SOURCE, BEHAVIOR AND FATE OF ORGANIC POLLUTANTS IN AN AGRICULTURAL ECOSYSTEM

C. Sablayrolles[1,2] and M. Montréjaud-Vignoles[1,2]

1- Université de Toulouse; INP; LCA (Laboratoire de Chimie Agro-Industrielle); ENSIACET, 4 Allées Emile Monso, F-31029 Toulouse, France

2- INRA; LCA (Laboratoire de Chimie Agro-Industrielle); F-31029 Toulouse

Context and objectives

Biological treatment of organic waste is perceived as an environmentally-sound waste management option as it relies on "natural" processes. However, environmental benefits and potential drawbacks of exogenous organic matter return to soil are difficult to assess.

The use of sewage sludge on agricultural land is controlled under Directive 86/278/EEC. The European Commission Working Document on sludge *(CEC, 2000)* will standardize limit levels of trace organic compounds in sewage sludge. These organic compounds are Polycyclic Aromatic Hydrocarbons (PAHs), PolyChloroBiphenyls (PCBs), Phtalates, Nonyl Phenol Ethoxylates (NPEs), LaurylAlkylBenzene Sulphonates (LAS). In Europe, the annual production of sludge from wastewater treatment plants is about 9 000 000 tons dry matter and 40% of this is agriculturally recycled, which means 3 600 000 tons dry matter concerned by this Legislation.

A review of environmental fate of sludge organic contaminant when applied to agricultural land is carried out in order to appreciate the potential impact of these Trace Organic Compounds on human health.

Presentation of trace organic compounds

To begin, PAHs have been described as ubiquitous compounds in the environment. They are considered as persistent organic pollutants. PAHs are lipophilic and volatiles. PAHs emissions results mostly from incomplete combustion of organic materials and fossil fuel. They are known to be carcinogenic.

PCBs are also considered as persistent organic pollutants. PCBs are very lipophilic and semi-volatile existing in the gas phase and associated to particule in the atmosphere. Due to their chemical and thermal stability, PCBs were mainly used in transformers and capacitors as hydraulic fluid. They were banned since the seventies due to their toxicity but they are still present in the environment. They are said to be cancer producer.

The third family concerns the phthalates esters. Di-ethyl-hexyl-phthalate (DEHP) is the most present. They are widely used as additives to plastic industry. They might cause endocrine effects.

Nonylphenols ethoxylates (NPE) are a group of non ionic surfactants. Three compounds are studied: *n*-nonylphenol (NP), nonylphenol monoethoxylate (NP1EO) and nonylphenol diethoxylate (NP2EO). They are used as emulsifiers. As the toxicity is concerned, NPE are known to mimic the effect of oestradiol.

Lauryl alkylbenzene sulfonates (LAS) are a group of anionic surfactants characterized by both a hydrophilic and a hydrophobic group. The congeners from ten carbons to thirteen carbons were summed. LAS are most widely used as anionic surfactants in cleaners and detergents.

The levels of these organic compounds are regulated in sludge and in compost by individual European Union member states.

Data available: two types of numerical data

Two types of numerical data can be found as trace organic compound uptake by plants is studied. The most often met concerns concentration in the cultivated plant or in different organs of this plant. However, it is quite never possible to calculate fluxes with data provided in publications. Initial concentrations in spread by-product, initial concentrations in soil and plant yields are not always provided. Thus, this concentration is a data difficult to exploit since a comparison between concentration data is not possible because results are dependent for experimental conditions.

The second type of data concerns the bioconcentration factor (BF) in the plant. This factor is the ratio between the concentration in the plant and initial concentration in soil – waste mixture. Also in this case, initial concentration in soil and waste, plant yield are not always provided. So, fluxes calculation is not possible for every publication. The advantage of BF is that data comparison is possible since they are free from several influential parameters such as the spread dose of by-product and the initial concentration in amended soil.

