HUMIC SUBSTANCES IN MUNICIPAL REFUSE DISPOSED OF IN A LANDFILL

Composition, Functions, Fate

ZDENEK FILIP

Department of Biochemistry and Microbiology, Institute of Chemical Technology, Hegstrauch 7, 35463 Fernwald, Germany, zdenek.filip@t-online.de

KATERINA DEMNEROV

Department of Biochemistry and Microbiology, Institute of Chemical Technology, Technicka 3–5, 166 28 Prague 6, Czech Republic

Abstract. Disposal of municipal waste in a landfill can create environmental and hygienic problems due to leakage water, odour and other nuisances until the disposed material becomes biologically and chemically stabilized. The stabilization process includes both mineralization and transformation of the waste organic matter, which may include humification of organic substances. Humic-like substances (HS) have been isolated from fresh municipal waste, and especially from that one aged for several months in a landfill. The amounts and structural composition of waste-related HS resembled those from a low-in-quality soil such as podzol. The HS have been found capable of forming Cu^{2+} and Fe^{3+} and other metal complexes. In laboratory experiments, however, the HS extracted from landfilled waste underwent strong microbial decomposition, especially if serving as sole sources of carbon or nitrogen for soil microorganisms. Indirectly, the experimental data reported here find their verification also in a more recent research results obtained by other authors.

Keywords: municipal refuse, landfill, microbial activity, humic substances.

1. Introduction

In a world with limited energy and raw material resources, the production of waste should be avoided or at least minimized as much as possible. Nevertheless, in the Member States of the European Union (EU) alone, about two billion tones of wastes are produced every year, and this figure is rather rising. In general, there

A.M. Bahadir and G. Duca (eds.), *The Role of Ecological Chemistry in Pollution Research and Sustainable Development*,

are two major ways of the solid wastes management: (i) utilization, and (ii) disposal in a landfill. Although a reintroduction of solid wastes into the product cycle should be preferred whenever ecologically possible and economically useful, their disposal in landfills remains widely spread. Therefore, the EU has laid down strict requirements for waste and landfills to prevent or reduce as far as possible the negative effects of the waste landfill on the environment, in particular on surface water, groundwater, soil, air, and human health [3]. Usually, a landfill can create some of these problems until biological and chemical stabilization of the disposed waste occurs. It has been widely documented, that in different natural environments refractory organic substances such as humic matter play an important role in stabilization processes [16, 25]. Rather less attention has been paid to humic substances eventually appearing in municipal refuse. In order to fill that gap experiments were performed some years ago [5, 7, 8, 10, 12–14, 24].

In this paper results of these investigations on the appearance, characteristics and fate of waste-related humic substances should be summarized. In addition, an actual development in the same field of applied science should be quoted.

2. Model landfill and material sampling

In a suburb of Braunschweig, Germany, big cylindrical containers of 40 m^3 in volume were constructed. The construction details of these thermally insulated and bottom-drained model landfills are described elsewhere [26]. Municipal waste originating from a domestic sector of the city was placed in the containers in amounts generated by some 5,000 people in a week. In some containers dewatered sludge was added, and waste was compacted mechanically. The top of containers remained open to the air but was covered with a soil layer. At intervals of 2 or 4 months, during a period of 20 months, samples of waste (1–2 kg) were taken using small openings in the container wall. Air-dried and finely milled samples were analyzed. For the description of analytical procedures, and other details refer to the original papers as cited in the paragraph 1 of this chapter.

3. Microbial counts and activities in municipal waste

Municipal waste delivered for disposal at the landfill was rich in different groups of microorganisms. The counts of aerobic bacteria capable of utilizing proteins for instance, was $2.5 \cdot 10^{12}$ g^{-1}. Figure 3.1 shows that the microbial counts were mostly reduced during the first weeks of the waste disposal. Later, the counts increased with maxima reached after 6 or 8 months. Simultaneously, the CO_2 release in samples of waste, which indicates the mineralization of decomposable organic matter, was reduced from 72 to 15 mg^{-1} $h^{-1} \cdot 100$ g (dw) in the course of disposal, i.e., between months 0 and 20. At the same time the addition of easily utilizable carbon (glucose), or carbon and nitrogen source (peptone) to the waste samples markedly enhanced CO_2 evolution. Thus, although rather stabilized after 20 months of disposal, the municipal refuse still contained microorganisms capable of mineralization activities. Probably, actinomycetes and fungi were strongly involved in these effects, since their numbers remained relatively stable in course of time in comparison to the counts of bacteria which were reduced from 100% to 0.1% after 20 months.

