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TOTAL, DEGRADABLE, LABILE, PERCOLABLE, COLLOIDAL, SOLUBLE FRACTIONS OF HYDROPHOBIC ORGANIC CONTAMINANTS IN FIVE SEDIMENTS BEFORE AND AFTER AEROBIC AND ANAEROBIC MATURATION

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ABSTRACT

This study aimed to quantify the potential for degradation and emission of hydrophobic organic contaminants (HOC: PAHs, PCBs and TPH) from different sediment in oxic and anoxic storage conditions. Degradable fractions were measured by monitoring concentrations for 1.5 year under drained condition and one year under waterlogged condition. Fractions of hydrophobic contaminants with fast, slow and very slow desorption rate were measured by adsorption on Tenax TA. The concentrations of HOC emitted during a standard percolation column tests were measured and the dissolved organic matter was speciated following standardized protocols. The free dissolved concentrations fractions were determined by passive sampler LDPE. These levels were compared with concentrations calculated by the classical equations of solubility in water according to various parameters based mainly on the hydrophobicity of the contaminants. Total concentrations change very little during maturation. The majority of HOC is desorbable only at a slow or very slow rate. The concentrations of the percolates are controlled by colloidal organic material, and are therefore much higher than the dissolved one, and are on the other hand not well estimated by the current equations of solubility. It is clear from this work that the emission of sediment contaminants should be measured by percolation tests and not calculated by equations that don't take into account the colloidal organic matter fraction.

Keywords: sediment, organic contaminants, emission, colloidal organic carbon, passive sampler

1. MATERIAL AND METHODS

Five marine, canals and road storm basin sediments contaminated by total petroleum hydrocarbons (TPH), polyaromatic hydrocarbons (PAHs) and polychlorobiphenyls (PCBs) were studied in the laboratory for 18 months in aerated conditions (wetting/drying cycle at a moderate water content between 40 and 60% retention capacity) and 12 months in saturated conditions. The composition of the sediment is presented at Table 1.

Origin	Evry, Highway storm basin	Dunkerque, Marine harbor	Lens, Canal	Marseille, Marine harbor	Nimy Blaton, Canal
Localization	48°36'34.99"N 2°25'56.15"E	51°2'33.01"N 2°21'34.36"E	50°26'13.77"N 2°53'0.24"E	43°19'21.50"N 5°21'37.05"E	50°30'9.26"N 3°41'56.53"E
Water column (m)	2	8	7	10	6
TOC (%)	3.20	2.85	13.9	4.93	10.6
Σ 14 PAH ¹ ($\mu\text{g kg}^{-1}$)	2550	7710	45700	37100	3360
Σ 7 PCB ² ($\mu\text{g kg}^{-1}$)	75	541	539	3530	318
TPH C ₁₀ -C ₄₀ (mg kg^{-1})	4590	3170	9580	5340	6310
Texture	Sandy-silty	Silty-sandy	Clayey silt	Silty-sandy	Clayey silt

¹: naphthalene, acenaphthene, acenaphthylene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, chrysene, benz[a]anthracene, benzo[a]pyrene, indeno[1,2,3-c,d]pyrene, dibenz[a,h]anthracene, benzo[g,h,i]perylene

²: CB28, CB52, CB101, CB118, CB138, CB153, CB180

Table 1: Initial characterization of the five tested sediments including total organic carbon (TOC) content; contaminant concentration; total petroleum hydrocarbons (TPH) and texture

The so-called "labile" and "recalcitrant" Tenax extractable fractions were measured by 13 successive extractions during 61 days. The example of results for some PAHs is given at Figure 2. A model with three first order kinetics (fast, slow, very slow) was fitted to the experimental results. Fastly desorbing fraction is recognized in the literature as potentially biodegradable fraction [1]. Fractions slowly and very slowly desorbed are recognized as "recalcitrant", and not biodegradable.

Percolation tests according to CEN/TS 14405 with 10 cm diameter column are presented at Figure 1. The recommended flow (15 cm/day in an empty column) has been divided by 2 due to poor hydraulic conductivity of the sediments.

True dissolved concentrations of HOC were measured by diffusion in low density polyethylene (LDPE) strips for 46 days, with control of performance by reference substances and control of absence of depletion of the solid phase [2]. The speciation of colloidal organic matter was done according to ISO/CD 12782-4 and -5.



