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Fate of organic pollutants after sewage sludge spreading on agricultural soils: a 30-years field-scale recording

¹Dominique Patureau, ¹Mireille Laforie, ²Eric Lichtfouse, ³Giovanni Caria,
⁴Laurence Denaix, ⁵Jens Ejbye Schmidt

¹INRA, UR050, Laboratoire de Biotechnologie de l'Environnement, Avenue des Etangs, Narbonne, F-11100, France, patureau@ensam.inra.fr; ²INRA-CMSE, Dijon, France; ³LAS INRA Arras, France; ⁴INRA UMR 1220 Domaine de la Grande-Ferrade, Bordeaux, France; ⁵Institute for Environment & Resources, Technical University of Denmark, Lyngby, Denmark

Abstract : Toxic organic compounds, such as the surfactants linear alkylbenzene sulfonates (LAS) and nonylphenol polyethoxylates (NPE), Polycyclic aromatic hydrocarbons (PAH) and residues derived from plastics (PAE-phthalates) end up in sewage sludge. In order to evaluate and quantify the potential environmental risks associated with the xenobiotic introduction into biological life cycle, the EU BIOWASTE project (QLK5-CT-2002-01138) devotes one task to the study of the fate of xenobiotic in a sandy soil after sludge spreading on a 30-year field-scale record experiment. Experimental maize crop fields from Bordeaux (France) have been amended with 100 tons per hectare each 2 years from 1974 to 1992. From 1992 to 2004, the fields were maintained and cropped with maize. This experiment shows that the concentration fluctuations in the sludge amended soil follow the same pattern of those in the sewage sludge showing that there is a real impact of the present xenobiotics in the sewage sludge on the concentration of the xenobiotics in the soil. Nonetheless, 12 years after the last addition of sewage sludge, the residual concentrations remain from 2 to 10 times higher than the content of the control soil, even though these levels are inferior to the Predicted Non Effect Concentration (PNEC). Only LAS level went back to the level in the control soil. However, only the LAS concentration is above the PNEC during all the experiment due to the very high level of LAS in the sludge (20 g/kg dry weight). These results show that even though this compound is much more degradable than NPE and PAE, it may have a long term effect in soil if high quantities are spread. To conclude, this study underlines the importance to fix maximum level for xenobiotic compounds for sewage sludge spreading on agricultural land, and also the central role of the sewage sludge processes in reducing the xenobiotic concentrations before spreading.

Keywords : biodegradation, bound residues, long term effect, sludge disposal, xenobiotic

Introduction

The environmental burden of organic pollutants contained in sewage sludge, after spreading on soil, depends on numerous factors related to the soil itself, the sludge (nature and way of spreading) and the chemical considered. A review concerning priority organic pollutants has recently been published by the European Union (EU, 2001).

Generally, nonylphenol polyethoxylates (NPE) are degraded in the soil to nonylphenol (NP), which adsorbs to soil particles. Under aerobic conditions, half-lives of these compounds are short. Half-lives for NP have been determined to be between 4.5 and 37 days depending on the conditions (lab scale, lysimeter) and for tested soils (sand, clay) (Staples et al., 1999; Topp and Starratt, 2000; Jacobsen et al., 2004). For Hesselsoe et al. (2001), the half-life was estimated to 3-6 days using ¹⁴C-NP with a residual 20-60% of radiolabelled compounds in the organic fraction. The authors also showed a correlation between oxygen diffusion and NP mineralization. Indeed, NP mineralization occurs in the soil depending on the oxygen availability and on the type of soil and sludge: it could be as fast as NP is supplied alone, but application of NP spiked sewage sludge delay the NP degradation and favour the adsorption and the formation of bound residues with organic matter. For example, addition of limed sludge increases NP adsorption and persistence in soils (Kollmann *et al.*, 2003; Dubroca *et*

al., 2005). NPE and NP do not show significant downward transport to underground soil layers (Jacobsen et al., 2004), and transfer to groundwater, whereas some uptake by higher plants have been observed.

