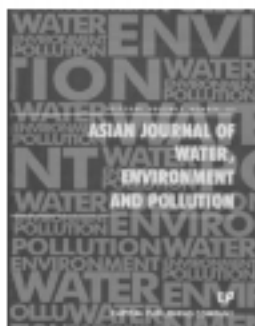


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Bioremediation of Contaminated Lake Sediments and Evaluation of Maturity Indices as Indicators of Compost Stability

Rekha P., D.S. Suman Raj, C. Aparna, V. Hima Bindu and Y. Anjaneyulu*

Centre for Environment
Institute of Science & Technology, Kukatpally
Jawaharlal Nehru Technological University, Hyderabad, India 500 072
✉ samy_12345@yahoo.com

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Abstract: Land contamination is one of the prominent and widely addressed problems and is gaining importance in many developed and developing countries. It is now widely accepted that contaminated land is a potential threat to human health and over recent years has led to international efforts to remediate many of these sites, either as a response to the risk of adverse health or essential effects caused by contamination or to enable the site to be redeveloped for use.

Traditional methods simply move the contaminant or may create significant risk in handling the hazardous materials involving cost intensive and potential liabilities. Physical and chemical methods can be effective but are technically complex and lack public acceptance. Bioremediation is an option that offers the possibility to destroy or render harmless various contaminants using natural biological activities. It uses relatively cost-effective low technology techniques, which have high public acceptance and can be carried out on-site.

In the present study, composting is demonstrated as a full-fledged bioremediation methodology for the stabilization of contaminated lake sediments. Lab scale studies were carried out to examine the various bioprocesses occurring in composting using simulated soils and optimized conditions are established for bioremediation of lake sediments contaminated with organics and heavy metals. In order to enhance microbial activity in composting, neutralization of the contaminated lake sediments was carried out by adding commercially available lime and then, organic and inorganic fertilizers like cowdung, poultry manure, urea, and superphosphate as initial microbial seeding amendments, bulking agents like sawdust and nutrients are provided and the impact of their variation was also studied. Continuous monitoring of process control parameters like pH, moisture content, electrical conductivity, total volatile solids and various forms of nitrogen etc. were carried out.

The stability of the compost was evaluated by assessing maturity indices like C/N, C_w (water soluble carbon), CN_w (C_w/N_w), nitrification index (NH_4/NO_3^-), cation exchange capacity (CEC), germination index, humification index, humification ratio, compost mineralization index (ash content/oxidizable carbon), sorption capacity index (CEC/oxidizable carbon). Enzyme activities of agricultural interest like urease, phosphatase, β -glucosidase, dehydrogenase and BAA-hydrolyzing protease, which are involved in the nitrogen, phosphorus and carbon cycles, were also assessed. Total content of macro and micronutrients in the final compost was also determined to assess the fertilizer value.

Introduction

Sediments are generally recognised to play a prominent role in ecosystem cycling, as the surfacial layer can be

considered to be intimately linked to surface waters through physical, chemical and biological processes. The continuous discharge of industrial wastes into the water bodies is increasing the risk of their contamination (Baudo, 2001). Sediments are globally considered the

* Corresponding Author

ultimate sinks for the particulate accumulation of organics and their environmental transformation in sediments has been well documented (Brown & Wagner, 1990; Lake et al., 1992).

Organic contaminants in sediment systems are mixtures of hundreds of aliphatic, chlorinated aromatic and other organic compounds, the relative proportions of which vary greatly between sources (Apitz, 1998). Inorganic contaminants also have very complex interactions with both anthropogenic and natural components in marine sediments.

The persistence of organo xenobiotics in the environment is a matter of significant public, scientific and regulatory concern because of the potential toxicity, mutagenicity, carcinogenicity and ability to bioconcentrate up the trophic ladder. These concerns continue to drive the need for the development and application of remediation techniques (Colleran, 1997).

It is now widely recognized that contaminated land is a potential threat to human health, and its continual discovery over recent years has led international efforts to remediate many of these sites, either as a response to the risk of adverse health or environmental effects caused by contamination or to enable the site to be redeveloped for use (Vidali, 2001). A key factor in both the degradability and bioavailability of the most recalcitrant fractions of anthropogenic contaminants is the long-term sorption that can occur between organic molecules and clays or other minerals in soils and sediments (Knaebel, 1994).

Hyderabad, the capital city of Andhra Pradesh, South India has almost 80 lakes in and around the city. With the growing industrial activities over the years about eight large industrial estates have been developed and these industries are unscrupulously dumping their effluents into the nearby lakes thereby depleting the natural flora, fauna and the ecological balance. The pollutants in these lakes tend to bioconcentrate up the trophic ladder and reach humans. So, rejuvenation of these lakes is a task of utmost importance and employing physico-chemical processes only transform the pollutants from one form to another but biological processes transform them into innocuous end products.

These concerns continue to drive the need for the development and application of viable and low cost remediation techniques (Stratton et al., 1998). Bioremediation is one such technology that offers the possibility to destroy or render harmless various contaminants using natural biological activity. Microorganisms have a unique ability to interact both chemically and physically with a huge range of both man-

made and naturally occurring compounds leading to a structural change to, or the complete degradation of, the target molecule (Head, 1998).