Figure 1: Percolation tests

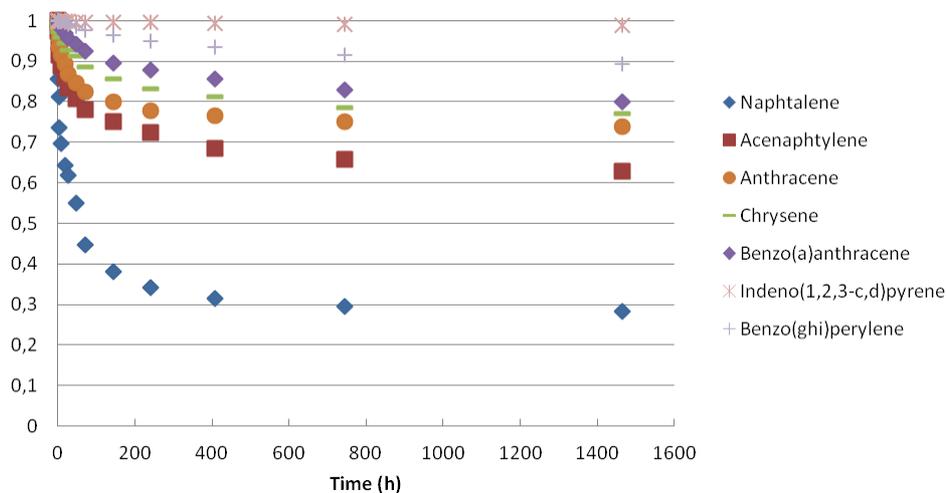


Figure 2: PAH extraction kinetics ($1-S_t/S_0$) for sediment of Lens

2. RESULTS

Effects of maturation on COH content

For the aerated condition, the pHs were stable and the ORP reached oxic values after 6 months.

In aerated condition, the TPH total contents were reduced by 4 to 10% (average of 9 %) during 18 months. Hydrocarbon maturity indices increased (the hydrocarbons were more weathered, results not shown).

The contents of total PAHs and PCBs did not decrease during maturation. However, PAH concentrations decreased by 13% on average for the lightest PAHs and some sediments (naphthalene 3 sediments, acenaphthylene 4 sediments, acenaphthene 3 sediment, fluoranthene 1 sediment) and did not decrease for all other PAHs. PCBs levels did not decrease. In saturated conditions, no significant changes in concentrations were observed for the three families for one year.

Speciation of the contaminants: biodegradable (fast desorbing), labile (slow desorbing) and recalcitrant (very slow desorbing) fractions

Three fractions with different desorption rate by Tenax are obtained (Figure 3). Caption of Figure 3 refers to the time to desorb 90 % of each fraction to the Tenax. The fast fraction (24% of the total content of PAH in Marseille) is considered as the maximum biodegradable concentration. The slow fraction is for PAHs in Marseille 17% of the total content, and the very slow fraction is 59% of the total content. Fast desorbing fraction for different PAHs and PCBs are given at Table 2.

In the literature, the parameters governing the desorption rates and the fractions could be linked to the content or amorphous condensed organic matter, sediment texture, the grain size, porosity, age of the pollution, composition of the solution, the aqueous diffusion and solubility of the compounds) [3]. We have found no correlation between the sediment texture and organic composition and the desorption rates (results not shown). This raises the question of the reliability of the models used.

For TPH, the mean fast fraction is 8 % of the total content, the slow fraction is 10 % and the very slow fraction is 82 % of the total content.

