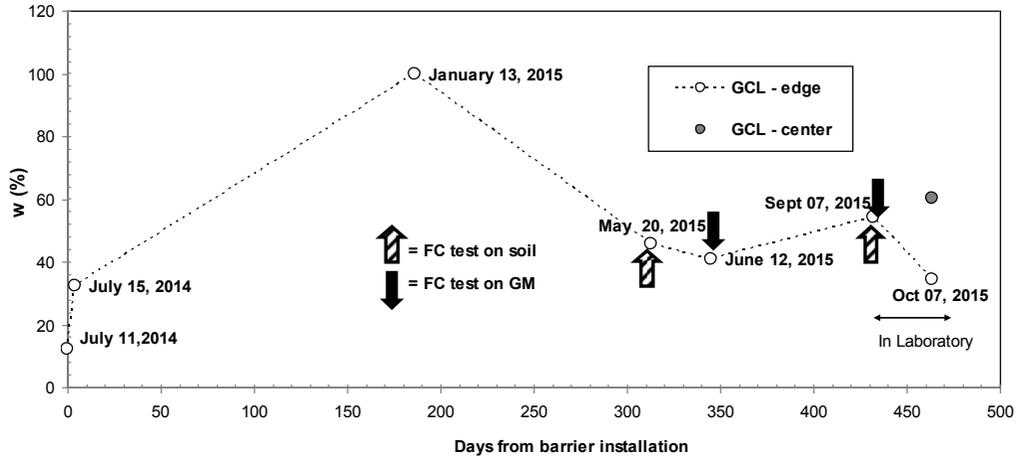


Figure 2. Water content of the GCL over time

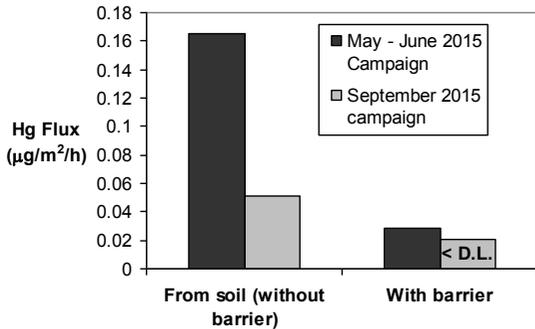


Figure 3. Measured flux of Hg vapours (D.L. = Detection Limit of the method)

was less than the detection limit of the method ($0.0205 \mu\text{g}/\text{m}^2/\text{h}$, also reported in Figure 3), whereas the flux from the soil, measured after removing the barrier, was $0.051 \mu\text{g}/\text{m}^2/\text{h}$.

With respect to September 2015 campaign, the tests were performed within a few days from each other, under very similar atmospheric conditions, therefore the reduction in the observed flux (by a factor >2.6) can be ascribed solely to the barrier. For the May-June 2015 campaign, the tests on soil and GM were delayed of about three weeks to allow diffusion through the composite barrier to approach steady-state (Xie et al., 2016). The base flux of Hg may have changed in the meantime, being influenced by several factors such as air and soil

temperature, barometric pressure and wind velocity (Di Sante et al., 2016). In any case, the peak daily temperature, T , and average barometric pressure, P , of the testing days were very similar ($T=28.6 \text{ }^\circ\text{C}$, $P=1008 \text{ mbar}$ and $T=30.1 \text{ }^\circ\text{C}$, $P=1016 \text{ mbar}$ on May 20, 2015 and June 12, 2015, respectively). Therefore, under the assumption of constant base emission from the soil, the reduction in the observed flux (by a factor of 5.6) can be ascribed to the screening effect of the barrier.