A similar behavior occurs concerning linear alkylbenzene sulfonates (LAS). A wide range of half-lives are reported in the literature from 1 to 87 days (Jensen, 1999; Scott and Jones, 2000) depending on soil types, LAS formulation, incubation conditions and route of LAS exposure (direct LAS application or LAS-spiked sewage sludge). Gejlsberg et al. (2003), using ^{14}C -LAS, showed from 48 to 82 % of mineralization of LAS in biometer flasks: the lowest mineralization occurs with sludge amendment where adsorption is higher. In more realistic conditions as lysimeter with non spiked sewage sludge, Jacobsen et al. (2004) found that LAS are rapidly degraded firstly with a slower secondary degradation step as already shown by Marcomini et al. (1989). They also observed low downward transport of LAS because of strong sorption on the sludge. This also underlines that the fate of LAS in soil is a combination of mineralization and binding to soil particles and LAS may be stabilised as bound residues in soil with time (Amundsen et al., 1997). Indeed, LAS has also a potential for uptake by plants.

The plasticizers phthalates have also distinct burdens according to their chemical structures. Di(2-ethylhexyl) phthalate (DEHP) is rapidly degraded in soil under aerobic conditions (EU, 2001). However, Roslev et al. (1998) using ^{14}C -DEHP applied on sludge amended soil, showed a two phase degradation with a 58 d half-live in the initial phase and 147 d in the late phase : more than 40% is not mineralized after one year and remained in the soil. Numerous esters lead to the formation of phthalic acid. This compound follow the same behavior as the DEHP but is faster degraded (Roslev et al., 1998). Another field study indicated that there is no long-term accumulation of dioctylphthalate in soil after following repeated sludge application (Rhind et al., 2002).

Polycyclic aromatic hydrocarbons (PAH) exhibit distinct behavior in soil according to their molecular weight (number of rings). The lightest are volatile, undergo biodegradation and can be mobile, whereas the heaviest are recalcitrant, strongly adsorb, and poorly transferred. Half-lives of month (phenanthrene) to years (benzo(a)pyrene) have been determined (Heitkamp et al., 1987; Goodin and Webber, 1995).

To conclude, the behavior of these compounds in soils is a combination of degradation-mineralization (from 30 to 80%) and adsorption-bound residues formation (from 20 to 70%) on organic matter, few downward transport are observed as well few plant transfer. A large range of half lives from 1 to 147 days have been determined depending on the experimental conditions showing that real field experiments and long-term experiments are needed to complete all these data. In this way, one task of the EU BIOWASTE project (QLK5-CT-2002-01138) was devoted to the measurement of 4 families of xenobiotics in soil after sludge spreading on a 30-year field-scale record experiment.

Methods

Field set-up

Experimental maize crop fields from Bordeaux (France) have been amended with high load of sewage sludge of up to 100 tons per hectare each 2 years from 1974 to 1992. From 1992 to 2004, the fields were maintained and cropped with maize. Sandy soils were yearly sampled, air-dried, sieved (2mm) and stored at ambient temperature from 1974 to 2004. The following samples were selected for analysis : 1) 0-20 cm sludge amended soils from years 1976, 1978, 1979, 1981, 1986, 1989, 1993, 1997, 2004; 2) 0-20 cm non-amended soils (control soils) from years 1989, 1999, 2004; 3) four sewage sludge used for amendment from years 1976, 1981, 1989, 1991. The four families of xenobiotics were analysed: PAH, LAS, NPE and PAE. Each sludge and soil sample was analysed in triplicate in 2005.

Xenobiotics analysis

PAE extraction was done adding 1 to 10 g of dried sample in a 250 ml Erlenmeyer flask with 20 ml of ethyl acetate and the flask was placed in an horizontal shaker (30 minutes of extraction on a Yellow line RS 10 basic). After extraction, 1 ml is sampled for analysis. If necessary a purification step may be added.

NPE, LAS and PAH are extracted with the ASE-200 procedure (DIONEXTM -Moduleware v.3.01 Bios 30.0). The principle of ASE system is the combined use of high pressure and high temperature to extract the target compounds. Some differences have to be pointed out : sample amount, solvent mixture, cell filling as summarised in table 1.

Table 1 : ASE condition for the extraction of NPE, LAS and PAH from sludge and soil samples.