Composting is one of the bioremediation strategies which when carried out under controlled conditions in the presence of oxygen results in the biological decomposition and stabilization of the biodegradable components. The process of composting includes four main phases, which are the initial phase, the thermophilic phase, the mesophilic phase and the maturation phase after which the compost can be used as an organic amendment. For the compost to be used as an organic amendment it has to be assessed for certain parameters like nitrification index, cation exchange capacity, germination index, humification index, water soluble carbon, compost mineralization index and sorption capacity index etc.

Since stabilization or maturation also implies the formation of some humic-like substances, the degree of organic matter humification is generally accepted as a criterion of maturity (Chefetz et al., 1996). The humification process produces functional groups and so increased oxidation of the organic matter leads to rise in cation exchange capacity. So compost with high cation exchange capacity is regarded as an index of maturity (Iglesias-Jimenez and Perez Garcia, 1992). The degree of maturity can also be revealed by biological methods involving seed germination and root length (Zucconi et al., 1981). However, immature composts may contain phytotoxic substances such as phenolic acids and volatile fatty acids (Kirchmann and Widen, 1994). Therefore a study of the changes occurring can be useful for assessing compost maturity.

The aim of the present work is to monitor the process of composting for the contaminated lake sediments and observe the changes occurring in the two piles set up by taking sediment from different strata and discuss few of the maturity indices and thus validate their use as matured composts resulting from the biological stabilization.

Materials and Methods

Initially a 100 × 100 sq m plot on the lakebed was chosen and the top layer was dredged and sent to a treatment storage and disposal facility located near the outskirts of city for landfilling; thereby getting rid of the uppermost polluted layer on the lakebed. The next 0.25 sq m of the lakebed was removed and a portion of the sediment was set up as Pile I. A further 0.25 sq m was dredged whose part was set up as Pile II. The two piles were set up by taking the sediments from two different strata of the

lakebed in a view to assess the leaching potential of pollutants into the different strata of the lake sediments and their amenability to composting.

Pile I—Sediment from upper stratum.

Pile II—Sediment from lower stratum.

Lime Stabilization

The polluted sediments from the two different strata were initially mixed with lime at 1% (w/w, dry weight basis) which raised the pH to 9.2. The addition of lime helps in the stabilization of heavy metals because metals get precipitated as metal hydroxides at high pH's (Akrivao, 2000). The sediments were kept as such for five days and then mixed with organic amendments like poultry manure and bulking agent sawdust which brought down the pH to 6.8.

Lab scale experiments for composting were set up by taking sediment, poultry manure and sawdust in the ratio of 2:1:2. The lab scale set up for the aerobic composting pile is shown in Figure 1. The organic amendment poultry manure is high in nitrogen and is used for the adjustment of carbon/nitrogen ratio and saw dust is used as a bulking agent to increase the porosity of the mixture. The sediment was mixed with the organic amendment to maintain the total solids content between 35 and 45% and then homogenized. The aeration was given through natural ventilation and by turning over the piles at an interval of seven days. The piles were protected with a layer of sawdust and straw on the surface to avoid odours and influence from wind.

Composting

The composting process lasted for a period of 14 weeks, including four stages such as the initial phase, the thermophilic phase, end of thermophilic phase and the mesophilic phase. The sludge-conditioner mixture was placed on a bed of wire mesh, at an altitude of 30 cm. The material was spread on a layer of wood shavings, which was covered with a layer of sawdust and straw. The moisture content was initially adjusted to 55% and later there was no addition of water. Once the pile was set up, the decomposition of the organic matter by thermophilic microorganisms started, which elevated the temperature to 58° C, causing the destruction of the pathogens. The aerobic conditions were assured by aeration through turning. Thermophilic phase remained for a period of 50 days in the pile. Within a period of 14 weeks, complete stability of the compost and the removal of odours were assured. The mixtures were then kept for another six weeks for maturation. All the parameters were assessed for this matured compost. Sifting was done to matured compost to separate the conditioning material and to obtain a homogenous product.

Analytical Methods

All the parameters such as moisture content, electrical conductivity, pH, organic matter and nitrate nitrogen were estimated using standard APHA methods (APHA, 1998). Total Kjeldahl nitrogen and ammonical nitrogen were analysed using Kjeldahl assembly (Kjel Plus DISTILL M KPS 020, India), the oxidizable carbon (Co)

