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Assessing natural clays of a contaminated site to stabilize and reduce the ecotoxicity of a coal tar

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Abstract

Stabilization/solidification is widely used for the immobilization of pollutants in matrices. This work addresses the effect of illite amendment to a liquid coal tar on organic compounds (OCs) immobilization, especially PAHs and BTEX. For practical purpose, illite was selected as raw clay material available on the coal tar contaminated site. Contaminants availability and ecotoxicity of clay/tar matrices at various ratios and considering several treatments were assessed. Varying the tar mass fraction from 1 to 0.12, strongly viscous pastes, pellets and powders were obtained successively, with minimal contaminant mobility observed for tar fractions ranging from 0.28 to 0.80. Pellets obtained for the tar fraction of 0.33 were particularly studied for toxicity tests, because of their ease of handling. Using the land snail *Cantareus aspersus* as an ecotoxicity probe, mechanisms of PAHs bioavailability considering several treatments were studied. Considering either land snails for direct contact or exposed to vapors, or *Lymnaea stagnalis* for contact with leachates, toxicity of matrices decreased with ageing or even better with incineration.

Keywords

Contaminated land; polycyclic aromatic hydrocarbons (PAHs); Solidification and stabilization; Risk assessment; Ecotoxicity

1. Introduction

Coal tars are hazardous waste materials originating from various industrial activities such as steel industry, former gas production or wood impregnation plants. These dense and viscous substances are complex mixtures that contain a high fraction of persistent organic pollutants (POPs), such as polycyclic aromatic hydrocarbons (PAHs), benzene derivatives (BTEX) and phenols. Pollutions are often the result of accidental spillages from tanks (INERIS, 2005; Mahjoub *et al.*, 2000) resulting sometimes in the release of dense non-aqueous phase liquids (DNAPLs) hard to remove. On the ground, unconfined tars represent a risk for health by physical contact and the release of toxic volatile compounds such as BTEX. These DNAPLs are also a permanent threat for groundwater quality, because of their density, their low biodegradability and the toxicity of POPs (Jurys *et al.*, 2013). In France, most pollution problems involve organic compounds (OCs) (about 70%) and PAHs compounds arise in 15% of the reported situations (MESD, 2013). Their levels in soil and water are regulated, because many of them are genotoxic and are classified as possible human carcinogens (IARC, 1987, 2002 and 2004; USEPA, 1999).

Possible management options are very limited because of the restrictive regulation on PAHs containing wastes and acceptance conditions. The most obvious are incineration above 800°C for energy production in cement kilns, disposal in landfills for solid materials, on-site oxidation (Milne *et al.*, 1986; Pironi *et al.*, 2009) and *in-situ* stabilization using costly sorbents like activated carbon (Cho *et al.*, 2009; Hilber and Bucheli, 2010). Their management often requires their handling and thus their solidification/stabilization (S/S), since for example landfilling requires the absence of free liquids. Sawdust is largely used for this purpose when incineration is selected, but the sticky material obtained does not reduce the emissions of OCs in the atmosphere. Then, huge volumes of foul-smelling highly contaminated material must be transported. Since the immobilization of liquids occurs mainly through capillary trapping and adsorption, the use of powdered natural sorbents like clays, abundant and easily available close to contaminated sites, is especially a way to be explored since OCs and clay are major base materials for cement production.

Contaminant mobility and toxicity are critical points when considering management options of coal tars. S/S is a fast process that uses additives to prevent the release in the environment of contaminants from hazardous matrices. S/S was found the best remediation strategy for source zones of PAHs contaminated sites based on analyses considering sustainability of technologies (Reddy and Chirakkara, 2013). Solidification aims at the production of monolithic blocks of solid waste with high structural integrity, whereas

stabilization reduces the mobility or the hazard of contaminants (Wiles, 1987). However, it is known that S/S is less compatible with organic liquids, since they are held by physical mechanisms onto surfaces and into pores (Trussel and Spence, 1994). Moreover, they may hinder reaction between binders to make hard materials, because of the dewatering of their surfaces. The binders used to develop strength, like Portland cement, are hardly efficient to prevent POPs leaching when directly mixed with highly HC-contaminated materials and stabilization agents must be added first. Mulder *et al.* (2001) demonstrated the stabilizing effects of clay and another sorbent on PAHs-leaching from weakly contaminated soils; unfortunately, no information is available about these additives. The use of hydrophobically modified clays to immobilize OCs is expensive. However, strong and irreversible interactions between natural clays and polar compounds in asphalt have been reported when clays are dehydrated first (Dean and McAtee, 1986; Marlow *et al.*, 1987). Thus, do polar OCs strongly bounded to soils like asphaltenes, that are largely present in coal tars, act as chemical binders between the rest of OCs and natural dry powdered clay materials ? Is that enough to make efficient S/S and reduce the toxicity of the tar ?

Management method of coal tars must not only facilitate their handling and/or recovery, but also limit their environmental impact both on terrestrial and aquatic organisms. Regarding the ecotoxicity assessment of coal tars, few data are available (Picot and Montandon, 2012) despite the fact that various bioassays are now available (Le Guédard *et al.*, 2017). The interest of bioassays to assess the efficiency of remediation method has been demonstrated (Chibwe *et al.*, 2015). Among soil invertebrates that can be used to assess the impact of solid contaminated matrices and/or to evaluate the efficiency and safety of waste treatment methods (ISO 15952; de Vaufléury, 2015), land snails are primary consumers living at the soil-plant-air interfaces. Their ability to accumulate pollutants is known, especially for metals; thus they can contribute to soil contaminants transfers to their predators (de Vaufléury, 2015). Relationships between toxicity and bioaccumulation in snail tissue was demonstrated for metals, but much more rarely for organic contaminants (Regoli *et al.*, 2006), despite the fact that their ability to reveal the genotoxic potential of soil contaminated with mineral coal tailings was evidenced (de Souza *et al.*, 2015). Snails suffer effects of pollutant from various sources (soil, air, food) and ways (cutaneous, digestive, respiratory), allowing experimental designs to explore the effect of exposure to polluted matrices by various ways. In the aquatic environment, the pulmonate snail *Lymnea stagnalis* is a widely encountered species that represents a significant biomass in freshwater ecosystems and is the subject of standardized bioassay (Ducrot *et al.*, 2014). The embryotoxicity of leachate can be evaluated

on embryos of *Lymnaea*, as early stages of development are often recognized to be highly susceptible to chemicals (Gomot, 1998) and also because hatching success is a key parameter for population development and maintain (Bandow and Weltje, 2012).