	NPE	LAS	PAH
Sample amount	0.5 g sewage sludge	0.5 g sewage sludge	2.00 ± 0.01 g
	2 g soil	2 g soil	2.00 ± 0.01 g
Solvent mixture	hexane/acetone (50/50, v/v)	methanol	Solvent 1 : acetone/methylene chloride 50-50 v/v, Solvent 2: acetone/hexane 50-50 v/v
ASE condition	Two extractions: 120°C; 100 bars; 2 cycles of extraction; static time, 5 minutes, cell flush, 60% and purge time, 100 sec.	Two extractions: 100°C; 100 bars; preheat, 0 min; heat, 5 min; 3 cycles of extraction; static time, 5 minutes, cell flush, 60% and purge time, 100 sec.	two extractions: 103.4 bar, 100°C with solvent 1, then 103,4 bar, 150°C with solvent 2
Cell filling	alumina and hydromatrix	hydromatrix	4 to 5 g celite and sand

The two PAH extracts are mixed then adjusted to 100 mL with acetone. 40mL extract are mixed with 0.5 mL 1% *n*-dodecane in hexane. The remained volume of extract is discarded. Extracts are rotary concentrated (vacuum pump, 500 mbar, 60°C water bath) to about 2 mL (never to dryness), then to dryness under a gentle nitrogen flow. Extract are diluted in 2 mL methanol, then allowed to stay at least 30 min before further analysis.

The two NPE extracts are soft evaporated under nitrogen flow to dryness. They are dissolved and pooled in 5 ml (sludge) or 2 ml (soil) of hexane. The extract is then agitated vigorously (10 min.), let diffused (30 min.) and stored (-20°C) for further analysis.

The two LAS extracts are soft evaporated under nitrogen flow to approximatively 10 ml each. They are pooled and soft evaporated to a final volume of 10 ml of methanol for sludge sample and 2 ml for soil sample. The extract is then agitated vigorously (10 min.) or sonicated, let diffused (30 min.) and stored (-20°C) for further analysis.

Two ml of the PAE extract is purified on a florisil (magnesium silicate, Prolabo ref 24 279.185) glass column. Silice (silice gel 60, CarloErba RS) or aluminium oxide (ICN Alumina N, Ecochrom) can be used instead. The florisil is dried 4 hours at 400°C before used. 1 g is used in the column. It was conditioned with ethyl acetate and then the 2 ml extract is purified and eluted with ethyl acetate. The purified extract is then soft evaporated and resuspended in 2 ml of ethyl acetate with DaIP at 100 µg/l.

NPE, LAS and PAH are analyzed by HPLC coupled to fluorescence detection. Table 2 summarises the main difference in the HPLC analysis conditions.

Table 2 : HPLC conditions for the analysis of NPE, LAS and PAH

Conditions	NPE		LAS	PAH
matrix	sludge	soil	Sludge and soil	Sludge and soil
column	Purospher® STAR greffée NH ₂ , 5 µm, 4x250	Purospher® STAR greffée NH ₂ , 5 µm, 4x250	Lichrospher 100 RP-18 5 micron, 4x250 mm	100 x 4.6 ed Hypersil PAH column (5 µm phase)
temperature	30°C	30°C	25°C	40°C
Elution solvent	98.5% (V/V) hexane and 1.5% isopropanol	98.5% (V/V) hexane and 1.5% isopropanol	75% methanol: 25% water NaClO ₄ 12 g/l	water/acetonitrile (v/v): 50/50
Flow and gradient	Isocratic 1.5 ml.min ⁻¹	Isocratic 1.5 ml.min ⁻¹	3 min. of isocratic elution, 2 min of linear gradient from 75 to 88 %, 15 min. at 88%, 1 min. of gradient from 88% to 75% methanol and 11 min. of isocratic rinsing of the column 1 ml/min	5 min isocratic, then 50/50 to 0/100 in 20 min
Wavelength for fluorescence	ex:228, em:305 nm	ex:228, em:305 nm	ex: 232 nm , em: 290 nm	0-7.8 min (226, 322), 7.8-15 min (268, 462), 15-18.10 (234, 420), 18.10-21.5 (268, 398), 21.5-25 (302, 500)*
Injection volume	7 µl	20 µl	20 µl	10 µl
Calibration	0.5 to 5 mg/l	25 to 500 µg/l	0.5 to 120 mg/l	40 to 1000 µg/l