One hundred publications have been identified. Forty five publications have been analyzed and thirteen have been selected as priority references. Indeed, a lot of publications give qualitative results very interesting but no data or quantitative results where data are not enough explained without protocol detailed. Therefore, these publications were not considered appropriate. And, we need absolutely numerical data to proceed to an environmental and sanitary assessment. By-product used is in great majority sewage sludge. We found only 2 publications on compost. And the authors have followed PAHs and PCBs levels in sludge-soil-plant system.

Trace organic degradation in soil

A persistence of heavy PAHs (molecular weight up to 254 g/mol) after spreading was noticed *(Wild et al., 1991) (Diercxsens et al., 1987)*. PAHs can have strong affinity for the soil organic matter *(Kacher et al., 2002) (Eun-Jung et al., 2003)*. Besides, PAHs provision by land application in soil is low compared with atmospheric provisions *(Wild et al., 1994)*. On the other hand, after 10 years of land application with sludge, PAHs concentration in treated soil is superior to PAHs concentration in the control soil *(Shuttleworth et al., 1995).*

PCBs persistence in soil increases with the number of chlorine atoms *(Fries et al., 1981)*. The PCBs monitoring in soil amended with sewage sludge showed that PCBs are not degraded after one year (*Marcomini et al., 1989)*. Besides, there is no leaching of PCBs in soil. PCBs are adsorbed on the soil organic matter. More the PCB is heavy more the PCB is adsorbed *(Strek et al., 1982)*.

Phthalates are faster degraded in aerobic conditions than in anaerobic conditions (*Petersen et al., 2003)*. A 50 % degradation of DEHP brought by sludge after three months has been observed. This behavior is explained by its properties: it is not very soluble in water and it has a very big affinity with organic matter *(Diercxsens et al., 1987) (Kirchmann et al., 1991).*

In anaerobic conditions, nonylphenols ethoxylates are degraded into NP. And then NP is degraded in carbon dioxide and water under aerobic conditions *(La Guardia et al., 2001) (Hesselsoe et al., 2001)*. Moreover, Mougin and Cravedi (2004) have shown that NP degradation in soil was slower when sludge is added. NP would disappear almost completely 3 months after spreading *(Diercxsens and al., 1987)*. The most important source of LAS in soil is the use of sludge and compost as fertilizers. LAS are well degraded in aerobic condition, while they are it little in anaerobic conditions (*Gron et al., 2001) (Jensen, 1999).* According to Gron et al. (2001), a weak transfer of LAS by root and leaves has been observed with no proof of translocation.

Trace organic uptake by plants

An accumulation of heavy PAHs in carrot peel have been observed *(Sablayrolles et al., 2004) (Sablayrolles et al., 2007)*. This observation is confirmed by Duarte-Davidson and Jones model which is based on physico-chemical properties of PAHs *(Duarte-Davidson & Jones, 1996)*. PAHs are able to adsorb on root but they have very week potential of translocation. Only PAHs with low molecular weight are able to absorb onto foliar parts of the plant *(Sablayrolles et al., 2004) (Sablayrolles et al., 2007)*. The following pathway is an atmospheric uptake *(Kampe, 1989)*.

PCBs plant uptake is principally observed in the peel and in a general way in plants rich in lipids *(Sablayrolles, 2004) (Wild & Jones, 1991) (O'Connor et al., 1990)*. It is interesting to know, for example, that peeling a carrot remove 95% of PCBs transferred. The peel behaves as a barrier restricting the penetration of PCBs in the middle of plants. However, less the PCB is chlorinated, more the transfer takes place *(O'Connor et al., 1990)*.