The present work aims to investigate the efficiency of natural clay widely available onto a contaminated former steelwork megasite to make S/S of the liquid coal tar. First, the effect of clay addition on S/S of the waste was studied considering mobility of the pure phase, leaching and evaporation. The ecotoxicity of the coal tar and a coal tar-clay in blend solid matrix was assessed using mollusks. Effects of ageing in the open air and incineration were assessed both through physicochemical measurements and with an *ex situ* bioassay using the land snail *Cantareus aspersus*. Measured endpoints for toxicity tests were survival, fresh mass variation and behavior. At the end of exposure, internal concentration of PAHs were measured to characterize their bioaccumulation potential in snails and possible mechanisms involved in toxicity. The freshwater snail *Lymnaea stagnalis* was used to assess the ecotoxicity of leachates.

2. Material and methods

2.1 Materials

Analytical reagents were n-hexane (Acros organics, 99%), concentrated nitric acid (VWR Prolabo, normapur), hydrochloric acid (Alfa Aesar, 37%), sodium hydroxide (Merck, > 97%), mineral oil (for the C10-C40 total petroleum hydrocarbon (TPH) index, LGC standards), n-pentane, n-hexane, isooctane, toluene and 1,2,4-trimethylbenzene (for the C5-C9 TPH index, Dr Ehrenstorfer Techlab), and Florisil (MgO-SiO₂, Macherey-Nagel GmbH&Co. KG). Standards for the 16 US-PAHs in hexane were obtained from LGC Standards. All solutions for analytical measurements were prepared with de-ionized water.

Coal tar (density: 1.2 g.cm⁻³) was collected in Hunedoara (Romania) from a former steelwork industry megasite used between 1884 and 1999. Many dumps and spillages of coal tar were present in the site, but the main dangers resulted from damaged open air tanks on the bare ground, that contained several hundreds cubic meters of liquid waste. The coal tar sample was collected from a damaged tank. The measured PAHs represent a large fraction of the C10-C40 TPH index present in that tar.

The site underground contained impermeable strata of Miocene clays. These formations were situated between 1 and 5 m below the artificial ground and had a thickness ranging from 8 to 32 m. The clayey material was collected from the 2-4 m horizon in a rift and let to dry for 1 year, before crushing and screening (125 µm). It was identified as illite from X-ray

diffraction (D8 Advance Brucker) and water-content (Karl-Fischer titrator) was found to be 4%. Specific surface area of illite is about $120 \text{ m}^2.\text{g}^{-1}$, its cation exchange capacity ranges from 10 to 40 cmol.kg^{-1} and its zero-point charge is 2.5 (Hussain *et al.*, 1996).

2.2 Experimental set-up and procedures

Weighed amounts of the liquid tar and of clay powder were thoroughly mixed manually with a stainless-steel blade in a glass cup. Specimens were characterized by their mass fraction of coal tar (χ_{tar}) in the binary mixture. The mobility potential of the liquid specimens was qualitatively assessed by spilling them, following their flow for 10 min. The mobility of volatile compounds in specimens was assessed through their loss of mass (analytical balance Mettler Toledo), while they were stored in an outside shelter with no direct solar light for 60 d in summer (min. 8°C , max. 39°C , average 21.3°C). The specimens were stored in PEHD cups covered with aluminum foils to prevent their physical contact with plastic. In addition, loss of mass was specifically studied for $\chi_{\text{tar}} = 0.33$, using volatilization in the open air under extraction hood for 3 wks. (Vol) and incineration (Inc) at 850°C for 45 min (oven Nabertherm P310). Alternatively, considering the effect of ageing conditions, some samples were stored under the same conditions, but in airtight 100 ml flasks for comparison with those let to open air. The leaching of OCs from samples was assessed at 20°C using demineralized water according to the NFX31-210 method. A given mass of sample was introduced into a 100-ml amber glass bottle equipped with a Teflon cap, before water was added at a water to sample mass ratio of 10. pH-dependent leaching tests were carried out from 3 to 12 using concentrated solutions of nitric acid or NaOH. The samples were shaken for a given time using a rotating table (250 rpm), then suspensions were filtered and filtrates were kept at 4°C for less than 7 d (Zhang, 2007), before chemical oxygen demand (COD), total organic carbon (TOC) and nitrogen (TON), PAH and BTEX quantification. All experiments were duplicated.

Ecotoxicity tests of solid matrices were assessed on sub adults *Cantareus aspersus* Müller, 1774 (syn. *Helix aspersa aspersa* O.F.) ($4.78 \pm 0.68 \text{ g}$). Snails were bred under controlled conditions as described by Gomot de Vaufléury (2000). They were exposed to the coal tar (Tar) or to the coal tar-clay mixture with $\chi_{\text{tar}} = 0.33$ immediately after preparation (J0) and after various alterations (volatilization (Vol), volatilization and crushing (Vol_d) and incineration (Inc)) (Table 1 SM).

For each matrix, three replicates of two snails were placed in 500 ml glass jars. For the control treatment (T), snails were exposed to the clay powder. Two modalities of exposure

were considered: snails in contact with the matrix under test (allowing cutaneous, digestive and respiratory exposure) or snails separated from the matrix by a layer of gravel to allow only exposure to the volatile fraction (g) (Table SM1). For each replicate, mass of the matrix was 15 g for the crude coal tar, 45 g for J0, 43 g for Vol and Vol_d and 33 g for Inc, to keep the same initial mass of coal tar. For the crude coal tar, only exposure to vapors was tested (Tar+g).

The snails were fed *ad libitum* with a plant-based food (Helixal®, SAS Antigny Nutrition, 85 510, France) placed in a Petri dish left on the bottom of the glass jar. The photoperiod was 18L/6D and the temperature was 20±2°C. The relative humidity was kept at 80–95%. Three times a week, the containers were cleaned, food was renewed and demineralized water was sprayed to prevent drying of soil.

