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Rachida Bamze Attoumani, Annette de Vaufleury, Nadia Crini, Nicolas Fatin-Rouge. Assessing natural clays of a contaminated site to stabilize and reduce the ecotoxicity of a coal tar. *Ecotoxicology and Environmental Safety*, 2020, 190, pp.110081. 10.1016/j.ecoenv.2019.110081 . hal-02469705

HAL Id: hal-02469705

<https://hal.science/hal-02469705v1>

Submitted on 21 Jul 2022

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

3
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12
13 **Abstract**

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

27 **Keywords**

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

30

31 1. Introduction

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

46 Possible management options are very limited because of the restrictive regulation on
47 PAHs containing wastes and acceptance conditions. The most obvious are incineration above
48 800°C for energy production in cement kilns, disposal in landfills for solid materials, on-site
49 oxidation (Milne *et al.*, 1986; Pironi *et al.*, 2009) and *in-situ* stabilization using costly
50 sorbents like activated carbon (Cho *et al.*, 2009; Hilber and Bucheli, 2010). Their
51 management often requires their handling and thus their solidification/stabilization (S/S),
52 since for example landfilling requires the absence of free liquids. Sawdust is largely used for
53 this purpose when incineration is selected, but the sticky material obtained does not reduce
54 the emissions of OCs in the atmosphere. Then, huge volumes of foul-smelling highly
55 contaminated material must be transported. Since the immobilization of liquids occurs mainly
56 through capillary trapping and adsorption, the use of powdered natural sorbents like clays,
57 abundant and easily available close to contaminated sites, is especially a way to be explored
58 since OCs and clay are major base materials for cement production.

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

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

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

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

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

113

114 2. Material and methods

115 2.1 Materials

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

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

129 The site underground contained impermeable strata of Miocene clays. These formations
130 were situated between 1 and 5 m below the artificial ground and had a thickness ranging from
131 8 to 32 m. The clayey material was collected from the 2-4 m horizon in a rift and let to dry for
132 1 year, before crushing and screening (125 μm). It was identified as illite from X-ray

133 diffraction (D8 Advance Brucker) and water-content (Karl-Fischer titrator) was found to be
134 4%. Specific surface area of illite is about $120 \text{ m}^2\cdot\text{g}^{-1}$, its cation exchange capacity ranges
135 from 10 to $40 \text{ cmol}\cdot\text{kg}^{-1}$ and its zero-point charge is 2.5 (Hussain *et al.*, 1996).

136

137 2.2 Experimental set-up and procedures

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

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

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

167 were considered: snails in contact with the matrix under test (allowing cutaneous, digestive
168 and respiratory exposure) or snails separated from the matrix by a layer of gravel to allow
169 only exposure to the volatile fraction (g) (Table SM1). For each replicate, mass of the matrix
170 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
171 the same initial mass of coal tar. For the crude coal tar, only exposure to vapors was tested
172 (Tar+g).

173 The snails were fed *ad libitum* with a plant-based food (Helixal®, SAS Antigny
174 Nutrition, 85 510, France) placed in a Petri dish left on the bottom of the glass jar. The
175 photoperiod was 18L/6D and the temperature was 20±2°C. The relative humidity was kept at
176 80–95%. Three times a week, the containers were cleaned, food was renewed and
177 demineralized water was sprayed to prevent drying of soil.

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

187 Ecotoxicity of leachates was assessed on adult freshwater snails (*Lymnaea stagnalis*)
188 sampled in the ponds of a producer of water plants (Acorus, 70700 Autoreille, France). They
189 were placed in dechlorinated tap water and fed with lettuce. Photoperiod and temperature
190 were the same as for *C. aspersus*. Egg masses were sampled and then incubated in glass Petri
191 dishes (60 ×15 mm) in 10 ml of leachate, not renewed until hatching. Leachates from the
192 clay/tar matrices ($\chi_{\text{tar}} = 0.33$) J0, Vol and Inc were used. pH of leachates were 6.7±0.1 (J0),
193 7.1±0.3 (Vol) and 10.9±0.2 (Inc). For each leachate, based on preliminary tests the final
194 dilutions tested were 10, 15, 20, 25, 50 and 100% for J0, 10, 25, 33, 50 and 100% for Vol, and
195 10, 25, 50 et 100% for Inc. Dilutions were prepared using tap water. The hatching rate was
196 determined after 25 d as well as abnormalities of embryos development (Gomot, 1998). At
197 least three replicates were prepared for each leachate concentration.