*Two fluorimetric detectors are coupled in series to avoid peak overlapping. The first detector is used for naphthalene, acenaphthene, fluorene, fluoranthene, benzo(b)fluoranthène, benzo(a)pyrène and indeno(123-cd)pyrene. The second detector is used for phenanthrene, anthracene, pyrene, benzo(a)anthracene, chrysene, benzo(k)fluoranthene, dibenzo(ah)anthracene and benzo(ghi)pyrene.

PAE are analyzed by GC-MS (Varian GC3400Cx/saturn 3 ion trap). The conditions are as follow : injection volume 1 µl; injector temperature 250°C; injection mode splitless; capillary column Factor Four Varian 30 m*0.25 mm*0.25µm; program of temperature : 3 min at 70°C, gradient to 280°C at 13°C/min, 20 min at 280°C; transfer line temperature 290°C; mass temperature 230°C; helium 5.5; impact electronic 70 mEV; target ion 149 for DBP, DEHP and DaIP. Each sample or standard is injected 2 times.

Results and discussion

The analysis of sewage sludge (four samples, year 1976, 1981, 1989, 1991) for PAH, NPE, PAE and LAS reveals concentrations varying between mg/kg to g/kg DW (figure 1). These concentrations fit the average values found for sewage sludge in Europe (Bennie et al., 1998; Webber and Lesage, 1989; Icon, 2001; Zurmühl, 1990) with very high level of LAS (10 g/kg), medium level of NPE and PAE (200-500 mg/kg) and low level of PAH (mg/kg for the sum of 16 PAHs, Lichtfouse et al., 2005). However, these levels are all above the proposed limits of the third draft of the EU sewage sludge directive (EU, 2001), except for the PAHs.

The same evolution with time is observed in the sewage sludge for the NPE, PAE and LAS: the concentrations decrease from 1976 to 1981 and increase from 1981 to 1989. This evolution could be explained by the highest requirements for the wastewater treatment plant during the 80th, i.e. increment of the collected waters, implementation of nutrient treatment.