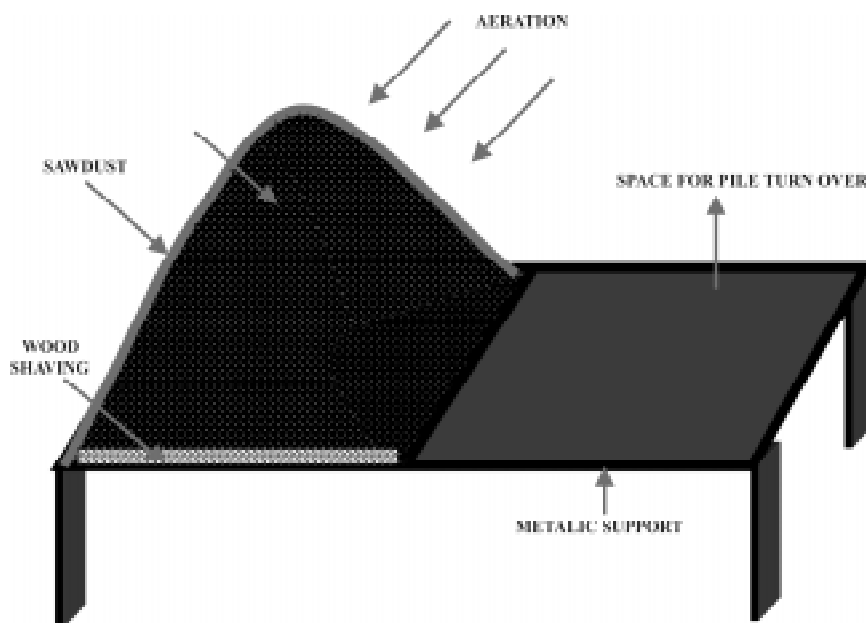


Figure 1: Setup for turning mode of composting.

was determined by oxidimetric method (Jerzy Drozd et al., 1997) and the ash content by gravimetric method after burning off the dry mass at 550° (Jerzy Drozd et al., 1997). In the water extracts (compost/water ratio of 1:10) the water soluble forms of carbon (Cw) and nitrogen (Nw) were determined. Total phosphorous (ascorbic acid method) (Gupta, 1999) and cation exchange capacity (CEC) was determined according to the method described by Gupta (1999).

Humic Substances

Humic acids, Fulvic acids and non humic fraction were estimated by the method as described by Hsu and Lo (1999). Humification index (HI), i.e., the ratio between humic acids and fulvic acids is deduced from the equation.

$$HI = HA/FA$$

$$\text{Humification Ratio} = \frac{\text{Extractable Carbon/}}{\text{Total Organic Carbon}} \times 100$$

Water-Soluble Carbon (Cw)

20 gms of compost was weighed and extracted with 200 ml of deionized water by shaking for 24 hrs. The extracts were centrifuged at 10,000 RPM for 25 mins and filtered through 0.45-µm filter membranes (mdl, India). Water extracts are immediately analysed for organic carbon (Hsu & Lo, 1999).

Enzyme Assay and Measurement

Assays of hydrolases (β-Glucosidase, BAA-Hydrolyzing Protease, Urease and Phosphatase) and dehydrogenase activities were performed as described by Garcia et al. (1993b,c). Dehydrogenase assay was based on the combination of two methods (Benefield et al., 1997; Trevors, 1984).

To determine β-Glucosidase activity 0.05 M 4-nitrophenyl-β-D-gluconopyranoside (PNG) was used as substrate (Hayano and Tubaki, 1985) while 0.115 M p-nitrophenyl-phosphate (PNPP) was used as substrate to measure the phosphatase activity. The para-nitrophenol (PNP) produced by both hydrolases was extracted and determined spectrophotometrically at 398 nm (Tabatabai and Bremner, 1969). To determine the BAA-hydrolysing Protease and Urease activities, 0.03 M N-α-Benzoyl-L-Argininamide (BAA) and 6.4% urea, respectively were used as substrates. The ammonium released by the two hydrolytic reactions was measured by an ammonium selective electrode (ORION, Model. 95-12).

To determine dehydrogenase activity, 0.4% 2-p-iodophenyl-3-p-nitrophenyl-5-tetrazolium chloride

(INT) was used as substrate. Iodonitrotetrazolium formazan (INTF) produced in the reduction of INT was measured spectrophotometrically at 490 nm.

Germination Index

The absence of phyto-inhibitory substances that reflect maturity of compost was tested by seed germination. Germination tests were performed with garden cress (*Lepidium sativum* L.). Seeds were soaked in compost extracts in water (1: 10 w/v) for 48 h. *Lepidium sativum* seeds were used because of their rapid germination and sensitivity to phytotoxic compounds (Zucconi et al., 1981). The germination index, inversely related to the presence of phytotoxic substances in compost, was calculated as the percentage of seeds germinated on filter paper in petri dishes with 10 ml of compost extract multiplied by the average length of roots in mm expressed as percentage of a control with distilled water (Hirai et al., 1983). The percentages of relative seed germination, relative root elongation and germination index (GI) are calculated by the following formula:

Relative seed germination (%)

$$= \frac{\text{Average length of roots in mm}}{\text{Average length of roots in mm of control}} \times 100$$

Relative Root Growth (%)

$$= \frac{\text{Percentage of seeds germinated}}{\text{Percentage of seeds germinated of control}} \times 100$$

Germination Index

$$= \frac{\text{Relative seed germination (\%)} \times \text{Relative Root Growth (\%)}}{100}$$

Results and Discussion

The physico chemical analysis of the poultry manure and saw dust and sediments from two different strata used in the present study are presented in Tables 1 and 2 respectively. A representative composite homogeneous replicated sample was taken by picking up material from different points of the two piles.

The evaluation of various parameters during composting and maturity are discussed.