198

199 2.3 Analytical Methods

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

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

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

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

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

241

242 2.4 Statistical analysis

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

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

254

255 3. Results and discussion

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

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

268

269 Table 1. here

270

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

290

291 Figure 1: here

292

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

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

301 equation. Experimental data were described considering the second Fick's law solved for
302 semi-infinite media (eq. 6 in supplementary material). However, whereas accurate fits were
303 obtained for solid matrices ($\chi_{\text{tar}} \leq 0.33$), non-random deviations were observed for semi-liquid
304 materials. This is explained by variations in the diffusion coefficient of OCs caused by
305 permeability reduction at the material/air interface with ageing. Variations of the fitting
306 parameters extracted from the volatilization kinetics considering the mass fraction of tar are
307 shown in Figure 2. First, it can be observed that the releasable fraction of OCs from the
308 matrices is systematically lower than the fraction of VOCs in the coal tar (Table 1). An
309 important fraction of VOCs, ranging from 30 to 80 %, was sequestered due to matrix effect
310 and ageing. Especially, it is believed to be the result of a gas-tight interface resulting from the
311 precipitation of the non-volatile OCs after VOCs removal (Luthy *et al.*, 1993). Second, a
312 minimum for the releasable fraction of OCs is observed for the viscous paste ($\chi_{\text{tar}} = 0.4$). This
313 amount decreased linearly with the fraction of clay in the mixture up to 60%, where a 50%
314 reduction of releasable OCs was achieved with respect to pure tar. Above 60% of clay, the
315 increase in the specific surface area of the solid materials resulted in an increase of VOCs
316 mobility. Especially, the released OCs reached 165% of that for pure coal tar for the
317 contaminated material with the highest mass fraction of clay ($\chi_{\text{tar}} = 0.12$), probably due to its
318 highly porous structure. Considering the calculated ratio of the concentration boundary layer
319 thickness to the square root of the diffusion coefficient, δ/\sqrt{D} , a maximum is seen for χ_{tar} in
320 the range from 0.6 to 0.8. Considering that for given hydrodynamic conditions, the
321 concentration boundary layer thickness is almost constant and is about 10^{-4} m (Labille *et al.*,
322 2007; Li *et al.*, 2005), the calculated diffusion coefficients ranged from 3.4×10^{-10} to 6.7×10^{-9}
323 $\text{m}^2 \cdot \text{d}^{-1}$. The lowest diffusion coefficients were calculated for the semi-liquid materials (χ_{tar}
324 ranging from 0.6 to 0.8), which were about 20-times lower than for the extreme matrices. This
325 range corresponds to strongly viscous semi-solid matrices. In contrast, powdered matrices
326 obtained for χ_{tar} lower than 0.27 showed slightly faster kinetic rates for VOCs transfer in the
327 gas phase than for pure tar. This phenomenon is explained by the enhanced interfacial surface
328 of the powdered matrices.

329

330 Figure 2: here

331

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

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

354
355 Figure 3: Here

356
357 The effect of clay amendment on the mobility of OCs is summarized in Figure 4. A
358 risk of spillage still exists for matrices with χ_{tar} larger than 0.5.

359
360 Figure 4: Here

361
362
363 The effect of ageing on dissolved organic matter in leachates, and especially mobile
364 toxic compounds like BTEX, depended strongly on storage conditions. When the matrices
365 were stored in sealed boxes, only small reductions in COD of leachates were observed. More
366 accurately, considering changes over 30 d for confined pellets, benzene and toluene remain
367 unchanged, but ethylbenzene and xylenes were decreased by 30 to 50% (Table SM2), because
368 their hydrophobic nature encouraged their sequestration within the matrix (Al-Turki, 2009).
369 In contrast, samples let in the open air often changed in appearance with time as discussed

370 earlier, and COD in leachates decreased with aeration time. Considering the effect of an air
371 exposure period up to 60 d before leaching tests, COD in leachates decreased linearly with
372 exposure time for compact solid matrices (χ_{tar} from 0.25 to 0.4) by $5.5 \pm 0.5\%$, whereas the
373 sum of the PAH concentration decreased from 4.9 to 0.7 mg.l⁻¹ and BTEX were no more
374 detected. In contrast, for pure tar and powdered matrices, a stabilization of COD in leachates
375 appeared after 50 d of air exposure and decreases amounted to 12 and 20 %, respectively.
376 Strong decreases were observed after 30 d aeration, since the sum of PAH concentrations
377 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,
378 respectively. Considering BTEX in pure tar, huge decreases in concentrations were observed
379 for all molecules, while after aeration only benzene still exceeded the regulatory limit
380 concentration (Table SM2).

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

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

400

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

404 observed, possibly due to the presence of metals. Indeed, embryos of *Lymnaea* are known to
405 be sensitive to metals (Gomot, 1998; Bandow and Weltje, 2012). The EC50 (mean \pm CI 95%)
406 were respectively $16 \pm 2\%$ and $27 \pm 1\%$ for the leachates of J0 and Vol. Thus, the ecotoxicity
407 of leachates was strongly reduced by incineration, more efficiently than by the amendment of
408 clay and/or the volatilization of the coal tar. The toxicity of leachate decrease in the order J0 >
409 Vol > Inc, as the concentrations of TOC and PAHs do. It cannot be excluded that other toxic
410 compounds may be involved in the toxicity, e.g. BTEX or heterocyclic PAHs (Blum *et al.*,
411 2011).