DEHP has been found in peel, root and leaves of plants *(Aranda et al., 1989) (Gron and al. (2001) (Sablayrolles et al., 2003) (Sablayrolles, 2004)*. It can be due to a soil-plant uptake or atmospheric deposition on leaves. Indeed, there is no correlation between DEHP present in plant and DEHP in the soil-by-product mixture (*Gron and al. 2001) (Sablayrolles et al., 2003) (Sablayrolles, 2004).*

It seems that NPE can be transferred towards plants; however, very weak quantities were observed in barley *(Kirchmann et al., 1991)*, carrot *(Laturnus et al., 1999) (Mougin & Cravedi, 2004)* and tomato *(Sablayrolles et al, 2003).* NP can be absorbed by roots and transported towards the upper parties as hydrophilic metabolite *(Pryor et al ., 2002).*

Conclusions

This review showed the complexity of trace organic compounds transfer in soil - byproduct – plant system. Indeed, the percentages of transfer can vary from a case to the other one. It can be explain by the number of influential parameters, such as the type of soil, the type of by-product, application rate, the type of plant. This complexity does not allow us to choose a unique value of percentage of transfer for each compound. What we can do is giving a mean value according to the type of cultivated plant on the amended soil.

Consequently, an important research work has to be performed in this domain of trace organic compounds uptake by plants.

References

[1] CEC, 2000, Working Document on Sludge. Third Draft, Brussels 27 april 2000, DG. Environment, 18 pp.
[2] KACHER, T., *et al.*, 2002. Chemosphere 21:117-131.
[3] EUN-JUNG, K., *et al.*, 2003. The Sciences of Total Environment 311:177-189.
[4] DIERCXSENS, P. and TARRADELLAS, J. 1987. Intern. J. Environ. Anal. Chem. 28:143-159.
[5] KAMPE, W. 1987. Korrespondenz Abwasser 34 (8):820-827.
[6] WILD, S.R., and JONES, K.C. 1991. Chemosphere 23:243-251.
[7] WILD, S.R., BERROW, M.L., and JONES, K. C. 1991. Environmental Pollution 72:141-157.
[8] KIRCHMANN, H. and TENGSVED, A. 1991. Swedish Journal of Agricultural Research 21 (3):115-19.
[9] NAKAJIMA, D., *et al.*, 1995. Chemosphere 30 (3):409-418.
[10] KIPOPOULOU, A.M., *et al.*, 1999. Environmental Pollution 106:369-380.
[11] SABLAYROLLES, C. *et al.*, 2004. WEF, Salt Lake City, USA, 22-25 February, session 15, 18 pages
[12] SABLAYROLLES, C. *et al.*, 2006. Acta Horticulturae, 700, 10-16
[13] DUARTE-DAVIDSON, R. and JONES, K.C. 1996. The Sciences of the Total Environment. 185: 59-70.
[14] DIERCXSENS, P., *et al.*, 1987. Gaz, eaux, eaux usées 3 (67ème année):123-132.
[15] KIRCHMANN, H. *et al.*, 1991. Swedish J. Agric. Res. 21:107-113.
[16] PETERSEN, S.O. *et al.*, 2003. Soil and Tillage Research 72:139-152.
[17] GRON, C. *et al.*, 2000. ACS Symposium Series 772:99-111.
[18] ARANDA, J.M. *et al.*, 1989. J. Environ. Qual. 18:45-50.
[19] SABLAYROLLES, C. *et al.*, 2005. Journal of chromatography A, 1072, 233-242
[20] SABLAYROLLES, C. *et al.*, 2004. 4^{th} IWA World Water Congress, Marrakech, Maroc, 19-24 septembre, 12 pages
[21] FIGGE, K., and SCHOEBERL, P. 1989. Tenside, Surfactants, Detergents 26 (2):122-8.
[22] LITZ, N. *et al.*, 1987. Ecotoxicology and Environmental Safety 14 (2):103-16.
[23] JENSEN, J. 1999. The Sciences of the Total Environment 226: 93-111.
[24] HESSELSOE, M. *et al.*, 2001. Environ. Sci. Technol. 35:3695-3700.
[25] MOUGIN, C., and CRAVEDI, J.P. 2004. Dossier de l'Environnement de l'INRA 25:85-90.
[26] LATURNUS, F., and GRON, C. 1999. 5th International In-Situ and On-Site bioremediation Symposium, at San Diego.
[27] FRIES, G.F., and MARROW, G.S. 1981. J. Agric. Food Chem. 29:757-759.
[28] GAN, D.R., and BERTHOUEX, M. P. 1994. Water environment Research. 1994 66 (1):54-69.
[29] XINHUI, B. *et al.*, 2002. Ecosystems and Environment 89:241-252.
[30] MARCOMINI, A. *et al.*, 1989. J. Environ. Qual. 21 (1-2):251-262.
[31] STREK, H.J., and WEBER, J.B. 1982. Environmental Pollution (Series A) 28 (4):291-312.
[32] MOZA, P. *et al.*, 1979. J. Agro. Food. Chem. 27 (5):1120-1124.
[33] IWATA, Y., and GUNTHER, F.A. 1976. Archives of Environmental Contamination and Toxiclogy 4 (1):44-59.
[34] PAHREN, H.R. *et al.*, 1979. Journal WPCF 51 (11):2588-2601.
[35] BOBOVNIKOVA, TS. I. *et al.*, 1999. The Sc. of the Tot. Env. 246 (2000):51-60.