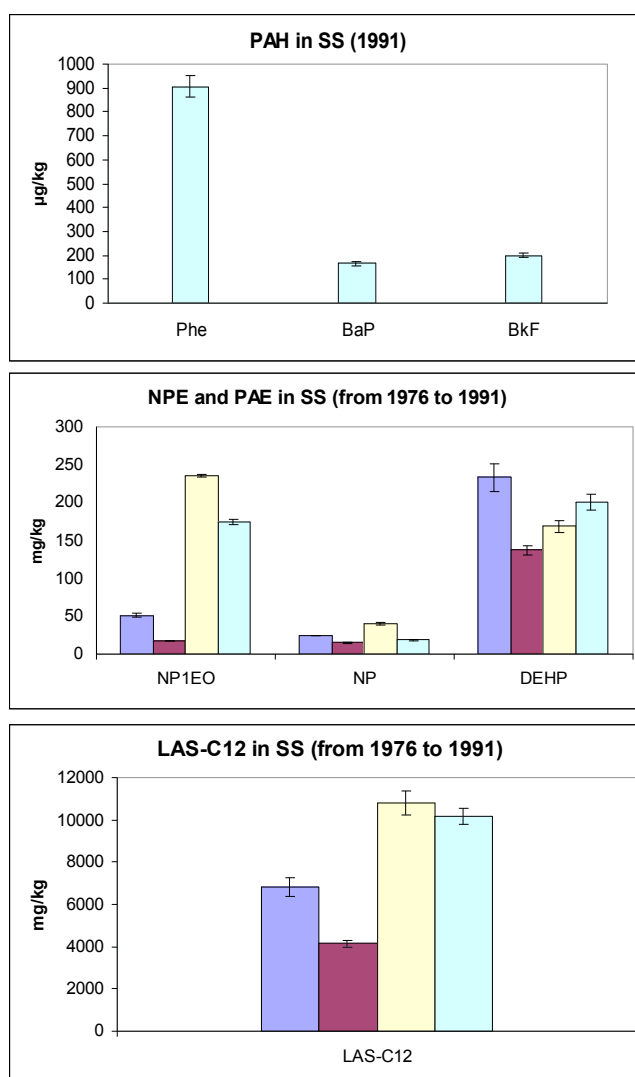


Figure 1: Level of polycyclic aromatic hydrocarbons (PAH), nonylphenol polyethoxylates (NPE), esters of phthalate (PAE) and surfactants (LAS) concentration of the sewage sludge (SEWAGE SLUDGE) used for application on the Bordeaux soil in 1976 (left), 1981, 1989 and 1991 (right). EU third draft proposed limits are : 2600 mg/kg for LAS (sum of LAS-C10, C11, C12, C13, longer of the alkyl chain), 50 mg/kg for NPE (NP1EO, NP2EO and NP), 100 mg/kg for DEHP, 6 mg/kg for PAH (sum of 11). DEHP, Di(2-ethylhexyl) phthalate. Phe, phenanthrene. BaP, benzo(a)pyrene. BkF, benzo(k)fluoranthene.

Levels in the control soil are around 5 (BaP, BkF, NP1EO), 14 (Phe), 30 (NP), 150 (DEHP) and 700 (LAS-C12, 1600 for the sum of the 4 LAS) $\mu\text{g/kg DW}$ (table 3). The DEHP and LAS levels are in accordance with those reported in literature for soil background. Carlsen et al. (2002) reported LAS concentrations of 500-1000 $\mu\text{g/kg DW}$ in soils from a preserved area not cultured for 50-100 years. EU (2001) reported DEHP values from 249 to 667 $\mu\text{g/kg DW}$ for soils in the area of Stuttgart, Germany. However, Vikelsoe et al. (2002) reported for an uncultured reference soil 2.9 (NP2EO), 0.47 (NP), and 16 (DEHP) $\mu\text{g/kg DW}$. EU (2001) also reported value for PAH in rural or urban soils lower than those we have found. These highest levels could be assumed to come from atmospheric deposition (DEHP and PAH) or from cross contamination from artificial fertiliser used on other soils (NP1EO and NP).

Table 3: PAH, NPE, PAE and LAS concentration ($\mu\text{g/kg}$ dry weight soil) on control soil, in sludge amended soil during the period of application and 12 years after the stop of spreading. Average and standard deviation values on three extractions. For PAH analysis, the analytical deviation extended from a minimum of 1.5% to a maximum 11%.

		Control soil 2004 (1999 for PAH)	Soil during sewage sludge spreading 1989	Soil 12 years after the stop of spreading 2004	PNEC (EUSES2.00 model)
PAH	Phe	14	109	35	700
	BaP	5	26	18	0.2
	BkF	4	23	45	-
NPE	NP1EO	4.5 \pm 1	410 \pm 0.65	43 \pm 3	492
	NP	26.5 \pm 5	118 \pm 9.8	25 \pm 0.07	367
PAE	DEHP	137 \pm 20	1469 \pm 30	881 \pm 73	10000
LAS	LAS-C12	521 \pm 0.7	2176 \pm 118	595 \pm 40	-
	LAS	1223 \pm 2.8	6654 \pm 372	1665 \pm 89	1600

During the period of sewage sludge spreading (table 3), levels in soil increase sharply particularly for the compounds with high concentrations in sewage sludge (LAS, DEHP and NP1EO). In the same way, the distribution of the compounds is consistent with the mixing of sewage sludge and control soil underlying the impact of sludge quality onto soil concentrations during the period of spreading. For example, PAH, LAS and NP1EO levels are either higher than or close to the Predicted Non Effect Concentration (PNEC, table 3). This imply that application of sewage sludge with high load (100 tons/ha each 2 years) but with a common EU pattern of xenobiotics may have an impact on the terrestrial environment.