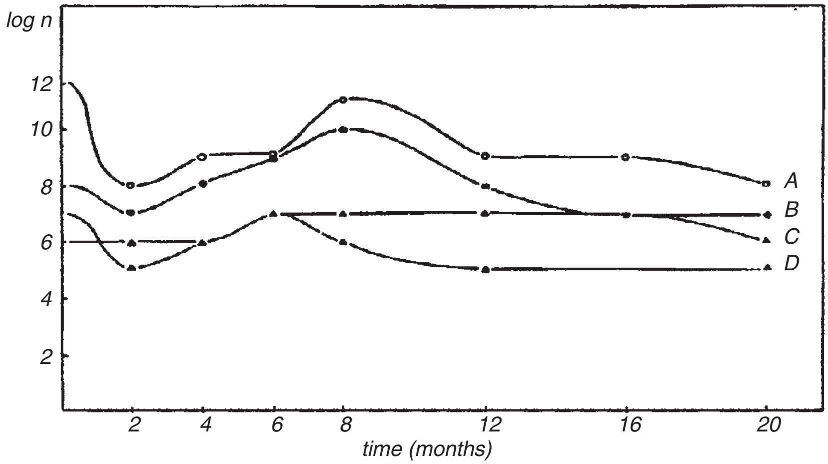

Fig. 3.1. Numbers of aerobic microorganisms in municipal waste disposed of in a landfill. A: aerobic proteolytic bacteria; B: anaerobic proteolytic bacteria; C: actinomycetes; D: microscopic fungi.

From earlier investigations it is known that different fungi and actinomycetes are capable of forming dark polymers that resemble humic substances in many respects [11, 18]. It was also possible to isolate numerous strains of microscopic fungi from municipal waste, which were capable of oxidizing simple phenolic compounds into dark coloured polymers. In the waste material they belonged to the complex microbial population. In individual experiments the ability of the waste-related microbial population was examined to produce humic-like polymers from two individual substrates which cannot be easily oxidized by microbial exoenzymes, i.e., casein (protein), and starch (carbohydrate). After a 2 months of aerobic incubation at 35°C, the cultures containing casein yielded a total amount of 830 mg C L^{-1} in humic-like substances. The adequate number for cultures containing starch was significantly lower (74 mg C L^{-1}). The cultures with starch, however, yielded 3.800 mg L^{-1} microbial biomass, whereas those enriched in casein yielded 1.800 mg C L^{-1}, and non-supplemented control cultures yielded only 33 mg biomass per liter. Since spectral characteristics indicated Because similarities in spectral characteristics between the microbially formed humic substances and groundwater-related humic acids could be observed, one can speculate about introduction of humic substances from a municipal landfill into groundwater aquifer, e.g., via landfill leachate, to occur.

4. Humic substances in municipal waste – their contents and characteristics

Humic substances were extracted from municipal refuse in a N_2-atmosphere using a mixture (1:1) of 0.1 M $Na_4P_2O_7$ and 0.1 M NaOH, and were allowed to precipitate 24 h at pH 1.5. The representative yields are shown in Table 4.1.

Table 4.1. Yields of humic substances from municipal waste (mg/l00 g waste).

	Period (months)				
Source	0	2	6	12	20
Compacted refuse	271	300	405	260	250
Uncompacted refuse enriched 2: 1 with sewage sludge	275	588	990	403	610
Compacted refuse enriched 2: 1 with sewage sludge	275	488	998	251	220

Evidently, humic substances were present even in fresh municipal waste, and their contents increased and decreased again during the disposal period. When compared with fresh waste, the maximum increase was reached after 6 months in waste disposed of with sewage sludge added. Later on, the content of humic substances decreased again, and finally, after 20 months, in compacted waste with or without sewage sludge added it was lower than in the fresh one.