Temperature, Moisture Content, pH and Electrical Conductivity

The temperature variation during composting followed a pattern similar to many other composting systems (Gray & Biddlestone, 1981). Initially heat was generated due to rapid breakdown of readily degradable organic matter and nitrogenous compounds in the pile which resulted

Table 1: Characteristics of Amendments Used

<i>Parameters</i>	<i>Poultry manure</i>	<i>Sawdust</i>
pH	7.8	5.7
Moisture content %	30	10
Total organic carbon %	47	65.1
Total Kjeldahl Nitrogen %	2.46	0.18
C/N ratio	19.0	361
Total Phosphorus (%)	3.7	0.008
K g kg ⁻¹	11.5	ND
Na g kg ⁻¹	3.1	ND
Ca g kg ⁻¹	49.5	ND
Mg g kg ⁻¹	7.3	ND
Fe g kg ⁻¹	2.7	ND
Cu p.p.m	435	ND
Mn p.p.m	246	ND
Zn p.p.m	311	ND

Table 2: Compost Product Characteristics

<i>Sl. Parameter No.</i>	<i>Mixture before composting</i>		<i>Composted product</i>	
	<i>Pile I</i>	<i>Pile II</i>	<i>Pile I</i>	<i>Pile II</i>
1. pH	6.8	6.7	7.6	8.2
2. Humidity %	55.0	55.0	42	30
3. Total Organic Carbon %	48.9	48.7	34	21
4. Total Kjeldahl Nitrogen %	1.6	1.65	1.75	1.76
5. C/N	30.5	29.5	19.4	11.9
6. Phosphates %	0.62	0.52	0.50	0.47
7. Potassium %	0.37	0.28	0.28	0.31
8. Water Soluble Carbon %	1.35	2.02	1.29	1.32
9. Water Soluble Nitrogen %	13.5	13.5	7.2	5.2
10. Ash Content %	4.51	4.94	5.28	6.19
11. Oxidizable Carbon %	19.5	2.04	16.2	14.1
12. Humic Substances %	15	31	25	52
13. Humic Acids %	3.2	5.2	10.8	21.9
14. Fulvic Acids %	6.1	8.2	5.4	5.4
15. Non-Humic Fraction %	14	18	17	12

in a rapid increase in temperature. High temperatures are consequences of microbial activity whereby heat is liberated through respiration of microorganisms and built up within the pile (Bertoldi et al., 1983). In Pile I, the temperature rose only upto 46° because of the presence of highly toxic compounds and thus low microbial activity while in pile II there was a steep increase in temperature upto 58° due to the availability of comparatively more degradable organic matter and hence intense microbial activity. The thermophilic phase lasted for nearly seven weeks. After this period of elevation the temperature gradually decreased to ambient levels and this marked the end of the thermophilic phase of

composting. At this stage the decomposition rate stabilized with a consequent decrease in temperature and microbial activities.

During composting the moisture content of the piles decreased which is due to the evaporation of water as a consequence of turning the piles and microbial heat generation. The continuous decrease in moisture content during composting is an indication of organic matter decomposition (Miller and Finstein, 1985). The moisture content in Pile I decreased upto 42% while that in Pile II decreased to 30%.

The intense microbial activity and organic matter degradation during the first weeks of thermophilic phase led to the formation of ammonia as a consequence of ammonification of organic nitrogen. The solubilization of ammonia led to the formation of ammonium and an increase in the pH values in the composting mixtures from an initial of 6.8 to 7.6 in pile I and from 6.7 to 8.2 in pile II.

The nitrification began after the thermophilic stage, where the pH fell and thereafter remained stable. Highly significant direct correlations were found between nitrate concentrations and electrical conductivity values. NO₃-N production explains the increase in conductivity found in both the piles. This is important from an agricultural point of view since an increase in electrical conductivity is a direct consequence of the increased concentration of nutrients, such as nitrate.

Changes in the Carbon/Nitrogen Ratio

The changes in the C/N ratio reflect organic matter decomposition and stabilization during composting and is represented in Figure 2. In the initial stage of composting intense mineralization process takes place which is manifested by a considerable decrease in carbon and increase in ash content in both the piles, the C/N ratio decreased due to the mineralization of the organic matter. Inorganic forms of nitrogen were in a very low concentration indicating a certain degree of inorganic nitrogen immobilization. This fact results from the incorporation of such forms into the microbial tissue during the thermophilic phase of composting (Bishop & Godfrey, 1983). The total nitrogen content increased during composting from an initial of 1.6% to 1.75% in Pile I and from 1.65% to 1.76% in Pile II. These nitrogen increases are probably due to a concentration effect caused by the decrease of the substrate carbon resulting from CO₂ lost (Kapetanios et al., 1993) as a consequence of the degradation of non-nitrogenous organic matter (carbohydrates etc.).

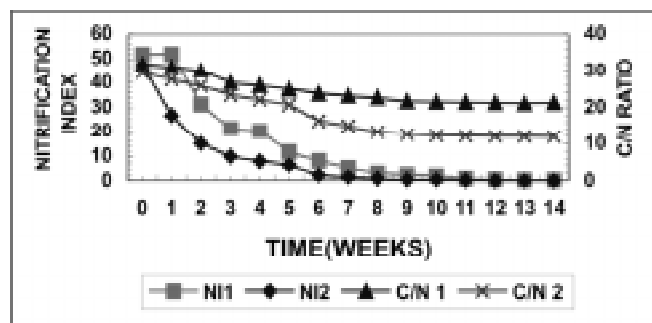


Figure 2: Variation of nitrification index and c/n ratio during composting.