Looking at the most persistent PAH, it is worthily to note that the BaP level is 10 times less in sewage sludge than the French policy level but the sewage sludge application was 10 times higher than the normal quantity which finally corresponds to the application of a standard EU sewage sludge at the French policy level. Unfortunately, the level in the soil increases during the period of application being 100 times higher than the PNEC. Twelve years after the stop of spreading, the concentration profile seems to be always influenced by the period of application with for all compounds, excepted LAS-C12 and NP, a higher level than the control soil levels. This implies that addition of such compounds to soil by the way of sewage sludge may have a long term impact with high residual level in the soil compared to a control soil despite many years of maize cropping and weather exposition. Particularly, the less degradable one (BaP) remains in the soil after 9 years at a level 100 times higher than the PNEC. This means stabilization of BaP : no degradation, no desorption from the bound residues pool. Surprisingly, the BkF concentration increases at the end of the studied period : this can be explained by external contamination or by desorption from the non-extractable fraction. It has already been shown that the kinetics of adsorption-desorption and degradation

of one PAH could influence another PAH (Cornelissen et al., 1999 ; White et Pignatello.,1999).

The evolution with time allows to understand and explain better the fate of the different compounds in the sandy soil. The evolution with time is shown on figure 2. Once added to the soil, the xenobiotics may (1) be degraded, (2) form bound residues as demonstrated by many other experiments like microcosms with radiolabelled compounds (Mougin et al., 2006) or (3) transfer to plant/water/air, this later part being generally little compared to the two other mechanisms. In our experiment, we measure a residual concentration corresponding to the fraction extracted by our analytical methodology: this residual concentration results from either degradation or/and adsorption on the soil organic fraction. Therefore, the evolution with time of the different compounds could be well correlated to the degradability of the molecules. Indeed, for the most degradable one, the LAS, the highest concentration was at the beginning of the studied period.

During the spreading period, the level does not increase whereas the quantity added is the highest, in counter part it stabilizes around 6 mg/kg. After the stop of spreading it decreases rapidly to reach the control soil level. In this case of easily degradable compound (by comparison to PAH, PAE or NP), the degradation may occur simultaneously to the addition of a high contaminated sludge. However, the remaining quantity in the soil is 12 years after stop spreading closed to the PNEC for soil (1.6 mg/kg), implying that even if the compound is well degraded it could have a long term impact on the environment. For the most persistent compound, the BaP, the behavior is completely different with increase of concentration during the spreading period (increase of the extractable pool) and then a level off meaning that once this compound is added to the soil, it remains for very long period. NP1EO and DEHP present an intermediate behavior. During the spreading period, their levels increase with the supply of the sewage sludge meaning that there is an increase of the extractable pool of the molecule but after the end of sewage sludge supply their levels decrease sharply during the 6 first years and then gently during the 7 following years. In 2004, their levels remain higher than in the control soil, particularly the DEHP with only 75% of disappearance. It means that degradation occurs at the beginning but after many years (ageing of the molecules), it may be much more difficult for the microorganisms to degrade the compounds that finally stabilise in the soil. It underlines thus the importance to fix limit for xenobiotics concentration in sewage sludge for spreading onto soil.