4.3 Post-test GCL properties

The saturated hydraulic conductivity, k , of the unused GCL and the exhumed GCL is shown in Figure 4. The k of unused GCL was $3 \times 10^{-11} \text{ m/s}$, typical for needle-punched GCL at relatively low stress level (Bouazza, 2002). The k of the exhumed GCL was $6 \times 10^{-10} \text{ m/s}$ (center) and $7.6 \times 10^{-8} \text{ m/s}$ (edge). Swell index results were 27 ml/2g for unused bentonite (compatible with sodium bentonite) and 9 ml/2g for exhumed bentonite, which indicates conversion into a less swelling form (e.g., into a divalent calcium form). The actual post-test cation population of bentonite was however not determined. While the k of the center of the sample is of the order of magnitude of intact GCLs with multivalent bentonite (e.g., calcium), the k of the edge of the

sample probably reflects the presence of desiccation cracks (e.g., Lin and Benson, 2000).

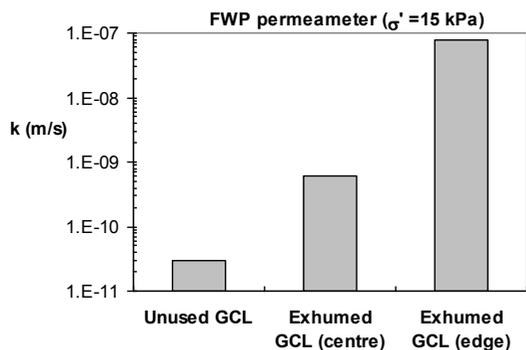


Figure 4. Saturated k of the unused and exhumed GCL

5 DISCUSSION

The obtained results suggested a good performance of the composite GM-GCL barrier in reducing the flux of Hg from the soil to the atmosphere, in accordance with the theoretical modelling by Xie et al. (2016). The reduction in the flux of vapours contribute to risk mitigation in the context of risk assessment. With regard to inhalation, calculation of risks for human targets is performed by entering the flux from soil into a box model (ISPRA, 2008), that simulates mixing with atmospheric air. For example, with reference to the May-June 2015 campaign, the calculations for C_{POE} yield 7.4×10^{-7} mg/m³ in case of free volatilisation, and 1.33×10^{-7} mg/m³ considering the flux through the barrier. Thus, as the flux of vapours and C_{POE} are linearly related in the box model, the reduction ratio is the same.

The results of the study also pointed out a relatively rapid (≤ 1.3 ys) conversion of sodium bentonite into a less swelling form upon field installation. Several studies have reported similar results with reference to landfills covers, (e.g., Meer and Benson, 2007). The particular subgrade (local soil mixed with process residues) and the thin covering layer adopted in this study may have favoured or accelerated cation exchange.

The type of adsorbed cations affects the water retention and field saturation of GCLs. According to simulations by Xie et al. (2016) concerning benzene the saturation degree of the GCL affects significantly the vapour flux for $S_r \geq 0.5$. Accurate determination of actual S_r of GCLs is difficult; apparent saturation, w/w_{ref} , (where w_{ref} is the equilibrium water content of the GCL hydrated under a given stress) has been used to assess saturation (Rouf et al., 2016). The final w of the GCL after permeability test (84%) was assumed as w_{ref} . The apparent saturation of the centre of the GCL sample under the field conditions was thus estimated as $0.6/0.84 = 0.71$.

6 CONCLUSIONS

Field measurements of Hg vapours emission from the ground surface and through a composite GM-GCL barrier test section were performed at an actual contaminated site using open dynamic flux chambers. Emissions through the barrier were measured by placing the flux chamber apparatus directly onto the GM. The results suggest that, under the adopted experimental conditions, the GM-GCL barrier significantly reduced the Hg emission from soil and may contribute in mitigating risks from volatilisation when used in caps A reduction in bentonite swelling capacity was observed, likely as a result of cation exchange. Therefore, to preserve the overall efficiency of the barrier, including the performance against gas diffusion, the design and installation conditions should ensure that the GCL remains sufficiently hydrated in the long term, e.g., by adequately thick covering layers (compatibly with redevelopment requirements), installation on wet subgrades, avoid direct exposure of the GM to sunlight during installation.

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