The organic carbon concentration in Pile II degraded much more intensely during the thermophilic phase of composting due to greater activity of the microorganisms and the presence of easily degradable substances. After 14 weeks of composting the organic matter in Piles I and II decreased from 48.9% to 34% and from 48.% to 21% respectively.

The C/N ratio decreased due to the mineralization of the organic matter. In pile I the carbon/nitrogen ratio decreased from an initial value of 30.5 to 19.4 at the end of the process while for the same period of time in pile II the initial carbon/nitrogen ratio decreased from 29.5 to 11.9.

According to Rao et al. (1995) a carbon/nitrogen ratio between 10-15 of the compost indicates a good degree of maturity.

Nitrification Index

The nitrification process has been used as maturity index of composting (Bernal et al., 1998). The changes in Nitrification Index expressed as $\text{NO}_3^- \text{--N} / \text{NH}_4^+ \text{--N}$ during the composting process is presented in Figure 2.

The $\text{NH}_4^+ \text{--N}$ content in pile II increased from 658 mg/kg to 725 mg/kg during the thermophilic phase. This increase could be due to conversion of organic N to $\text{NH}_4^+ \text{--N}$ via the ammonification process and then the $\text{NH}_4^+ \text{--N}$ content decreased to 144 mg/kg towards the end of maturation phase. A similar trend was observed by Mahimairaja et al. (1994) and Tiquia & Tam, (2000). This decreasing trend guaranteed that ammonification was ending and can be used as a criterion of compost maturity (Sesay et al., 1997). The ammonia produced during the thermophilic phase is oxidized to $\text{NO}_3^- \text{--N}$ and thus the concentration of ammonia decreases with the increase in $\text{NO}_3^- \text{--N}$. In Pile I the increase in ammonical nitrogen was not very significant and so was the decrease.

The NO_2 concentration was negligible in both the piles, indicating that aerobic conditions prevailed during the composting process.

Appreciable amounts of $\text{NO}_3^- \text{--N}$ could be observed in Pile II and the values increased from 0.01% to 4.5%, which were reached after maturation. A $\text{NH}_4^+ / \text{NO}_3^-$ ratio in favour of the oxidized form is considered desirable for a mature compost. In Pile I, the $\text{NH}_4^+ / \text{NO}_3^-$ ratio was 0.28 while in Pile II the ratio was 0.03 towards the end of composting. At the end of the process the concentration of nitrates should be higher than that of ammonium indicating that the process has been prepared under adequate conditions of aeration (Miller & Finstein, 1985). A high concentration of $\text{NH}_4^+ \text{--N}$ in compost indicates instability and according to Zucconi and de Bertoldi (1987) it should not exceed 0.04% in mature compost. Bernal et al. (1998) established a limit of 0.16 as a ratio between ammonium nitrogen and nitric nitrogen as an index of maturity in composts.

Water Soluble Carbon (Cw)

The water-soluble carbon variation with composting time is presented in Figure 3. Water-soluble organic carbon is the most readily biologically active compound in composts applied to soils. The water extract from fresh composting mixtures was yellowish green and as composting proceeded, the intensity of colour increased to dark black during seventh week and gradually changed to light brown at the end of composting. These changes in colour imply changes in type and concentration of water-soluble organics. Water-soluble organic carbon level in Pile I gradually increased from 1.35% to 1.44% in the 7th week and then gradually decreased to 1.29% towards the end. While in Pile II the water-soluble organic carbon level gradually increased from 2.02% to 2.41% in the 7th week and then gradually decreased to 1.32% towards the maturation phase. As carbon component that are easily available to microbes organic and amino acids, proteins were degraded during the thermophilic stage of the decomposition, breakdown products were continuously released resulting in an increase in water soluble carbon (Hsu & Lo., 1999). A decline in water-soluble carbon is often used as an indicator of compost maturity (Garcia et al., 1991). In matured compost most of the soluble organic carbon is present as humic substances, which are resistant to further decomposition, thus explaining its increased stability observed with time during composting.

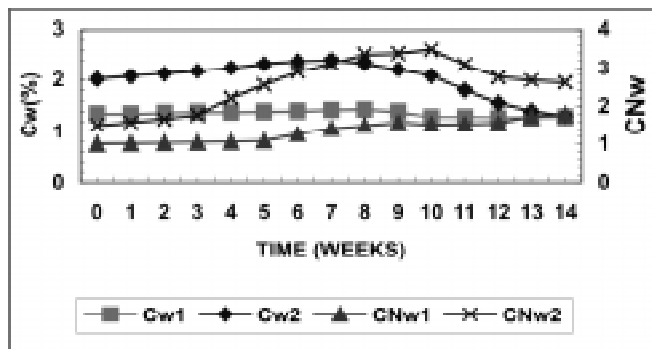


Figure 3: Variation of water soluble carbon and cnw during composting.

A limit of $C_w < 1.7\%$ can be used to reflect a good maturation degree. (Bernal et al., 1998).

CN_w (Water Soluble)

The water-soluble carbon and nitrogen index is presented in Figure 3. Water-soluble organic carbon level in Pile I gradually decreased by about 4.4% while in Pile II the decrease was 34.6%. The easily biodegradable carbon components that are highly available to microbes were degraded during the thermophilic stage of the decomposition, and the breakdown products were continuously released resulting in an increase in water soluble carbon (Hsu & Lo, 1999).