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

419

420 Figure 5 : Here

421

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

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

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

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

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

471

472 Table 2: here

473

474

475 4. Conclusion

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

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

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

498

499 Acknowledgement

500 Funding of this study was provided by an OSU Théta grant. The authors acknowledge
501 gratefully the municipality of Hunedoara, ECO-SID, Pr. Ioan Bica and Dr. D. Ganadataru for
502 their help in getting samples, Ms J. Brand for ecotoxicological tests, Dr V. Moutarlier for
503 XRD-analysis and Ms M. Remery for Karl-Fischer measurements.

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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.

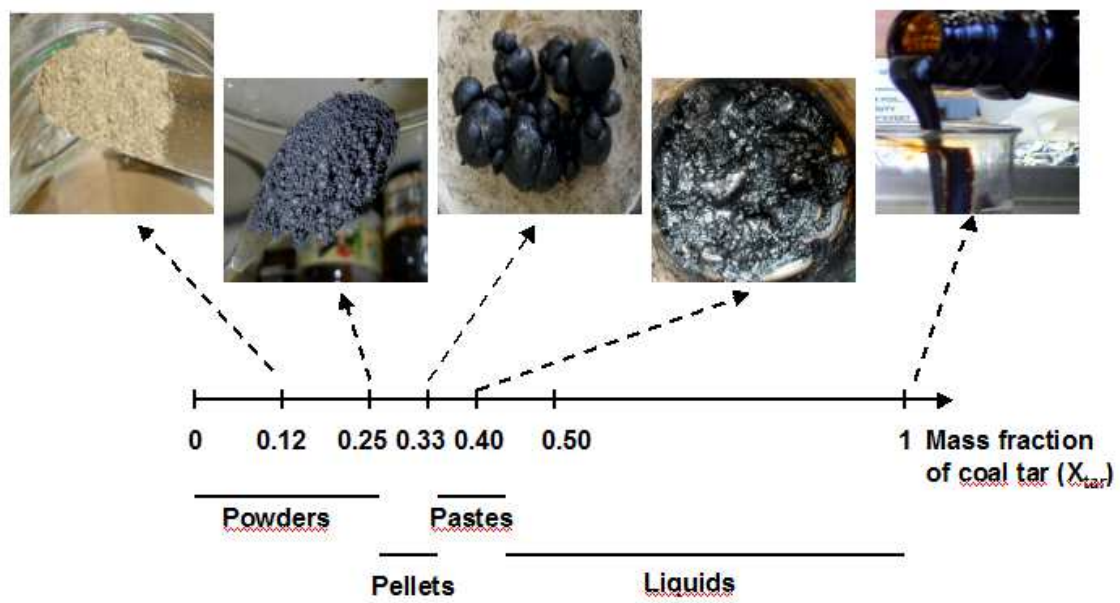


Figure 1

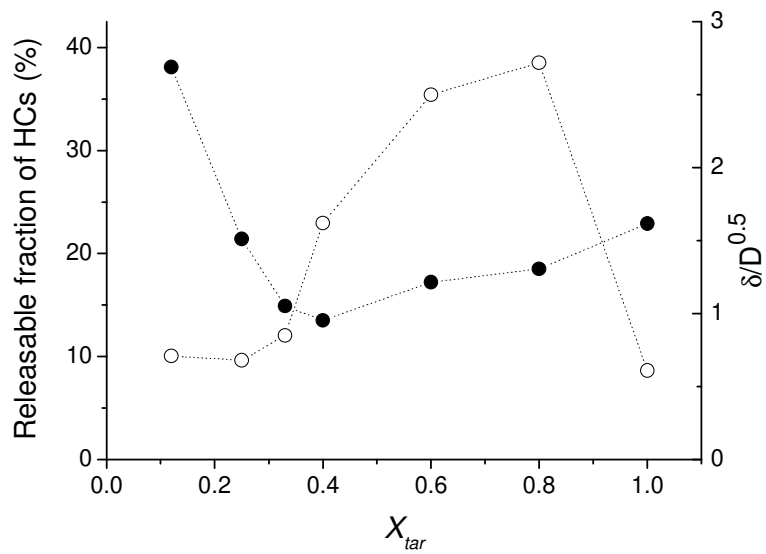


Figure 2

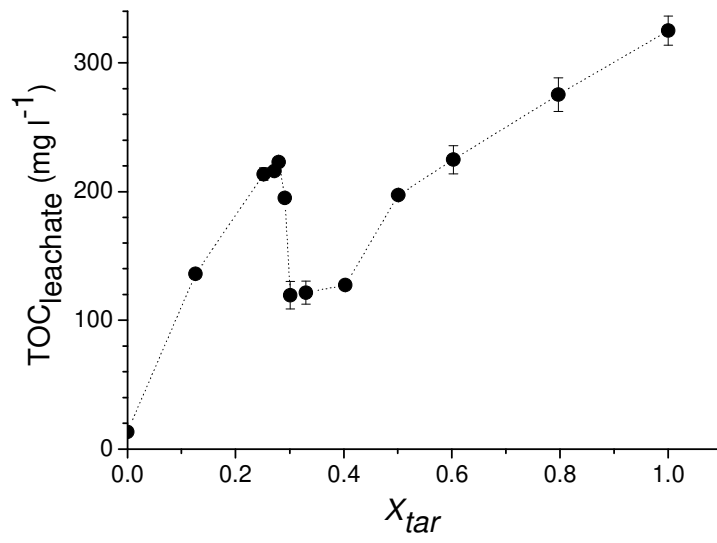


Figure 3

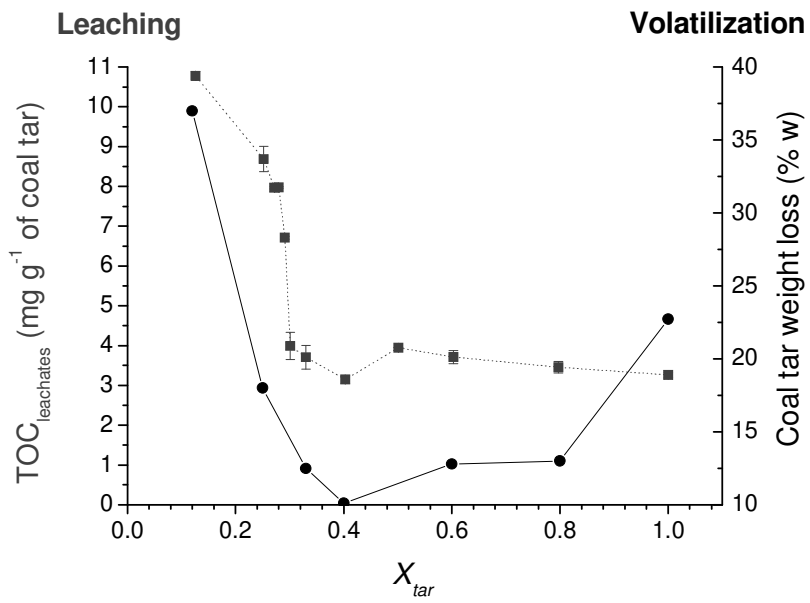


Figure 4

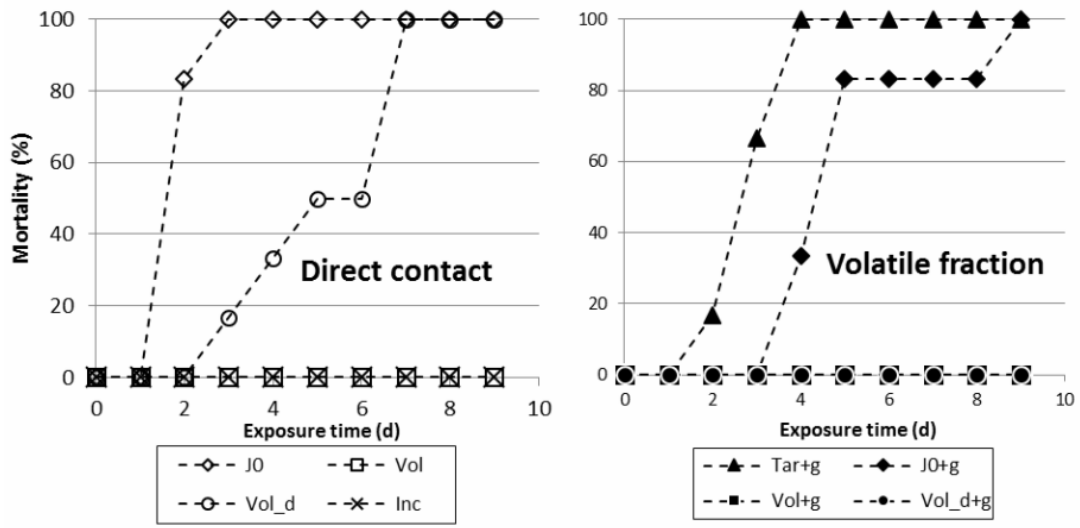


Figure 5

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

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 ($p > 0.05$).