Growth was assessed weekly by weighing the fresh mass (whole body) and measurement of shell diameter as described in ISO 15952. Survival and behavior were observed daily. Snails were considered as dead when they do not react to a stimulation of the foot or tentacles. All visible signs, such as lethargic behavior, extended edematous body (EE), and drooping eyestalk (DE), as previously described by Coeurdassier *et al.* (2001) were noted. Dead snails were frozen at -20°C. After 28 d exposure, which corresponds to the classical duration of the ecotoxicity test (ISO 15952), snails were placed in clean containers for a 48h period of fasting, frozen and kept at -20 °C. After thawing, the whole soft body was removed from the shell and the foot and the visceral mass separated.

Ecotoxicity of leachates was assessed on adult freshwater snails (*Lymnaea stagnalis*) sampled in the ponds of a producer of water plants (Acorus, 70700 Autoreille, France). They were placed in dechlorinated tap water and fed with lettuce. Photoperiod and temperature were the same as for *C. aspersus*. Egg masses were sampled and then incubated in glass Petri dishes (60 ×15 mm) in 10 ml of leachate, not renewed until hatching. Leachates from the clay/tar matrices ($\chi_{\text{tar}} = 0.33$) J0, Vol and Inc were used. pH of leachates were 6.7±0.1 (J0), 7.1±0.3 (Vol) and 10.9±0.2 (Inc). For each leachate, based on preliminary tests the final dilutions tested were 10, 15, 20, 25, 50 and 100% for J0, 10, 25, 33, 50 and 100% for Vol, and 10, 25, 50 et 100% for Inc. Dilutions were prepared using tap water. The hatching rate was determined after 25 d as well as abnormalities of embryos development (Gomot, 1998). At least three replicates were prepared for each leachate concentration.

2.3 Analytical Methods

The water content in coal tar was measured in triplicate using the Karl Fischer method. The volatile and semi-volatile fractions of petroleum hydrocarbons were measured as the C5-C9 (headspace/FID according to the XP T 90-124 norm) and C10-C40 (according to the NF EN ISO 9377-2 norm, see details in Hanafiah *et al.*, 2018) TPH indices, respectively. The lower heating value (LHV) of the coal tar was measured according to the ASTM D240 method. Metals in coal tar were assessed after their transfer in aqueous phase after putting it into contact with 1M HNO₃ solution for 24h under gentle stirring. After phase separation using a funnel, metals in the aqueous phase were measured using ICP OES (Spectroblue). COD measurements were performed according to standard NF T 90-101. TOC and TON in leachates were measured using a TOC-L instrument (Shimadzu). PAHs and BTEX were measured in leachates from pure tar and from the specimen $\chi_{\text{tar}} = 0.33$ immediately after preparation and 30 d later using GC-MS (Thermo Trace Ultra GC coupled to a Thermo DSQ mass spectrometer), Restek Rxi-5Sil MS (30 m \times 0.25 mm i.d., 0.25 μ m film thickness) and Varian VF-624ms (30 m \times 0.25 mm i.d., 1.4 μ m film thickness) columns, according to the XPX33-012 and ISO 17993 methods, respectively.

PAHs were analyzed in the viscera of *C aspersus* after death or after 28 d of exposure. Viscera were selected for analysis as they contain various organs, especially the digestive gland (Gomot de Vaufleury and Pihan, 2000), known as a major site of detoxification, metabolizing and bioaccumulation of PAHs-like contaminants (Regoli *et al.*, 2006).

After defrosting, viscera of a same replicate (1.5g fw) were collected, homogenized and extracted with 20 ml of n-hexane at 20500 rpm for 2 min using an ultra-turrax (Ika T25 model, France) in a 50 ml conical flask, then centrifuged at 14500 rpm for 15 min at 4°C. After this step, the upper organic layer was transferred into a glass flask. This extraction process was again repeated twice with n-hexane (1 min each time) and the resultant extracts were pooled with the previous one, reduced to about 0.3 ml using a Syncore Analyst system (Büchi, Rungis, France) for hexane evaporation at 156 hPa. The concentrated extract was transferred into a volumetric flask containing 50 μ l of a mixture of 3 deuterated internal standards (ISTD, benzo[a]pyrene-*d*₁₂, acenaphthene-*d*₁₀ and pyrene-*d*₁₀) at 2 mg.l⁻¹ and the final volume was adjusted to 1 ml. Samples were analyzed by GC-MS/MS (Agilent, Massy, France) equipped with a (5 % phenyl)-methylpolysiloxane HP5MS column (30 m \times 0.25 mm i.d., 0.25 μ m film thickness, Agilent 19091J-433).

For the extraction procedure validation of PAHs in viscera, calibration curves were previously established, for each compound using *blank* samples spiked at seven increasing

concentrations, by plotting the PAH/ISTD peak area ratios versus the PAH-concentration. The spiked calibration samples were treated following the sample extraction procedure previously described. Three experimental replicates for each concentration level were carried out. Validation method was carried out through linearity ($R > 0.99$), limit of detection (DL, Table 2) which was defined as 3-times the signal to noise ratio, precision expressed by relative standard deviation (RSD between 11 and 21 %) and trueness expressed as average recoveries (between 101 and 107%), for all concentrations levels. A quality control was injected once every ten samples.

2.4 Statistical analysis

For mass variation and PAH concentrations, the homogeneity and normality of data were tested using the Bartlett and the Kolmogorov-Smirnov tests, respectively, after a logarithmic transformation of data. A multiple comparison test (HSD Tukey) was then used to find significant differences. When prerequisites were not respected, a non-parametric test (Kruskal-Wallis) was used. For the mass evolution, according to the Akaike index (AIC), a random effect between replicates was not necessary.

Considering the embryotoxicity for *L. stagnalis*, the effect concentration that reduces the hatchability by 50% (EC50) value was determined with the Hill's model using the macro application Regtox free version EV7.04 in Excel. Hatching rates were compared using a X^2 test ($p = 0.05$). All statistical analyses were performed with the R software at a p-value of 5% (<http://www.R-project.org/>; version 3.0.3; libraries pgirmess, multcomp, nlme).