During composting the total nitrogen content increases with simultaneous decrease of its solubility in water (N_w) and towards the maturation phase the amount of mineral water soluble forms of nitrogen increased (Jerzy Drozd et al., 1997). In Pile I the N_w decrease from 13.5% to 7.2% and in Pile II the decrease was from 13.5% to 5.0%. The CN_w increased from 0.99 to 1.7 in Pile I while in Pile II the CN_w increased from 1.4 to 2.6 at the end of composting period.

Humic Substance Content

Humic substances comprise the most important fraction of organic matter because of their unique properties, such as the capacity to interact with metal ions, the ability to buffer pH, and the ability to act as a potential source of nutrients for plants (Hsu & Lo, 1999).

The relative contents of humic substances and non-humic substances during composting are presented in Figure 4. The quantities of humic acids, fulvic acids and non-humic fraction in composting mixture at various stages of the composting process represent the humification process. In Pile I total humic substances increased from 15% of organic matter to 25% of organic matter after seven weeks, stabilizing at this value till the end of the process. The fulvic acid level gradually

decreased from 6.1% of organic matter to 5.4% in mature compost. The humic acid level increased from 3.2% to 10.8% in the mature compost.

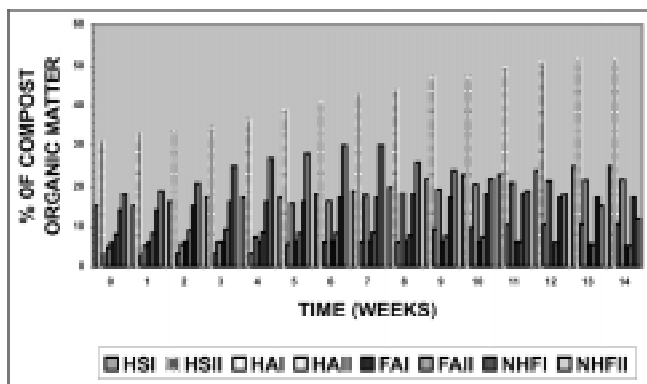


Figure 4: Variation of humic and non humic substances during composting.

In Pile II, total humic substances increased from 31% of organic matter to 52% of organic matter after seven weeks, stabilizing at this value till the end of the process. The fulvic acid gradually decreased from 8.2% of organic matter to 5.4% in mature compost. The humic acids increased from 5.2 to 21.9% in the mature compost.

The increasing level of humic acids during composting process represents the humification and maturity of compost. In general, fresh composts contain low levels of humic acids and higher levels of fulvic acids (Chefetz et al., 1996). During composting humic acids increased, whereas fulvic acids slightly decreased. The non-humic fraction in Pile I increased rapidly from 14% to 17% but then did not decrease further due to low organic matter degradation. In Pile II non-humic fraction increased rapidly from 18% to 30% of organic matter for the first seven weeks of composting, and then decreased to 12% in the mature compost, may be due to decomposition and humification of the breakdown products and presence of easily biodegradable organic matter during the maturation stage.

The Humification index and Humification ratio of the two piles are presented in Figure 5. Humification index in Pile I remained steady at 0.6-0.7 for the first four weeks and increased sharply to 1.3 in the seventh week and slowly increased to a final value of 1.8 towards maturity of compost. Humification index in Pile II remained steady at 0.6-0.8 for the first four weeks and increased sharply to 1.8 in the seventh week and slowly increased to a final value of 4.0 towards maturity of compost. The changes in humification index reveal that fulvic fraction and non-humic fraction extracted from sediment contain relatively high levels of biodegradable organic matter

that was mostly decomposed during first seven weeks of composting. The humification ratio in Pile I increased from 0.29 to 0.94 while in Pile II it increased from 0.4 to 1.04.

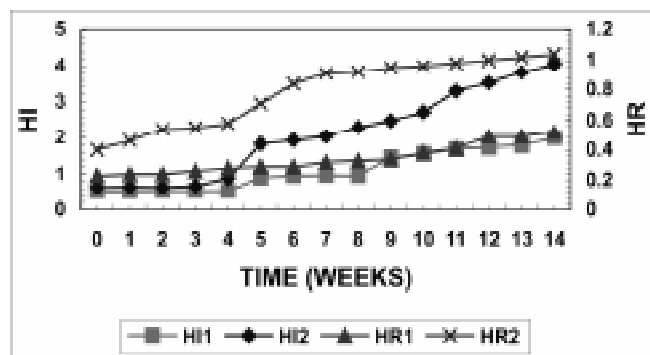


Figure 5: Variation of humification index and humification ratio during composting.

Cation Exchange Capacity

One of the variables that are frequently determined to estimate the degree of transformation reached by compost during the process of composting is cation exchange capacity (CEC). The changes in cation exchange capacity is presented in Figure 6. Its determination in an organic amendment is of great value because it allows us to know the stability degree of the amendment. Several studies accomplished with different kinds of compost have demonstrated that CEC increases with the stability degree of the compost. On the other hand, this parameter gives an indication of the amendment's capacity for catching nutrients and immobilizing phytotoxic substances as well as for buffering unforeseen pH changes. The obtained results showed that the CEC increased from an initial value of 31 cmol kg⁻¹ to final values of 38.9 cmol kg⁻¹ in Pile I while in Pile II the value increased from an initial value of 55.3 to 68.6 cmol kg⁻¹. The value in the Pile II was higher than the minimum recommended for mature compost (67 cmol kg⁻¹) (Iglesias-Jimenez and Perez-Garcia, 1992) thus indicating that the compost is mature.