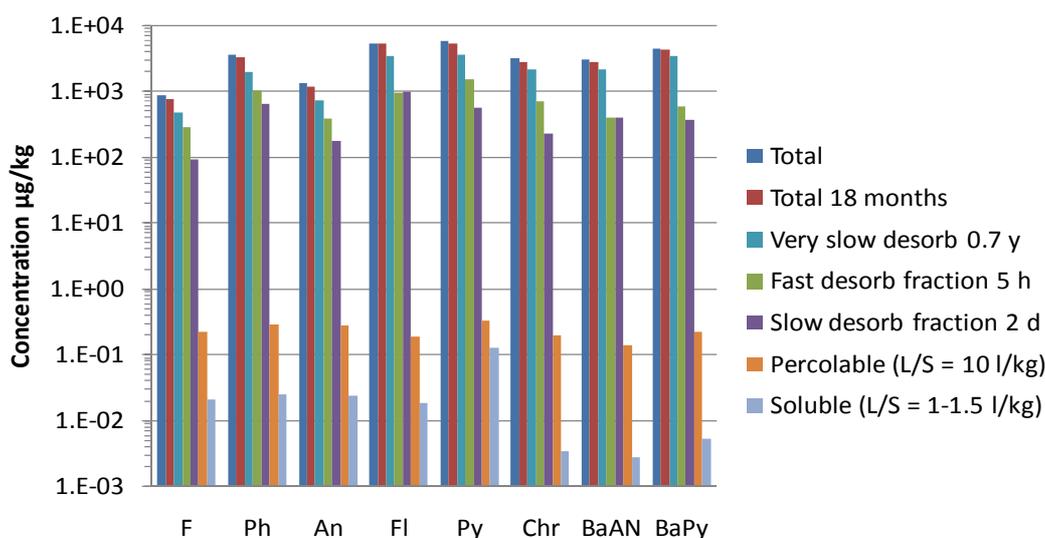


Figure 3: Total, total after 18 months, Tenax very slow, fast and slow desorbing fractions, dissolved percolable contents and free soluble contents of PAH for sediment of Marseille

PAHs	Min	Max
Naphthalene	0.25 (NB)	0.41 (Evry)
Acenaphthylene	0.19 (Lens)	0.34 (Evry)
Acenaphthene	0.21 (NB)	0.39 (Evry)
Fluorene	0.14 (NB)	0.32 (Evry)
Phenanthrene	0.12 (NB)	0.35 (Evry)
Anthracene	0.18 (NB)	0.28 (Evry)
Fluoranthene	0.10 (NB)	0.27 (Evry)
Pyrene	0.14 (NB)	0.33 (Evry)
Chrysene	0.13 (NB)	0.22 (Evry)
Benz[a]anthracene	0.06 (NB)	0.19 (Evry)
Benzo[a]pyrene	0.07 (NB)	0.16 (Lens)
Indeno[1,2,3-c,d]pyrene	0.08 (NB)	0.15 (Evry)
Dibenz[a,h]anthracene	0.08 (Mars)	0.22 (Evry)
Benzo[g,h,i]perylene	0.03 (Mars)	0.12 (Evry)

Table 2: Fast desorbing fraction for PAHs and PCBs (minimum and maximum relatively to the total content)

Speciation of contaminants: percolation tests

The concentrations and cumulated concentrations of PAHs measured in the 7 fractions of the European percolation test are presented at Figure 4 (some examples) and Table 3 (5 sediments and all the PAHs).

The cumulative amount of percolated contaminant represents between 0.04% (PAHs) and 0.52 % (PCBs) of the total contaminant concentrations. The emission is controlled by the presence of colloidal dissolved organic carbon (DOC), which has been split into individual components (fulvic acids, humic acids HA, hydrophilic organic carbon HON, and hydrophilic neutral organic carbon) according to standard ISO/CD 12782-4 and -5. The lightest PAHs ($3.37 < \log Kow < 5.22$) and PCBs are correlated with neutral hydrophilic organic carbon HON. PAHs with $\log Kow > 5.22$ are correlated to the humic acids HA.