3. Results and discussion

Measured characteristics of the tar are summarized in Table 1. Coal tars are complex mixtures with different characteristics considering their mode of production and storage (Birak and Miller, 2009; Leonard *et al.*, 2010; Milne *et al.*, 1986). The liquid tar used in this study was neutral. However, variations of the COD in water vs. pH of the leaching solutions showed the presence of a substantial amount of asphaltene bearing carboxylate and phenolic and/or amine functional groups as previously reported (Barranco and Dawson, 1999; Zheng *et al.*, 2001). The water content of the tar is consistent with the lowest values of the reported range from 0.03 to 28% (Birak and Miller, 2009). Its lower heating value (LHV, Table 1) higher than 34000 kJ.kg^{-1} makes it attractive as substitute for fuel oil in cement works. The volatile organic compounds (VOCs, including naphthalene) amounted to about 65% of the

coal tar weight, whereas naphthalene and BTEX concentrations were higher than 84 and 8 g.kg⁻¹, respectively.

Table 1. here

The effect of clay addition for solidifying the liquid tar was studied to prevent risk of spillage during storage. Upon clay addition to the tar, different materials were obtained (Figure 1); A strong rheo-thickening behavior of the tar was observed. The liquid tar turned into a viscous paste having no more spilling potential when χ_{tar} reached about 0.4, and further into low-tack pellets for χ_{tar} lower than 0.35. Further on, powders were observed when χ_{tar} was lower than 0.27. These observations can be interpreted as follows: in powdered samples, OCs are mainly adsorbed by clay; once the sorption capacity is exceeded, free OCs are trapped by capillary condensation (Gelb *et al.*, 1999; Zhang *et al.*, 2017) resulting in the cohesive structure of pellets. At larger tar fractions, capillary forces lower as the inter-grain distance increases and free phase of OCs results in pasty or liquid samples. The shear-thickening behavior of concentrated dispersions is well-known and explained considering the basic Einstein's model for suspension of particles into Newtonian fluids (Couarraze and Gossior, 1983). Reported adsorption capacities of illite for pure neutral hydrocarbons are up to ten of mg.g⁻¹ with the decreasing order: n-decane, toluene and methyl cyclohexane (Zhang *et al.*, 2017). However, Powers *et al.* (1996) observed that among a variety of non-aqueous phase liquids (NAPLs) including pure solvents, crude oils and coal tars, the latter displayed the strongest ability to alter the wettability of sands from water to oil wet. The special ability of coal-derived NAPLs to alter soil wettability is believed to result from their polar fraction, and more especially from organic amines.

Figure 1: here

Considering toxicological risks associated to contaminant transfer into the gas and water phases contacting the contaminated materials, the state of the latter and the effects of further treatments are examined in the following.

Volatilization kinetics of OCs from matrices with different coal tar fractions were followed through the lost mass fraction of OCs initially present in samples (Fig. SM1). The process occurred on time-scale from a week to a season, depending on the contaminated materials. The theory used for calculations about contaminant mass transfer is detailed in supplementary material. The first order kinetics observed agree with the mass-conservation

equation. Experimental data were described considering the second Fick's law solved for semi-infinite media (eq. 6 in supplementary material). However, whereas accurate fits were obtained for solid matrices ($\chi_{\text{tar}} \leq 0.33$), non-random deviations were observed for semi-liquid materials. This is explained by variations in the diffusion coefficient of OCs caused by permeability reduction at the material/air interface with ageing. Variations of the fitting parameters extracted from the volatilization kinetics considering the mass fraction of tar are shown in Figure 2. First, it can be observed that the releasable fraction of OCs from the matrices is systematically lower than the fraction of VOCs in the coal tar (Table 1). An important fraction of VOCs, ranging from 30 to 80 %, was sequestered due to matrix effect and ageing. Especially, it is believed to be the result of a gas-tight interface resulting from the precipitation of the non-volatile OCs after VOCs removal (Luthy *et al.*, 1993). Second, a minimum for the releasable fraction of OCs is observed for the viscous paste ($\chi_{\text{tar}} = 0.4$). This amount decreased linearly with the fraction of clay in the mixture up to 60%, where a 50% reduction of releasable OCs was achieved with respect to pure tar. Above 60% of clay, the increase in the specific surface area of the solid materials resulted in an increase of VOCs mobility. Especially, the released OCs reached 165% of that for pure coal tar for the contaminated material with the highest mass fraction of clay ($\chi_{\text{tar}} = 0.12$), probably due to its highly porous structure. Considering the calculated ratio of the concentration boundary layer thickness to the square root of the diffusion coefficient, δ/\sqrt{D} , a maximum is seen for χ_{tar} in the range from 0.6 to 0.8. Considering that for given hydrodynamic conditions, the concentration boundary layer thickness is almost constant and is about 10^{-4} m (Labille *et al.*, 2007; Li *et al.*, 2005), the calculated diffusion coefficients ranged from 3.4×10^{-10} to 6.7×10^{-9} $\text{m}^2 \cdot \text{s}^{-1}$. The lowest diffusion coefficients were calculated for the semi-liquid materials (χ_{tar} ranging from 0.6 to 0.8), which were about 20-times lower than for the extreme matrices. This range corresponds to strongly viscous semi-solid matrices. In contrast, powdered matrices obtained for χ_{tar} lower than 0.27 showed slightly faster kinetic rates for VOCs transfer in the gas phase than for pure tar. This phenomenon is explained by the enhanced interfacial surface of the powdered matrices.

Figure 2: here

Leaching tests were carried out on freshly prepared matrices. All the liquid phases were amounted, but the presence of a pure phase of light OCs (1 mm thick) was observed

only when pure tar was contacted to water. Besides, the amount of dissolved OCs was followed considering several factors including tar to clay ratios and pH of the leaching solution. First, dissolution kinetics were followed both globally through COD and for specific compounds, considering pure tar and pellets ($\chi_{\text{tar}} = 0.33$). COD in leachates followed first-order kinetics and reached several hundreds to tens of hundreds mg.l^{-1} for pellets and pure tar, respectively (Fig. SM2). On the basis of COD measurements, equilibrium concentrations of OCs in the water phase were reached within a month, pointing out their slow diffusion through the viscous interfaces. However, regarding specifically BTEX, equilibrium concentrations were reached within 1 d. The effect of the fraction of tar in matrices on equilibrium concentrations of OCs is shown in Figure 3. As expected, the dissolved OCs concentration globally rises as the fraction of tar in samples. However, three main domains are observed, showing the interest of the compact solid matrices: first, a strong decrease is observed when χ_{tar} reaches about 0.3, where a transition occurs from powdered to more compact matrices; the TOC-variation vs. χ_{tar} is 10-times lower for the compact matrices, showing the lower availability of OCs in the latter. Second, an important raise in TOC is observed when χ_{tar} is larger than 0.4, which corresponds to a transition from solid to viscous liquid (Fig. 1). There, the slope for TOC-variations with χ_{tar} raised more than 3-times as compared to the compact solid matrices. However, despite reduction in OCs release from compact solid matrices, dissolved OCs concentrations in leachates remain as high as 100 mg.l^{-1} .