In comparison with the soil humic acid from podzol or with a commercial humic acid (Fluka AG), the humic substances from municipal waste had a much lower optical density at first (Fig. 4.1. A, B). Later, however, the slopes of the extinction curves showed a strong increase in optical density, and this usually indicates a high degree of polymerization of the structural units in humic substances [2].

In order to obtain a better insight with respect to their structure, humic substances were analyzed by IR spectroscopy. Figure 4.2 shows the IR spectra of humic substances extracted from samples taken in three different layers of the waste disposed in a landfill. Apparently, all the waste-related humic substances, and especially those extracted from the middle layer, demonstrate structural similarity with soil humic acid.

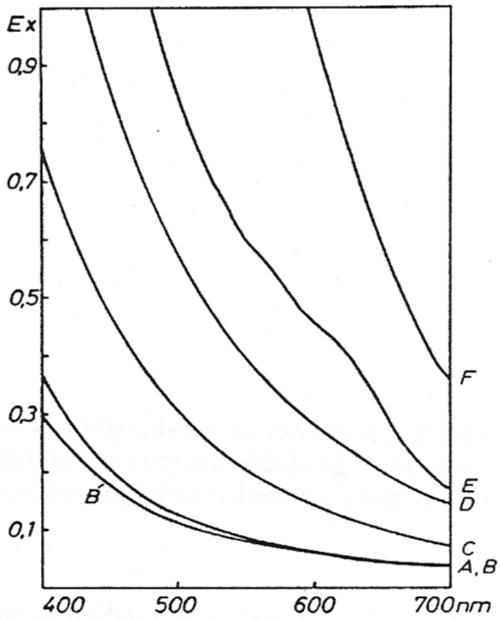

Fig. 4.1. Visible spectra of waste-related humic substances (HS), and reference humic acids. A: HS from fresh waste; B: HS from waste disposed of for 2 months; C: HS from waste disposed of for 6 months; D: HS from waste disposed of for 12 months; E: humic acid from podzol soil; F: commercial humic acid (Fluka AG).

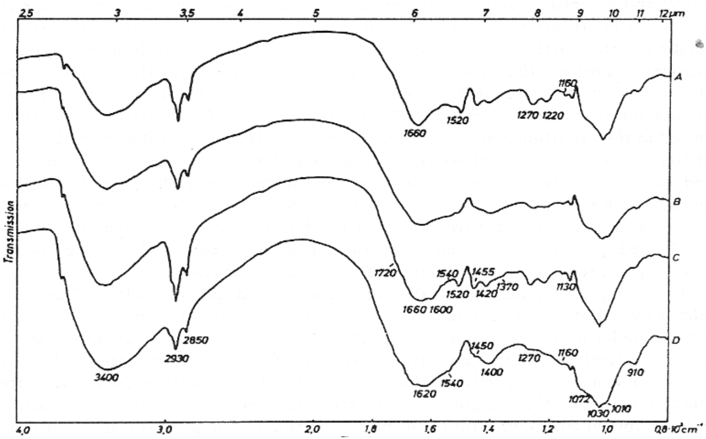

Fig. 4.2. IR spectra of humic substances (HS) from the municipal waste disposed of for 12 months, and a soil humic acid. A: HS from a bottom (60 cm) container layer; B: HS from a middle layer (120 cm); C: HS from an upper layer (180 cm); D: humic acid from podzol soil.

The NMR signals (not shown in Fig.) indicated the presence of chemical structures, which are likely to occur already in raw waste, such as proteins, lipids, carbohydrates and lignin-cellulose materials. With ageing of the waste in a landfill, the composition of humic substances changed. In particular, the concentration of proteinaceous material and lipids decreased, while the fraction of aromatic compounds increased.

The elemental composition of the waste-related and reference humic substances are compared in Table 4.2. The carbon and nitrogen contents of the waste humic substances were always higher than those of the soil humic acids.