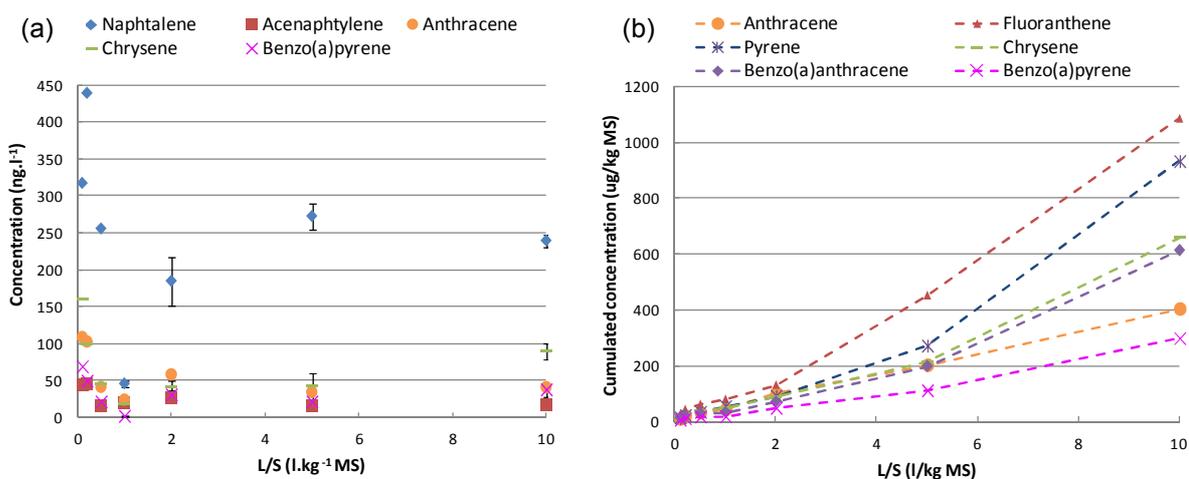


Figure 4: (a) Concentrations and (b) cumulated concentrations of some PAH during percolation test of the sediment of Lens

PAH	Marseille	Dunkerque	Lens	NB	Evry
Naphthalene	830.7 ± 15.7	5274.4 ± 156.7	2076.0 ± 124.2	763.9 ± 74.56	1181.8 ± 102.5
Acenaphthylene	273.3 ± 22.1	150.3 ± 12.7	172.2 ± 3.9	179.1 ± 4.7	150.9 ± 10.5
Acenaphthene	231.5 ± 7.9	159.5 ± 23.1	301.8 ± 41.8	176.8 ± 10.5	143.9 ± 8.5
Fluorene	228.1 ± 2.5	188.9 ± 17.0	290.6 ± 28.8	181.7 ± 12.3	181.3 ± 13.3
Phenanthrene	286.9 ± 6.7	199.1 ± 21.5	453.7 ± 31.1	190.7 ± 8.5	177.5 ± 12.3
Anthracene	272.5 ± 3.4	309.5 ± 26.7	404.1 ± 39.1	196.9 ± 5.2	n.d
Fluoranthene	258.3 ± 13.7	249.4 ± 49.5	1084.4 ± 91.3	152.6 ± 23.1	302.7 ± 17.6
Pyrene	330.3 ± 63.8	420.5 ± 54.5	931.1 ± 84.6	176.4 ± 20.8	145.6 ± 6.7
Chrysene	197.6 ± 10.0	358.2 ± 36.9	658.3 ± 75.4	233.8 ± 10.7	n.d
Benz[a]anthracene	137.9 ± 11.7	303.9 ± 29.2	612.6 ± 53.6	24.7 ± 1.7	n.d
Benzo[a]pyrene	226.9 ± 34.1	n.d	298.2 ± 14.2	26.8 ± 1.5	n.d
Indeno[1,2,3-c,d]pyrene	278.1 ± 38.5	n.d	n.d	n.d	n.d
Dibenz[a,h]anthracene	94.2 ± 12.0	n.d	n.d	n.d	n.d
Benzo[g,h,i]perylene	378.0 ± 28.2	n.d	n.d	n.d	n.d
Σ 14 PAH	4023.6 ± 102.3	7613.7 ± 210.3	6878.9 ± 184.6	2303.4 ± 89.6	2283.7 ± 149.8

Table 3: Cumulated percolated concentrations (ng.kg-1) of PAHs for the five sediments

Storage 18 months in aerated laboratory conditions reduced the overall emission of PAHs by 40%, TPH by 60%, and the PCBs concentrations fall below the limit of quantification. The emission is reduced by 50% for the lightest PAHs and 100% for compounds with a log K_{ow} > 5.1. The concentrations of humic acids HA in the percolates after maturation are below the limit of quantification, while the concentrations of dissolved organic carbon increased (results not shown). Speciation of dissolved organic matter thus explained the mobilization of hydrophobic contaminants.

Speciation of contaminants: concentration dissolved in water

Dissolved concentrations were measured by passive samplers (adsorption on strips of LDPE at 13 different times during 46 days in the laboratory) with levels of up to below 10-11 g/l for PAHs and 10-12 g/l for PCBs (Figure 3, case of Marseille). The dissolved fraction is 0.0037 % (PAHs) and 0.0005 % (PCBs) of the total concentration. Details can be found in [4]. These low levels are largely explained by the presence of a "natural" adsorbent, the soot (quantified as black carbon) (results not shown). The resulting K_d values are presented at Figure 5.