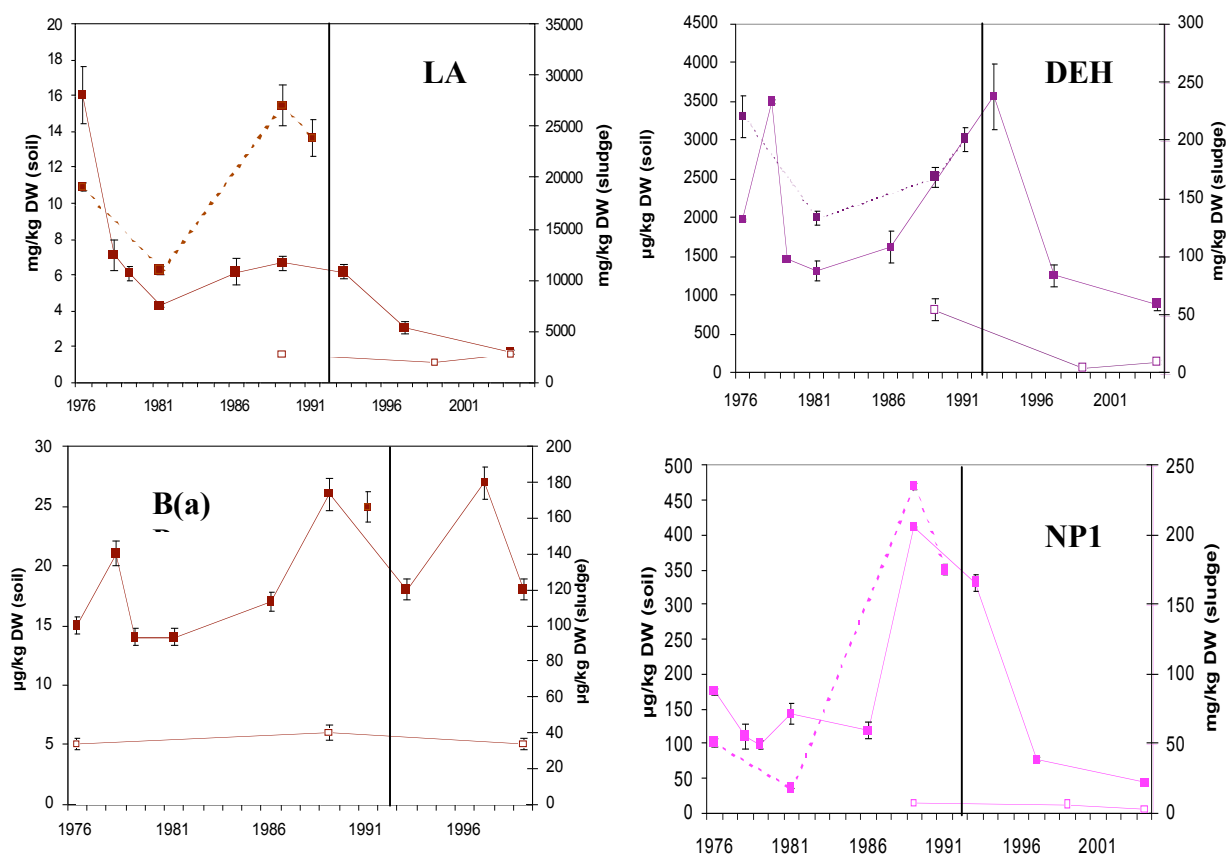


Figure 2 : LAS, DEHP, NP1EO and BaP evolution in sewage sludge (dotted line, closed square), control soil (open square) and sewage sludge amended soil (closed square) along the 30 years experiment. The dotted line represents the Predicted Non Effect Concentration (PNEC) for each compound. PNEC DEHP is 10000µg/kg DW soil. The vertical line represents the year of stop of spreading.

These experiments underline also the large influence of the treatment on the fate and impact of the compounds in the sludge amended soil. The NPE is the best example : WWTP are known to participate to the production of a more toxic by-product (NP) by the shortening of the ethoxylate chain of the NPE. In our experiment it seems that due to the characteristics of the WW treatment the shortening stops at the NP1EO level. As these compounds are less toxic and more degradable, their impact is lowest.

Conclusion

The field experiment shows that the concentration fluctuations in the sludge amended soil follow the same pattern of those in the sewage sludge showing that there is a real impact of the sewage sludge concentration on the soil concentration particularly for the less degradable compounds like PAH, PAE and NPE. During the spreading period, if there is no limitations, the level of such compounds in the soil can be higher than thresholds like PNEC : in our experiment this is the case for LAS, NP1EO and PAH. After spreading stop, the less degradable compounds (PAH, particularly B(a)P) remain in the soil at levels 100 times higher than the PNEC. This underlines that even though the PAH level in the sludge was low, it stabilises in the soil for long period of time on a human scale. The three other compounds NPE, PAE and LAS decrease in concentration with time. Nonetheless, 12 years after the last addition of SS, the residual concentrations remain from 2 to 10 times higher than the content of the control soils, even though these levels are inferior to the PNEC. These results show that whatever the degradability range of the target compounds, it may have short and long term effects in soil if high quantities are spread underlying the importance to fix maximum level for xenobiotic compounds for sewage sludge spreading. It also underlines the key role of the sewage sludge processes for reducing the concentration of xenobiotic before they reach the environment.

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