Figure 3: Here

The effect of clay amendment on the mobility of OCs is summarized in Figure 4. A risk of spillage still exists for matrices with χ_{tar} larger than 0.5.

Figure 4: Here

The effect of ageing on dissolved organic matter in leachates, and especially mobile toxic compounds like BTEX, depended strongly on storage conditions. When the matrices were stored in sealed boxes, only small reductions in COD of leachates were observed. More accurately, considering changes over 30 d for confined pellets, benzene and toluene remain unchanged, but ethylbenzene and xylenes were decreased by 30 to 50% (Table SM2), because their hydrophobic nature encouraged their sequestration within the matrix (Al-Turki, 2009). In contrast, samples let in the open air often changed in appearance with time as discussed

earlier, and COD in leachates decreased with aeration time. Considering the effect of an air exposure period up to 60 d before leaching tests, COD in leachates decreased linearly with exposure time for compact solid matrices (χ_{tar} from 0.25 to 0.4) by $5.5 \pm 0.5\%$, whereas the sum of the PAH concentration decreased from 4.9 to 0.7 mg.l⁻¹ and BTEX were no more detected. In contrast, for pure tar and powdered matrices, a stabilization of COD in leachates appeared after 50 d of air exposure and decreases amounted to 12 and 20 %, respectively. Strong decreases were observed after 30 d aeration, since the sum of PAH concentrations decreased from 13 and 13.3 to 5.7 and 0.7 mg.l⁻¹ for matrices where χ_{tar} was 1 and 0.33, respectively. Considering BTEX in pure tar, huge decreases in concentrations were observed for all molecules, while after aeration only benzene still exceeded the regulatory limit concentration (Table SM2).

Dissolved TOC-values increased slightly (< 20%) with the interfacial area between matrices and the leaching solution. Finally, after pellets ($\chi_{\text{tar}} = 0.33$) incineration, TOC in leachates decreased about 10-times, down to 16 mg.l⁻¹, whereas for pure clay they were 13 mg.l⁻¹. Comparison of the latter TOC-values in leachates shows that almost all the OCs were removed through incineration (Table SM3). The effects of the matrix, treatment and pH of the leaching solution on TOC and TON concentrations in leachates were measured (Table SM3). As expected, the clay material was poor in carbonaceous and nitrogenous organic matter. Furthermore, it presents small changes over the pH-range from 2.6 to 11.6. In contrast, dissolved organic carbon and nitrogen in leachates after contact with the tar are substantial and vary much with pH. Maxima of solubility are observed under strong acid conditions, but also at high pH for TOC. They are associated to the presence of carboxylic acids, phenols and to aromatic amines in coal tar (Birak and Miller, 2009; Seifert and Howells, 1969). Leachates from pellets displayed intermediate TOC-concentrations, whereas TON-concentrations remained very low. This behavior could be explained by electrostatic interactions between the negatively charged illite and organic cations.

Finally, considering standards for rejection of leachates from rainwater infiltration into the environment, ageing of the various matrices in the open air reduced the OCs concentrations that were conformed to the threshold values for PAHs and BTEX, but not for COD. Further treatment of pellets by incineration is required to agree with the regulation.

Considering the ecotoxicity of leachates on *L. stagnalis*, the hatching rate of control (T) was $93 \pm 8\%$. The hatchability of embryos exposed to the undiluted leachate of Inc varied strongly ($54 \pm 35\%$) and abnormalities of the development of the shell and the soft body were

observed, possibly due to the presence of metals. Indeed, embryos of *Lymnaea* are known to be sensitive to metals (Gomot, 1998; Bandow and Weltje, 2012). The EC50 (mean \pm CI 95%) were respectively $16 \pm 2\%$ and $27 \pm 1\%$ for the leachates of J0 and Vol. Thus, the ecotoxicity of leachates was strongly reduced by incineration, more efficiently than by the amendment of clay and/or the volatilization of the coal tar. The toxicity of leachate decrease in the order J0 > Vol > Inc, as the concentrations of TOC and PAHs do. It cannot be excluded that other toxic compounds may be involved in the toxicity, e.g. BTEX or heterocyclic PAHs (Blum *et al.*, 2011).

Regarding the effect of the pellets ($\chi_{\text{tar}} = 0.33$) on *C. aspersus*, the mortality was important and occurred rapidly for snails exposed by direct contact to J0 and Vol_d or to the volatile fraction of the crude coal tar (Tar+g) and (J0+g) (Figure 5, Table SM1). They showed similar symptoms: abundant production of mucus, narcosis, stop moving and feeding. After 28d of exposure, only snails exposed directly to the matrix after aeration (Vol) present a delayed growth (Figure SM3). Their shell did not get a lip, what corresponds to the end of the growth period and the maturation of sexual organs.

Figure 5 : Here

The first volatile fraction was the most toxic one. Kinetics of mortality were close for J0 and J0+g with a delayed mortality for snails exposed only to vapors. For Vol_d, the crushing of the matrix modified the bioavailability of the coal tar trapped within the pellets, enhancing the direct contact of snails with mobile contaminants and thus their mortality. This was not observed when pellets were not crushed (Vol, Fig. 5). Survival and growth of snails exposed to the matrix after incineration (Inc) were like control snails. In all cases, exposure to the volatile fraction of OCs was less toxic than exposure by direct contact (i.e. exposure by cutaneous and respiratory routes).

