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Analysis and Comparison of Toxicants Between Tunisian Activated Sludge and Produced Compost

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Abstract: In the research reported here, heavy metals and polycyclic aromatic hydrocarbons (PAH) were analyzed in selected Tunisian activated Sludge and the produced compost. The GC-MS study demonstrates that not PAH were detected in the activated sludge and the final compost contain only natural PAH compounds. Major differences were observed between the sludge and the mature compost studied as regards their total heavy metal contents. An increase in total Fe and Mn ions was observed in the produced compost Addition of green waste as co-compost to activated sludge caused a significant reduction of total Cd and Cu contents in the compost due to dilution effect and the sludge led to greater content of total heavy metal concentrations. The total metal contents in the final compost were much lower than the French limit values of composts to be used as soil fertilizer. Both GC-MS study and the total heavy metal analysis provided valuable information concerning amount of toxicants in the compost and the sludge.

Key words: Composting, sewage sludge, heavy metals, PAH

INTRODUCTION

The presence of organic and inorganic contaminants in compost, pose a grave danger to the environment of which heavy metal and micropolluants are the main obstacle factors leading to restricted agricultural use of compost. In the last years in Tunisia, we tried to give more interest to sludge composting. A major limitation of land application of sewage sludge compost is the potential for metal contamination related to the metal content of the original sludge (Zorpas *et al*., 2000). The concentration of heavy metals is probably the main factor to bear in mind, when sewage sludges are used as organic amendments. There are numerous legislations and regulations laid down by various organisations for sludge disposal. In the final regulations of USEPA, only metallic compounds are taken into account, since the levels of some organic compounds were not detectable and therefore had no significant effect on health and environment (Pérez *et al*., 2001). Now, the directive NFU 44095 provides the allowable content for some organic pollutants including Polycyclic Aromatic Hydrocarbons (PAH) for agricultural recycling of sewage sludge. The cut-off value of Total PAH is set to 12 mg kg^{-1} DW. The sewage sludge compost agricultural use implies knowing its content of the heavy metals present. Not only are these elements not biodegradable and become toxic at some concentrations, they tend to accumulate along the food chain where man is the last link (Dudka and Miller, 1999). Hsu and Lo (2001) show the increase of metal concentrations during composting of swine manure and suggest that the types of composting and raw materials are of major importance to metal condensation. Also, composts can contain significant levels of contaminants like PAH (Bûyûksônmer *et al*., 2000). The increased microbial activity of compost can increase degradation rate

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of PAH (Strom., 2000). Persistant organic polluants can increase in concentration as the volume of compost is reduced and can even release back into the environment as the compost degrades thereby posing a health risk (Bûyûksônmer *et al*., 2000). Accordingly, the objective of this research work was to examine the levels of total heavy metals Cd, Cu, Fe, Mn and Hg as well as PAH content in sludge and sludge compost.

MATERIALS AND METHODS

A laboratory research was conducted in the laboratory of Tunis International Center for Environmental Technologies. This research was commencing in Semptember 2005.

Selection of Parameters to Analyse

To determine the range of compounds to analyse, we used two criteria:

- The compound must be listed us high priority contaminant by the health and the environmental authorities.
- Included in other countries sludge or compost regulation guidelines.

Sampling

Sludge

Activated sludge was collected from the wastewater treatment plant of Charguia in Tunis town. Preservation of the sludge was conducted prior to experimental run. The Typical characteristics of sludge used in the composting process are shown in detail in Table 1.

Compost

The mature sludge compost was made from the above sludge with greenwastes (1/2 volume) and municipal sewage sludge (1/2 volume) following the Aerated Pile Method (Wilson *et al*., 1980). This compost met the French norm on composts made with materials of water treatment for pathogenic microorganisms and heavy metals (NFU 44-095). Characteristics of compost are shown in Table 1.

Physico-chemical Analysis

Nitrogen was determined by the Kjeldahl method (NF ISO 11261), the organic matter by Gravimetry (Rodier 8th edition). Total organic carbon is measured according to Colorimetry method (ISO 14235). Fe, K, Ca, Mg, P were analyzed by emission spectrometry -ICP (NF EN ISO 11885). The elements Cd, Cu and Mn were analyzed by emission spectrometry-ICP (NF EN ISO 11885). Mercury was determined by atomic absorption analysis (NF EN 1483).

PAH Extraction

A sample of about 20 g of compost and sludge were used. PAH extraction was performed on this amounts of matter with dichlorométhane and heaxane (95/5%). The organic phases were taken, dried on $Na_2 SO_4$, concentrated and purified on a silica cartridg. PAH were determined and quantified by GC-MS.

Table 1: Physico-chemical properties of activated sludge and produced compost (Results expressed in dry basis)

Properties	Sludge	Final compost
OM (g kg^{-1} DW)	522.00	251.00
TKN (g kg^{-1} DW)	38.30	14.80
C/N	8.85	13.37
TOC (g kg^{-1} DW)	339.00	198.00

GC-MS Analysis

A Perkin Elmer series gas chromatograph equipped with a mass detector and a data analysis station HP Chem was used for the GC-MS analysis.The column used for analysis was a HP-5 MS type (30 mL, 0.25 mm I.D., 320 μm film thickness). As carrier gas, high-grade helium was used at a flow rate of 1 mL min^{-1}. Injection was made in split less mode. The injection volume was 1 μL For PAH analysis, the oven temperature increased from 50 to 300°C over a 20 min run time.