[36] O' CONNOR, G.A. *et al.*, 1990. J. Environ. Qual. 19 (1):113-118.
[37] SABLAYROLLES, C. *et al.*, 2007, CODIS International Congress, Solothurn, Switzerland, Februar 27-28.
[38] SABLAYROLLES, C. *et al.*, 2003, European Biosolids and Organic Residuals Conference, Wakefield, UK, 24-26 novembrer, 2(16), 9 pages
[39] SABLAYROLLES, C. *et al.*, 2003, WEFTEC'03, Los Angeles, USA, 11-15 octobrer, session 43, 17 pages
[40] WEGMANN, M.A. *et al.*, 1987. Toxicological and Environmental Chemistry 14 (4):287-296.
[41] YE, Q. *et al.*, 1992. Chemosphere 25 (7-10):1475-1479.
[42] KÖMP, P., and LACHLAN, M.S. 2000. The Sc. of the Tot. Env. 250 (2000):63-71.
[43] TARRADELLAS, J. and P. DIERCXSENS, 1983. Schweiz. Arch. Tierheilk., 125:598-605.

Compound group	Physico-chemical properties	Concentration range in sludge (mg kg^{-1})	Degradation	Leaching potential	Plant uptake	Transfer to animals
PAHs	Limited water solubility Volatile Lipophilic	1-10	Week to 10 years **[7]** Strongly adsorbed by soil organic matter **[2] [3]**	Low **[4]**	Light PAHs Foliar absorption **[5] [6] [7] [8] [9] [10]** Very poor root retention Heavy PAHs Root retention Low translocation **[11] [12] [13] [14]**	Possible but rapidly metabolized not accumulated
Phthalates	Generally lipophilic Hydrophobic Non-volatile	1-100	Rapid Half-life < 50 days **[4] [15] [16] [17] [18]**	Low	Root retention Translocation ? **[18] [19] [8] [20] [21]**	Generally limited
LAS	Amphiphilic	50-15000	Very rapid **[18] [22] [23] [24]**	Low	Minimal No translocation **[18].**	Minimal
NPE	Amphiphilic	100-3000	Rapid < 10 days **[8] [25] [26]**	Low	Minimal **[8] [5] [27] [20]** Root retention	Minimal
PCBs	Low water solubility Highly lipophilic Semi-volatile	1-20	Very persistent Half-life several years Strongly adsorbed by soil organic matter **[28] [29] [15] [30] [31]**	Low **[32]**	Root retention **[33-40]** Foliar absorption **[28] [36] [40] [41] [42]** Minimal root uptake and translocation **[29] [5] [34]**	Possible into milk/tissues via sludge ingestion **[43]**