Coupling chemical and biological methods allowed to evidence that mixing the coal tar and clay limits its mobility and its ecotoxicity depending on the considered treatment. Simple volatilization for 3 weeks greatly reduces the impact of the matrix to snails, especially when pellets were not crushed. Incineration was found to be the most effective method to decrease the ecotoxicity of the coal tar-clay mixture, especially regarding the embryotoxicity of the leachate to *L.stagnalis*. For *C aspersus*, the toxicity of solid matrixes decreased in the expected order : J0 > Vol_d > Vol > Inc = T, showing that stabilization by clay followed by incineration is efficient to reduce the deleterious effects of coal tar. The experimental design

used allows to demonstrate the toxic effects of the volatile OCs to the land snail *C. asperses*. These effects were slightly reduced by clay amendment, but more after aeration of the pellets. To our best knowledge, it is the first time that toxicity of coal tar was demonstrated on snails. Indeed, if snails have been shown to be relevant to assess the effects of pollution by coal tar, it was mainly the genotoxicity of soil contaminated with mineral coal tailings that was measured (Leffa *et al.*, 2010; de Souza *et al.*, 2015; Filippi *et al.*, 2018). We also found that the cutaneous route of exposure to the volatile compounds, including PAHs, of the studied matrix is very important and can cause important deleterious effects. Similar observation was reported with dimethoate that is more toxic by cutaneous than by digestive exposure, whereas the opposite occurred with Cd (Coeurdassier *et al.*, 2001; Coeurdassier *et al.*, 2002).

In the viscera of *C. aspersus* the mean concentration of PAHs in control snails (T) were always lower than the detection and quantification limits (Table 2), showing that snails, food, control matrix and gravel were uncontaminated. There is no significant difference between internal concentrations of PAHs in control and Inc snails. The highest internal PAHs concentrations were observed for the most volatile ones, especially NAP, which were also the most abundant in the coal tar. According to Sverdrup *et al.* (2006), mainly the lightest PAHs and a medium lipophilicity reduced the survival and reproduction of collembolan; it is possibly what occurred for snails that survived only few days when exposed to the freshly prepared matrices. The heaviest PAHs were quantifiable only in snails exposed directly to the crushed pellets (Vol_d) that also present the highest PAH concentrations excepted for NAP. Internal concentrations of PAHs in snails directly exposed to J0 and Vol_d and to J0+g could be involved in the toxicity inducing snails' death after 3 to 6.5 d, respectively.

Comparison of internal PAH concentrations for the various ways of exposure is complicated by the fact that they have been measured after 3 to 28 d of exposure, depending on the survival of snails. However, the survival was considerably reduced for snails showing high PAH concentrations; These data are the first allowing to link survival and snail PAH internalization. Naphthalene concentration in snails exposed to the coal tar after various treatments ranged from 113 to 304 $\mu\text{g.g}^{-1}$ fw in the viscera, which is higher than those observed (about 110 $\mu\text{g.g}^{-1}$ fw) in snails caged for 1 month on a traffic-congested site in Italy. At this concentration, Regoli *et al.* (2006) reported DNA damages, but not increased mortality that remained lower than 10% on all the studied sites. Possibly other compounds may be involved in the observed toxicity, e.g. acenaphthene was not detected by Regoli *et al.* (2006), whereas its concentration was larger than 9 $\mu\text{g.g}^{-1}$ fw in the present study.

Table 2: here

4. Conclusion

Overall this work demonstrates the efficiency of clay amendment to ease handling of a liquid coal tar, reduce its mobility and its ecotoxicity to a terrestrial invertebrate, whereas it could be an interesting base material for cement production. While strongest mobility reduction of POPs was observed for blends with coal tar fractions ranging from 0.4 to 0.8, strongly viscous pastes hard to handle were obtained. Clay/tar pellets easy to carry were obtained for lower tar fractions, in the range from 0.27 to 0.33, but they could be more hazardous than pastes since contaminants mobility rises. Ecotoxicity measurements conducted on snails have shown the high toxicity of VOCs present in coal tar and risks associated to their transfer, especially in the atmosphere. However, a substantial fraction (30 to 80%) of volatile contaminants was sequestered thanks to matrix effects boosted by the precipitation of heavy OCs with ageing under aerated conditions. It also evidenced the impact of the size and way of preparation of the solid pellets; indeed, the ecotoxicity was amplified by a crushing of the pellets that allows the release of entrapped OCs. The complementarity of chemical/physical and biological approaches is clear.

The feasibility of using a natural material like clay present on site to stabilize a coal tar is demonstrated and the main constraint that must be considered to obtain a good compromise between contaminant mobility and possible handling were described. Considering this method for contaminated site management, it is advisable to prevent rainwater infiltration, capture vapors for one month at least, and make incineration at more than 800°C whenever possible to remove main hazards from these matrices.

Finally, the occurrence of chemical reactions induced that illite might induce deserves further study, since clay can catalyze polymerization of aromatic compounds like PAHs.

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666 Further reading

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675

Figure captions

Figure 1: Obtained materials for tar-clay mixtures at various coal-tar mass fractions.

Figure 2: Calculated values for released fractions of hydrocarbons (●) and ratios of the boundary layer thickness to the square root of the diffusion coefficient (○) as obtained from volatilization kinetics.

Figure 3: Dissolved organic carbon concentrations in leachates at the equilibrium vs. the mass fraction of coal tar in clay-tar matrices.

Figure 4: Mobilization of hydrocarbons in the atmosphere (●) and in water (■) for the various freshly prepared clay-tar matrices.

Figure 5: Mortality of *C. aspersus* snails exposed to different modalities: direct contact or contact with the volatile fraction only.