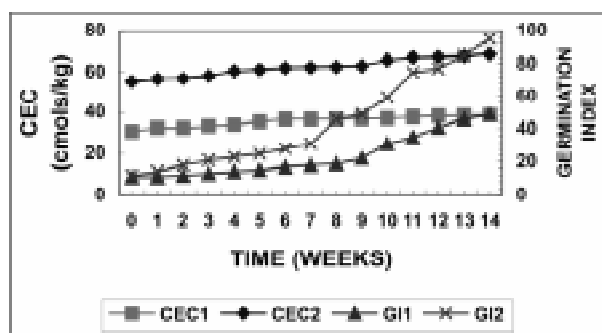


Figure 6: Variation of cation exchange capacity and germination index during composting.

Compost Mineralization Index

The compost mineralization index is expressed as Ash content/Oxidizable carbon. The changes in Compost Mineralization Index is represented in Figure 7. In the initial stage of composting (about seven weeks) the intense mineralization process takes place, which is manifested by a considerable decrease in carbon and increase in ash content. In Pile I, the ash content increased from 45.1% to 52.8%, the oxidizable carbon decreased from 19.5% to 16.2% and the compost mineralization index increased from 1.85 to 3.01. The ash content in Pile II increased from 49.4% to 61.9% and the oxidizable carbon decreased from 20.4% to 14.1% and the compost mineralization index increased from 2.5 to 4.65.

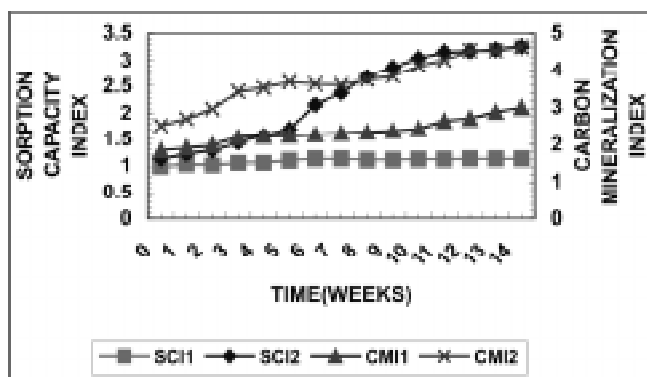


Figure 7: Variation of sorption capacity index and compost mineralization index during composting.

Sorption Capacity Index

The Cation Exchange Capacity/Corganic ratio reflects the degree of maturity of specific humic compounds and according to Inbar et al. (1990) it can be connected with the increase of the functional groups during humification process. The cation exchange capacity increases and organic carbon decreases with composting. The changes in Sorption Capacity Index is represented in Figure 7.

At the end of the active phase Pile I, had a sorption capacity index of 1.1 while Pile II had a value of 3.2 which was greater than 1.7—the lowest limit for describing well humified manures (Iglesias-Jimenez and Perez-Garcia, 1992).

Germination Index (GI)

The GI values increased during the composting process due to decomposition of the phytotoxic organic compounds. The changes in germination index is presented in Figure 6. These phytotoxic compounds, which were present in raw waste or produced during the first days of composting as intermediate products of microbial metabolism, were degraded during the process,

giving mature composts which could safely be used with plants. The sample taken from Pile I had a GI of 49 while Pile II had a GI of 95 which is greater than 80 and, according to Zucconi et al. (1981) and Tiquia et al. (1996), indicates a phytotoxic-free compost.

Profiles of Enzymatic Activities

The degradation of the labile substrates contained in organic matter can be followed by studying specific hydrolases, which are relatively easy to determine, and specific to the substrate. The hydrolases monitored in the present work (BAA-Hydrolysing Protease, Urease, β -glucosidase, Dehydrogenase and Phosphatase) could represent a good index of qualitative fluctuations of substrate during composting since they are substrate-inducible enzymes. The changes in enzymatic activities in Piles I and II are shown in Figure 8.

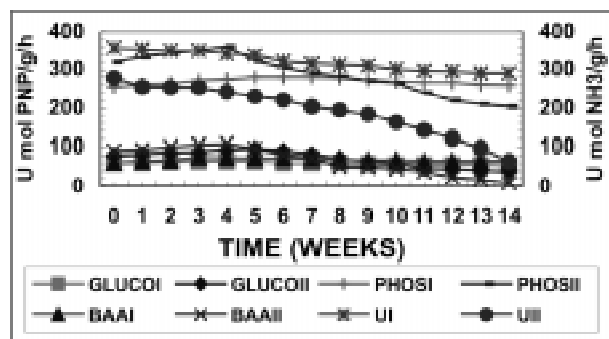


Figure 8: Activities of various enzymes during composting.

The high initial activity of these enzymes reflected the high microbial activity. The presence of a high content of degradable compounds in Pile II might have stimulated enzyme synthesis. As substrate decreased, the enzyme activity decreased as well (Ceccanti & Garcia, 1994).

