# Occurrence of micropollutants in final sludges and fate during treatment

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# Priority and emerging substances in sludge and fate during sludge treatment

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## Context

Wastewater treatment plants produce a large quantity of sludge. The European Union (EU-27) production is estimated at almost 11 million tons of dry sludge in 2005, probably exceeding 13 million tons up to 2020 (Kelessidis & Stasinakis 2012). Different pathways are possible for these wastes, principally incineration, disposal or agricultural use (Fytili & Zabaniotou 2008). Agricultural use and compost represents in Europe 53% of sludge produced (Kelessidis & Stasinakis 2012), while incineration and disposal reach respectively 19 and 17%.

A lot of contaminants such as metals and organic chemicals are sorbed to sludge during water treatment process because of their hydrophobicity or propensity to be adsorbed (Byrns 2001). Thus, the occurrence of many pollutants (Karvelas *et al.* 2003; Clarke & Smith 2011) in digested sludge has been well documented for many years since digestion is the most widespread technology used in medium and large scale treatment plants (Christensen *et al.* 2004). Furthermore, European regulations require a control of sludge quality regarding micropollutants (EC 1986, 1991, 2000). At the same time, disposal of sludge will progressively decrease until total banning in 2015.

In this context, assessing the sludge quality, as well as the fate of micropolluants during sludge treatments is very important. While several papers give information about anaerobic digestion (Carballa *et al.* 2007; Knoth *et al.* 2007; Barret *et al.* 2010), most of the time only for certain pollutant families, centrifugation, thermal drying or composting are still poorly documented. Finally, removal mechanisms during digestion are still not very well known, especially at industrial scale as majority of papers presents laboratory scale studies.

## Aims of this study

This study aims at investigating at an industrial scale:

1. The quality of final sludges for a large number of organic pollutants (n=120), particularly polybrominated diphenyl ethers (PBDE), pesticides, metals, polycyclic aromatic hydrocarbons (PAH), polychlorobiphenyls (PCB), alkylphenols, volatile organic compounds (VOC) and organotins,
2. The fate of micropollutants during 4 different sludge treatments, i.e. centrifugation, thermal drying, anaerobic digestion and sludge cake.

Sludge cake represents a digested sludge thermally conditioned (cooking) and then dewatered by press filtering.

## Methodology

Different sludge treatments on 3 wastewater plants were studied. These plants treat wastewater from the Parisian catchment, reflecting quite homogenous quality, and are supervised by Parisian sanitation service (SIAAP). SIAAP's large scale treatment processes (9 million population equivalents) produce almost 15% of the million tons of French sludge annually produced, in majority for land farming (70%) (Atlan 2003).

To evaluate the fate of compounds during sludge treatments, removals of pollutant loads were calculated using difference of contents and removal of dry matter. Average removal of dry matter (or matrix) during our campaigns on digestion (42%) was similar to common literature values (Moletta 2008).

Main results

*Quality of final sludge*

Out of the 120 molecules monitored, 33 are detected in sludge. The final sludges exhibit a comparable micropollutant pattern with concentrations not varying more than one order of magnitude. Pesticides and VOC were never quantified. Sludge cakes and digested sludges are the most contaminated while lower contents are observed in centrifuged and dried sludge. The contents found in final sludges are globally in accordance with literature for organotins (Clarke & Smith 2011), alkylphenols (Stasinakis *et al.* 2008), PBDE (Knoth *et al.* 2007), PAH (Abad *et al.* 2005), PCB (Stevens *et al.* 2002) and metals (Karvelas *et al.* 2003). On the other hand, DEHP contents are in the lower range of values reported in the literature (Marttinen *et al.* 2003; Clarke & Smith 2011). As regards regulations, metals, PCB and PAH contents are below European and French limit values (EC 1986; FG 1998).

*Fate of micropollutants during sludge treatments*

During centrifugation and thermal drying, no removal of metals, organotins, PAHs and DEHP are observed since pollutant loads are conservative. A difference is however observed for alkylphenols which are partially removed during thermal drying (50%), contrary to centrifugation. Heating to 260°C could enhance transfer to atmosphere by desorption and/or volatilization (Tuncal *et al.* 2011), and lead to an abiotic degradation, even if solid retention time is short (3 min). As regards digestion, differences of behaviours depending on the molecules under consideration are observed (Table 1).

**Table 1.1** Behaviours of micropollutants detected in studied sludge during anaerobic digestion

| Conservation of load | Removal of load similar to matrix removal | Higher removal of load than matrix removal |
|---|---|---|
| Metals | MBT | Alkylphenols (except NP) |
| DBT | TBT | DEHP |
| | NP | BDE 209 |

A conservation of loads between inlet and outlet for metals is observed which is consistent as they are not biodegradable and volatile. Organotins are degraded similarly to dry matter except dibutyltin (DBT) exhibiting stable load. Biodegradation of tributyltin (TBT) in DBT through dealkylation process has been observed at laboratory scale and in surface water and sediment in both aerobic and anaerobic conditions and could explain this result (Maguire & Tkacz 1985; Craig 2003; Stasinakis *et al.* 2005). Similarly, anaerobic biodegradation of carboxylate and ethoxylate compounds to nonylphenols (NP) balancing its own degradation could explain the lesser removal of NP compared to other alkylphenols (Salanitro & Diaz 1995; Ejlertsson *et al.* 1998). Globally, alkylphenols, DEHP and PBDEs are significantly removed (>50% in mass load), organotins and NP are moderately removed (40%) while metals and DBT are not removed.

This study provides interesting knowledge on i) the quality of final sludges and ii) the fate of some pollutants during sludge treatment. While centrifugation and thermal drying have no significant impact on the pollutant loads, digestion enable the removal of some pollutants. Specific studies on mechanisms involved in thermal drying, and on the fate during composting should be held to continue this work.

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