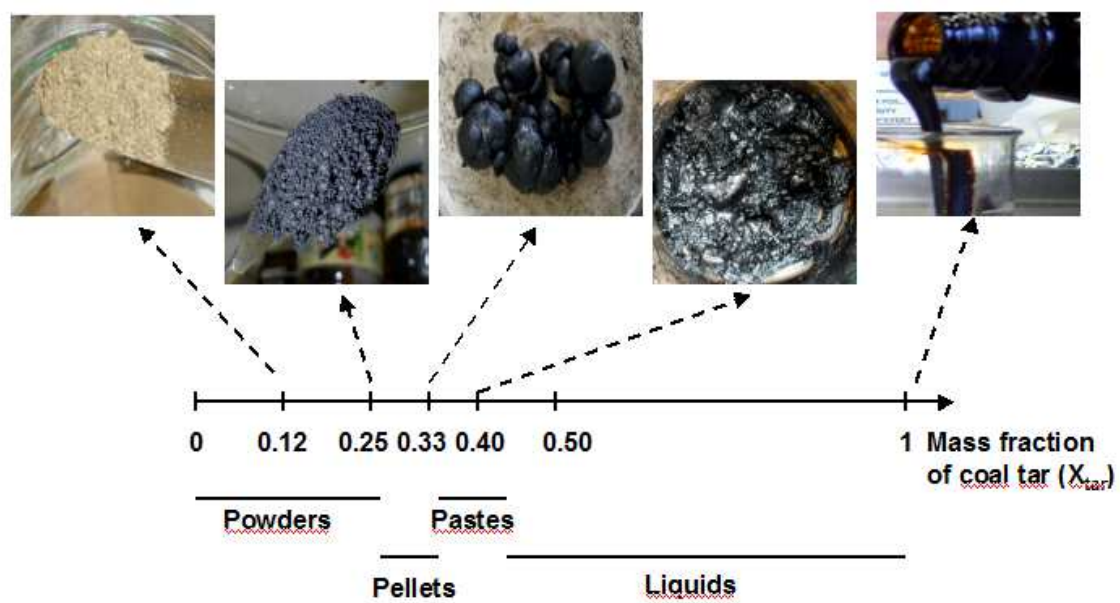


Figure 1

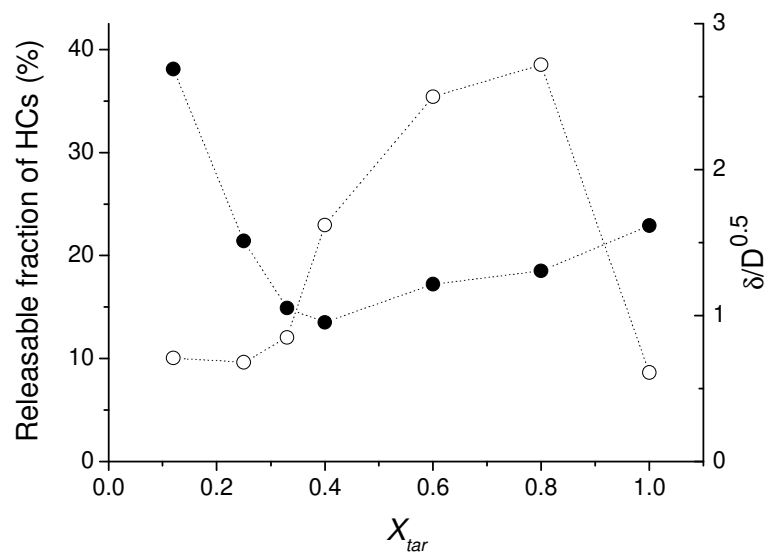


Figure 2

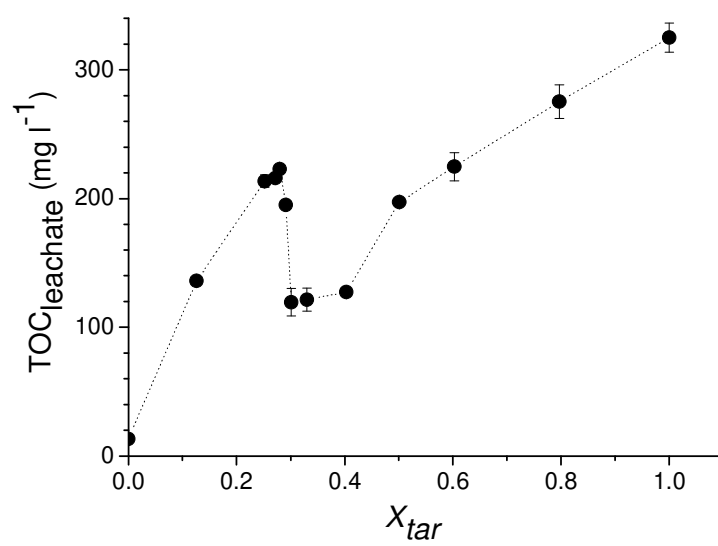


Figure 3

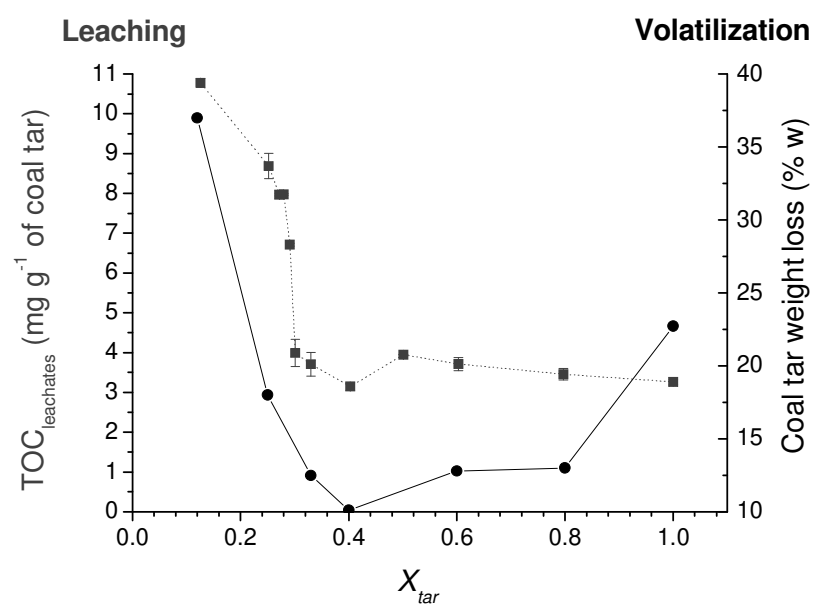


Figure 4

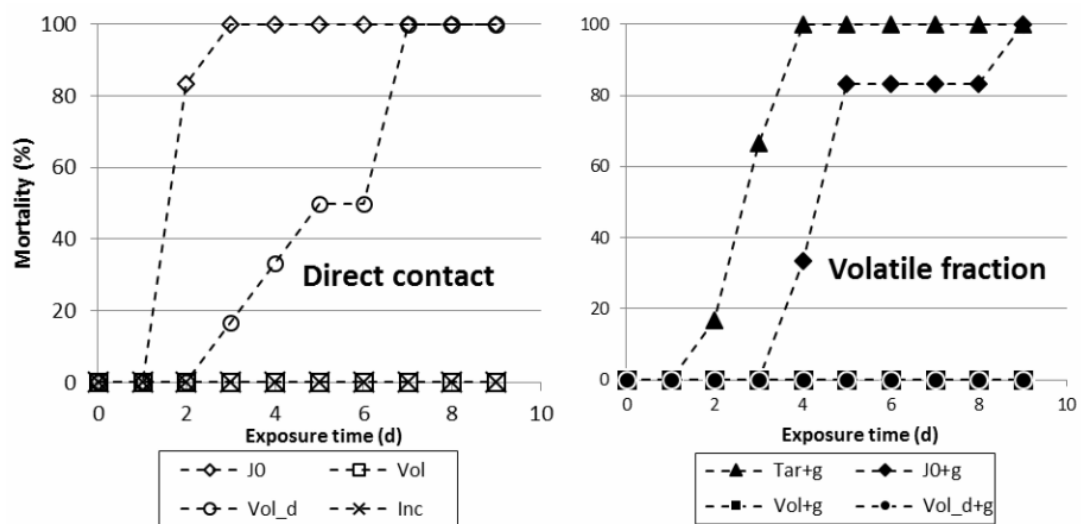


Figure 5

Tables

Table 1: Measured characteristics of the coal tar

Parameters	Values	Parameters	Values
pH	6.0	LHV ^a (kJ.kg ⁻¹)	37478
Water content (%)	0.035	BTEX (mg.kg ⁻¹)	
Petroleum indices		Benzene	2038 ± 864
(mg.kg ⁻¹)			
C5-9	567000	Toluene	2556 ± 956
C10-40	433000	Ethylbenzene	204 ± 44
PAHs (mg.kg ⁻¹)		Xylenes	3281 ± 556
Naphtalene (NAP)	84250 ± 3278		
Phenanthrene (PHE)	54513 ± 1067	Sum of BTEX	8079 ± 2297
Anthracene (ANT)	16827 ± 3108	Metals (µg.kg ⁻¹)	
Fluoranthene (FLT)	16675 ± 2977	Al	22.7 ± 4.1
Pyrene (PYR)	12452 ± 2103	As	< 3.4
Benzo(a)anthracene (BaANT)	8453 ± 1642	Cd	< 1.4
Chrysene (CHYChy)	9472 ± 3497	Cu	18.7 ± 3.3
Benzo(b)fluoranthene (BbFLT)	3320 ± 842	Fe	80.9 ± 15.7
Benzo(k)fluoranthene (BkFLT)	5738 ± 931	Mn	515.2 ± 98.2
Benzo(e)fluoranthene	3179 ± 630	Ni	2.8 ± 1.0
(BeFLT)			
Benzo(a)pyrene (BaPYR)	4262 ± 1119	Pb	7.5 ± 1.4
Indeno(1,2,3-c,d)pyrene (IcdPYR)	864 ± 145	Zn	25.3 ± 4.4
Sum of PAHs	221000 ± 21552	V	< 1.4

s.d. calculated as the 95% confidence level of three analyses. ^a LHV: Lower heating value of the coal tar

Table 2: PAH concentrations (ng.g⁻¹ FW) in the viscera of snails exposed to the various matrices

Modality of exposure			T	T + g	J0	J0+g	Vol_d	Vol_d+g	Inc