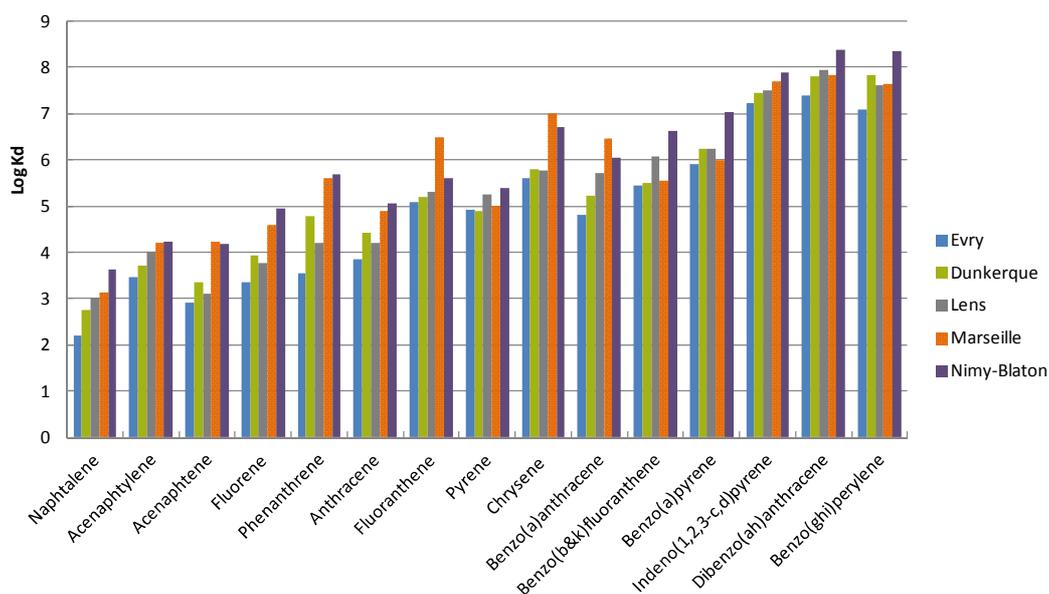


Figure 5: Partition coefficients of PAHs for the five sediments

PAHs are associated with each 20% or more (for naphthalene) to 99.9% or more (for the highest molecular mass) to organic colloids (Figure 7, case of PAHs of Nimy-Blaton). When detected (sediment Marseille and Lens), the PCBs 28 and 52 are associated with 81% or more to the colloidal fraction. The free fraction decreases as the hydrophobicity of PAHs and PCBs increases.

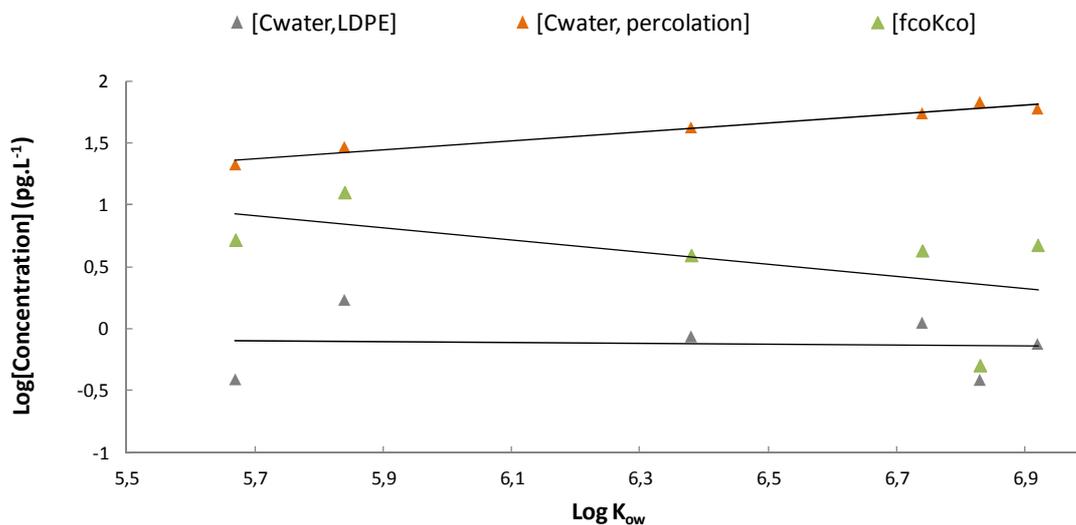


Figure 6: Concentrations of PCBs in pore water obtained by passive sampler (Cwater LDPE), percolation (Cwater, percolation) and by calculation with Kd (fcoKco) for sediment of Marseille