The β -glucosidase activity decreased throughout the composting process, in Pile II as may be expected, since carbonated structures are degraded as composting proceeded (Garcia et al., 1995) and only the most resistant and those with the smallest number of side chains remain at the end of the process. β -Glucosidase and BAA-hydrolysing protease which are enzymes involved in C and N cycles, respectively showed a sharp decrease during the first seven weeks, and then stabilized as a consequence of decrease in available organic substrates.

Urease activity is closely related with the nitrogen cycle and it is involved in the hydrolysis of proteins to ammonium hydrolysing urea-type substrates. It is

believed that denaturalization of the enzyme during composting due to high temperature does not occur since urease is stable up to 80° C (Nannipieri et al., 1982). There is a pronounced difference between the values of the initial and composted samples. This is perhaps because the enzyme depends on microbial biomass, which implies that when the biomass is degraded (due to composting) enzymatic activity decreases. The activity of urease which catalyses the hydrolysis of urea to CO_2 and NH_4^+ , increased during the first four weeks of experiment probably as a consequence of diminution of high initial concentration of NH_4^+ in the substrate which may be responsible for the inhibition of this activity (McCarty et al., 1992). Subsequently urease activity decreased until seventh week and then remained more or less stable till the terminal phase of the composting process.

Phosphatase is a key enzyme in the phosphorus cycle, which is induced by the substrate. Its activity is largely dependent on microbial biomass (Ceccanti & Garcia, 1994). Phosphatase activity showed a sharp increase during the thermophilic phase followed by a gradual decrease. The increase observed during the thermophilic phase can be associated to high microbial activity, which occurs during this stage. The phosphatase hydrolyses compounds of organic phosphorous and transforms them into different forms of inorganic phosphorous (Ayuso et al., 1996). Thus, the decrease in activity observed may be due to enzyme inhibition by inorganic phosphorous temporarily released from the mineralization of the organic phosphorous (Garcia et al., 1992). Phosphatases are enzymes with relatively broad specificity capable of hydrolyzing various organic phosphate esters (Alef et al., 1995). The high initial activity could be related to the presence of organic phosphate compounds which may act as inducers of enzyme synthesis (Garcia et al., 1993a). After a slight decrease during the first week phosphate activity stabilized at about 200 $\mu\text{mol PNP g}^{-1} \text{h}^{-1}$ in Pile II and at 260 $\mu\text{mol PNP g}^{-1} \text{h}^{-1}$ in Pile I.

Dehydrogenase activity in soils and other biological systems has been used as a measure of the overall microbial activity (Garcia et al., 1997) since it is an intracellular enzyme related to the oxidative phosphorylation process (Alef, 1991). The initial high dehydrogenase activity recorded might have been the result of high microbial activity due to the high water soluble carbon concentration. After two weeks dehydrogenase activity decreased until the end of composting. The dehydrogenase activity is represented in Figure 9.

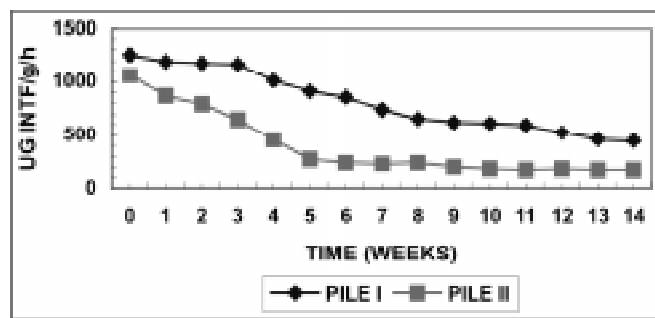


Figure 9: Variation of dehydrogenase activity during composting.

Characterization of Final Compost

A number of physical, chemical and biological indices have been linked to the maturity of composts (Mathur et al., 1993). The compost in Pile II was alkaline, pleasantly earthy in smell and dark down. The main parameters of the compost are presented in Table 2. According to the results obtained, compost in Pile II showed a C/N ratio of 11.9 which is in accordance with the recommended value between 10-15 (Rao et al., 1995) which shows that there was a considerable decrease in organic matter, there was decrease in water soluble carbon and nitrogen, increase in CEC values, showing a higher concentration of carboxyl and hydroxyl-phenolic groups which are mainly responsible for the higher value of CEC (Lax et al., 1986). Total N contents in composts were higher than the minimum level recommended (0.6% total N) by Zucconi and De Bertoldi (1987). The enzymatic activities are intracellular activities of proliferating microorganisms and not due to the activities of extra cellular enzymes. Thus these hydrolytic and dehydrogenase activities are sensitive indicators of the state and evolution of the organic matter and the overall quality of the compost. The macronutrient contents were above the minimum recommended (0.5% P_2O_5 ; 0.3% K_2O ; 0.3% MgO ; 2.0% CaO) by Zucconi and De Bertoldi (1987). Metal mobility and availability was reduced by increased pH values since cationic ions are less available at high pH conditions (Brady, 1974). Heavy metals present, in all the composts, were below the maximum values permitted for each element. Further studies on the regulatory standards of the composted product can validate the applicability of these stabilized sediments for successful application as biosolids.

Conclusions

It can be inferred from these studies that composting can be addressed as a full-scale bioremediation

methodology for contaminated lake sediments and the evaluation of maturity indices can be used as efficient indicators to assess the efficiency of compost activity.

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