For the carbon values at least, this is a reflection of the comparatively low ash contents. The soil humic acids contained much larger amounts of Fe, Mg, Na and P than waste humic substances, but similar amounts of Ca, Cu, Cd, K, S and Zn. According to Kerndorff and Schnitzer [19] high N and S contents of humic material appear to be the most valid indicators of a source material pollution, and this could be attributed also to municipal waste.

Metals are bound to humic substances usually as complexes, and therefore likely to be rather unavailable for organisms. Also, the concentration of Cu, Cd, Fe and Zn in the landfill drainage water was 10^2 to 10^3 times lower than in the humic substances [15]. This difference indicates that waste humic substances may play a role in retaining metal ions in the waste decomposing in a landfill if the complexes are stable enough.

Table 4.2. Elemental composition of waste-related humic substances and soil humic acids.

Source	C	N	Al	Ca	Cu	Cd[a]	Fe	K	Mg	Na	P	S	Si	Zn	Ash
	(%)							(ppm)							(%)
Fresh refuse	59.8	5.2	3600	1700	130	< 13.0	260	140	430	170	320	590	3800	170	0.74
Compacted refuse, aged for (months):															
2	59.6	3.7	5700	23000	130	< 2.0	1000	1000	2500	230	630	3000	4900	440	7.0
6	52.1	4.7	8100	14000	160	< 3.6	2000	1800	2900	590	1600	4700	9500	320	8.3
12	45.9	4.1	9800	20000	620	< 2.8	5300	2200	6500	1600	2200	7400	13000	610	12.2
20	52.7	3.9	2600	17000	160	< 0.9	1900	750	5600	1300	1800	6200	3500	390	7.1
Uncompacted refuse enriched 2:1 with sewage sludge, aged for (months):															
2	49.6	6.8	4300	14000	410	< 1.1	1800	760	3600	840	2100	5200	6000	750	6.9
6	48.4	7.0	3400	12000	660	< 3.9	4200	530	3000	710	1500	5000	5000	850	6.0
12	50.2	5.9	4200	19000	500	< 2.3	2500	770	5500	1500	3500	8800	7600	790	9.7
20	50.9	5.4	2000	13000	500	< 3.8	900	480	4100	850	2700	6500	5800	320	6.8
Compacted refuse enriched 2:1 with sewage sludge, aged for (months):															
2	50.5	5.8	9300	14000	260	< 2.3	4400	1800	3900	510	3200	7500	12000	440	10.4
6	54.5	5.3	12000	8500	110	< 2.5	4000	2000	2900	370	1800	5200	16000	280	10.1
12	49.7	4.9	7700	24000	180	< 1.6	3600	1700	5700	1500	2400	8600	9300	390	11.3
20	53.8	4.7	2200	12000	110	< 17.0	560	980	2800	830	970	5500	2800	420	5.1
Podzol	38.1	3.3	20000	25000	110	< 1.2	10700	2500	8800	2700	8700	4700	25000	670	19.5
Chernozem	42.1	3.5	7500	29000	560	< 1.9	11200	1200	9800	3200	4500	4000	12000	310	14.0

[a] < indicates limit of detection.

Because different heavy metals have been found to exert negative effects on microorganisms and their metabolic activities [6], the affinity of some health relevant bacteria to the presence of humic substances extracted from municipal waste was tested. Humic substances from a compacted municipal waste (anaerobic landfill) slightly inhibited the growth of *Pseudomonas aeruginosa,* and a strong inhibition was observed with a *Staphylococcus aureus* strain. Preparation extracted from a non-compacted mixture of waste and sewage sludge inhibited only the growth of *S. aureus*. The observed inhibition effects of waste-related humic substances were comparable to those obtained with a phenol solution (100–200 $\mu g \cdot mL^{-1}$).

As mentioned above, the municipal waste, which was disposed of in large-in-volume containers representing model landfills were covered with a soil layer. In some of them, thin soil layers also separated to individual 60 cm high layers of refuse. Since in soils, humic substances usually undergo a partial degradation by microbial activities [9], it was tested in laboratory experiments whether or not waste-related humic substances can be degraded and utilized under aerobic conditions as sources of nutrient by soil microorganisms. According to results obtained, up to 50% of humic substances were utilized as a supplementary source of nutrients in only 21 days. The microbial utilization was enhanced to over 80%, and for some preparations up to 98%, if the humic substances served as the sole source of carbon or nitrogen, respectively. Remaining humic substances which could be re-isolated from microbial cultures were lower in their carbon (up to 12%), and nitrogen (up to 2.3%) contents. Spectroscopic analyses (UV, Vis, FTIR) indicated losses, especially in aliphatic structural units, and a relative enhancement in aromatic structures.