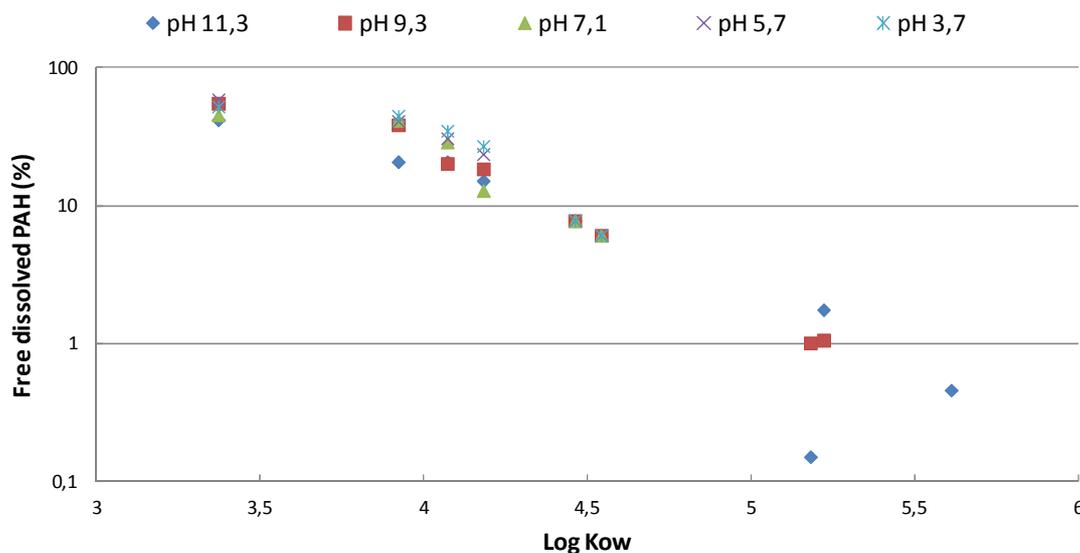


Figure 7: Proportion of free dissolved PAHs in leachate at different pH (sediment of Nimy-Blaton)

3. CONCLUSION

This study calls into question the use of total concentrations of contaminants instead of dissolved concentrations to assess the ecological risk. Sediments have inherent significant sorption properties for HOC. Despite high levels of contamination, the concentrations in the pore water are very low. The presence of thermally altered aged materials or hydrocarbon phase also leads to restrict the emission of hydrophobic contaminants to the environment.

It is shown that:

- Hydrophobic organic compounds of these old sediments are poorly or not degradable in 18 months under aeration;
- The fraction degraded in 18 months in the laboratory is moderately consistent with so-called "fast" (Tenax extraction) fraction for PAHs and not for PCBs;
- The percolable fraction is significant (between 0.04 % and 0.52 % of the total solids phase PAHs and PCBs) and is totally controlled by the colloidal organic carbon, and in particular humic acid and hydrophobic neutral organic carbon fractions. It is greatly reduced by the ripening;
- The free dissolved fraction (between 0.0037 % and 0.0005 % of the total solids phase PAHs and PCBs) can be measured either by the (time-consuming and long lasting) method of passive samplers, or by a simple method of flocculation of colloids in the eluates with aluminum sulfate;
- The approach of emission concentrations by solubility equations underestimates largely the concentrations by not taking into account the vectorization by organic colloids. The measurement must prevail on modeling to evaluate the emission of contaminants sediment, mainly due to colloidal emission.

The transfer of contaminants vectorized by colloids in saturated or unsaturated soil should be studied by field work.

Today the regulatory classification of these materials is achieved by the total amount of organic contaminants, despite very slowly desorbable fraction prevails, and that a very little part of the HOC can be mobilized.

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