RESULTS AND DISCUSSION

The sludge contained high levels of N and P, important properties for any sludge to be used in land application. Table 2 shows the total Cd, Cu, Fe, Mn and Hg contents of the sludges and the final compost. For comparative purposes, the same table shows the maximum levels of the heavy metals allowed in french norms for land-applicable waste (NF U 44-095). Mn and Fe were the predominant metals in the sludges. Thus, land application should be controlled to avoid potential Mn toxicity. The sample of sludge was taken in the January 2006. Generally, highest heavy metals concentrations were found on winter. Heavy metals are carried away by rains. Owing to this, heavy metals concentration is higher in winter. The highest concentrations were obtained in the sludge due to the highest mineralization of the sludges (Villar *et al*., 2006). Low total Cd and Cu concentrations were found in the selected sludge. Hg contents were also very low. The content of total Mn was 63.5 g kg^{-1} DW in the sludge. In the mature compost, the total Mn content was 155 mg kg^{-1} DW. These values show that Mn could produce appreciable environmental damage if the sludge was used as an organic-mineral amendment. A slight increase in Fe ions was observed in the produced compost. It can be caused by the reduction in volume of pile and therefore an increase in the concentration of Fe contents after composting. The composting process is generally marked by an increase in some metal concentrations due to the evident reduction of compost mass by decomposition (loss of matter) (Lazzari *et al*., 2000). The content of total Cu, Cd ions was 23.1 mg kg^{-1} DW of Cu and <0.003 mg kg^{-1} DW in matured compost, which were much lower than their respective initial concentration of 140 mg kg^{-1} DW of Cu and 1.95 mg kg^{-1} DW of Cd in the activated sludge (Table 2). This was simply due to the addition of large amount of greenwaste into the compost. This enlarged the volume and diluted the metal content in compost. Moreover, the reduction in volume of pile after composting resulted in an increased concentration of heavy metals. The GC-MS chromatograms of the sludge and compost are shown in Fig. 1. No PAH had been detected in any of the sludge and compost samples in this study. These results are very near to the more values reported in Sweden and Denmark (National Swedish Environmental Protection Board, 1992; Torslev *et al*., 1997). Only Natural hydrocarbons were detected in the mature compost. Generally, composting yielded a more stable and humified organic matter richer in aromatic structures. the organic matter of sewage sludge and composts was not completely aromatic in nature but that also polysaccharides and alkyl compounds were present in large quantities (Hernandez *et al*., 2005). Generally, the highest concentrations of PAH have been found on summer. Total PAH are highest in the month of October while in December it was the lowest. The sample of sludge was taken in the January 2006. In this month; PAH concentrations decrease, probably due to the first autumn rains. In this way it is possible to found a relationship between the typical south of

Table 2: Amount of heavy metals in the sludge and produced compost (Results expressed in dry basis)

Metal	Sludge	Final compost	Limit values (NFU 44095)
Mn (g kg^{-1} DW)	63.50	155.00	-
Fe (g kg^{-1} DW)	7.49	8.22	-
Cd (mg kg^{-1} DW)	1.95	<0.60	3
Cu (mg kg^{-1} DW)	140.00	23.10	300
Hg (mg kg^{-1} DW)	<0.091	<0.091	2

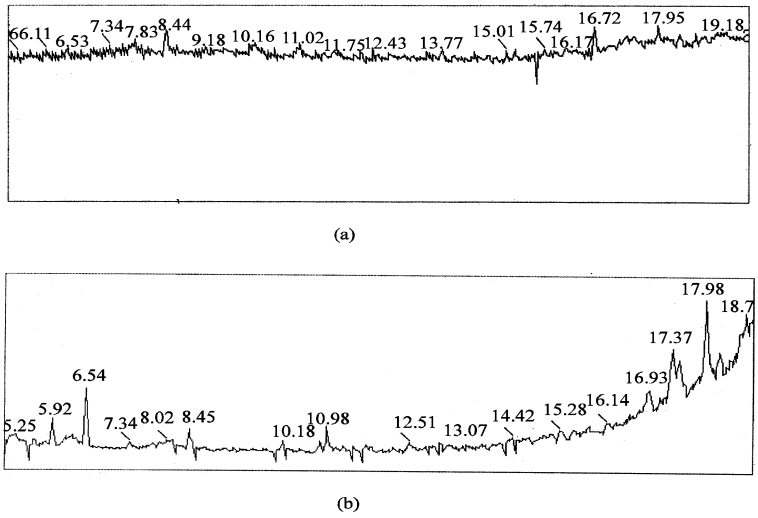

Fig. 1: GC-MS analysis of the sludge and compost samples during composting.
a): GC-MS chromatogram of the sludge and
b): GC-MS chromatogram of the final compost

Tunisia climatologic and the temporal evolution of PAH. Villar *et al*. (2006) observe an increase of PAH concentration on summer and a decrease in winter. It is associated to increase of traffic from inland zones to costal zones (beaches) due to extra holydays activities on summer.

CONCLUSIONS

It can be concluded that the composting procedure reduced the heavy metal levels in the produced compost. The analysis of total heavy metal showed a reduction of Cu, Cd and Hg contents and the increase of Total Fe and Mn contents in the mature compost. GC-MS analysis showed that any PAH has been detected in the samples studied of sludge and sludge compost. The activated sludge and its produced compost, studied here, do not represent a major threat for the environment but can require some follow-up over time, especially for Cu and Mn soil content before amendment. Composting sewage sludge with green waste appears an interesting avenue for an integrated management of waste management in Tunisia, but more research is required in this field. The results obtained in this study may contribute to the prevention of environmental damage, although they cannot be extrapolated directly for making predictions about *in situ* metal behaviour in the soil.

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