PAHs	DL	QL	(28)	(28)	(3)	(6)	(6,5)	(28)	(28)
NAP	4.9	16.3	NQ ^a	NQ ^a	207551 ± 45182 ^b	304215 ± 56333 ^b	113063 ± 22788 ^b	196 ± 261 ^c	NQ ^a
ACY	8.9	29.5	ND	ND	962 ± 299	1602 ± 146	2371 ± 240	NQ	ND
ACE	5.0	16.5	ND	ND	2351 ± 770	4137 ± 342	6274 ± 859	NQ	ND
FLU	3.3	11.0	ND ^a	ND ^a	2683 ± 1049 ^b	4406 ± 727 ^{bc}	9275 ± 1953 ^c	11.3 ± 2 ^d	ND ^a
PHE	4.1	13.7	ND ^a	ND ^a	2028 ± 842 ^b	2753 ± 718 ^b	9709 ± 1626 ^c	17.2 ± 6 ^d	ND ^a
ANT	4.3	14.3	ND ^a	ND ^a	261 ± 108 ^b	371 ± 131 ^b	1526 ± 386 ^c	NQ ^d	ND ^a
FLT	1.4	4.6	ND ^a	ND ^a	245 ± 85 ^b	276 ± 181 ^b	1439 ± 587 ^c	NQ ^d	ND ^a
PYR	1.3	4.2	ND ^{ac}	ND ^a	210 ± 59 ^b	228 ± 123 ^b	1115 ± 482 ^b	NQ ^c	ND ^a
BaANT	0.7	2.4	ND ^a	ND ^a	23 ± 7 ^b	23 ± 18 ^b	198 ± 164 ^c	2.6 ± 1,6 ^d	ND ^a
CHY	0.7	2.5	ND ^a	ND ^a	23 ± 6 ^b	27 ± 22 ^b	185 ± 133 ^c	3.8 ± 2 ^d	ND ^a
BbFLT	0.8	2.5	ND ^a	ND ^a	7.9 ± 5,4 ^b	8.1 ± 6,8 ^b	54 ± 48 ^c	3 ± 1,5 ^d	ND ^a
BkFLT	0.9	3.1	ND	ND	9.7 ± 8,5	8.9 ± 8,9	79 ± 69	3.9 ± 1,5	ND
BaPYR	1.5	5.1	ND ^a	ND ^a	8 ± 6 ^b	7.6 ± 6,7 ^b	66 ± 59 ^c	NQ ^{ab}	ND ^a
IcdPYR	0.7	2.3	ND ^a	ND ^a	NQ ^{bc}	NQ ^b	14 ± 13 ^c	NQ ^{ab}	ND ^a
dBahANT	1.2	4.2	ND ^a	ND ^a	ND ^{ab}	ND ^b	5.7 ± 5 ^c	ND ^{bc}	ND ^a
BghiPL	0.9	3.1	ND ^a	ND ^a	NQ ^b	NQ ^b	17 ± 15 ^c	NQ ^b	ND ^a

Duration of exposure before death is indicated in parenthesis. ND = not detected. NQ = not quantifiable. Values that share similar letters are not significantly different ($p>0.05$).