5. Recent developments in the research on humic matter in solid wastes

In Germany and some other countries a mechanical-biological pre-treatment of residual municipal solid waste prior to land-filling became preferred in recent years in order to minimize different harmful emissions, some of which might contribute to the greenhouse effect [4, 20]. Such a procedure appears quite necessary because otherwise, under landfill conditions the refuse, which contains biological degradable matter, might need around 22–30 years to become fully settled and mineralized according to results obtained in China [29]. A fine black soil-resembling fraction, however, could be obtained from a typical refuse landfill in Shanghai also already after 8–10 years of disposal but still, the refuse contained a large and metabolically diverse population of microorganisms [30]. On the basis of simulation tests and a mathematical method, [27] suggested different stabilization indicators of semi-aerobic landfill such as chemical oxygen demand (COD) $\leq$ 400 mg L^{-1}, NH_3-N $\leq$ 15 mg L^{-1}, and biodegradable matter (BDM) $\leq$ 5 %. Similar to our previous investigations, which were discussed in the paragraph 4, even actually several authors utilized alkali extractable organic carbonaceous matter (humic substances) to evaluate the stability of disposed wastes. Wu and Ma [28] found the content of fulvic acids (FA) but not that of humic acids (HA) correlate with CO_2 evolution, and thus, the authors recommended a FA-based test for the evaluation of stability of the disposed waste. In experiments carried out by Mondini et al. [21], water-extracted organic C did not provide reliable information on the transformation of lingo-cellulosic wastes but in contrast, the alkali-extracted organic C reflected organic matter changes during the waste disposal. An increase of the amount of humic-like carbon has been observed between the 7th and 12th weeks. Also similar to our results, Adani and Spagnol [1] found differences in the stability of waste-related humic acids. HA from a more evolved waste compost and disposed of for 150 days contained a higher portion of recalcitrant fraction based on aromatic carbon and a lesser amount of more labile aliphatic carbon than HA from a raw waste or that one disposed of for 11 days only. Fuentes et al. [17] performed complex structural analyses of humic substances extracted from domestic and other wastes. They found the humification process to be associated with an increase of the aromatic character of the systems, with the presence of phenolic groups as principal constituents and the decrease of oxygen containing carboxylic or carbonyl groups. The content of larger molecular size fractions also increased. Recently, Montoneri et al. [22, 23] reported structural composition and physical-chemical characteristics of humic acid-like substances isolated from fresh and composted green urban wastes. From the results obtained the authors postulated that extracts of these wastes can served as bio-surfactants and other chemical auxiliary for fabric cleaning and dyeing, and also for the photo-degradation of different dyes.

6. Conclusions

Municipal wastes contain diverse and a large number of metabolic active microorganisms. Basically, many of these microorganisms are not only capable of decomposing organic matter but also of formation of humic substances from simply structured C and N containing breakdown products.

The waste-related humic substances usually appear in complexes with metal-ions. In the course of waste disposal, humic substances become a subject of microbial transformation and degradation, and thus, their role in a long-term stabilization of organic wastes disposed of in a landfill seems rather questionable.

References

1. Adani F, Spagnol M (2008) Humic acid formation in artificial soils amended with compost at different stages of organic matter evolution. *J Environ Qual* 37: 1608–1616.
2. Chen Y, Senesi N, Schnitzer M (1977) Information provided on humic substances by E_4/E_6 ratios. *Soil Sci Soc Am J* 41: 352–358.
3. Council directive 1999/31/EC of 26 April 1999 on the landfill of waste. http://europa.eu/scadplus/leg/en/lvb/121208.htm
4. Felde von D, Doedens H (1999) Full-scale experience with mechanical-biological pre-treatment of municipal solid waste and landfilling. *Waste Manag Res* 17: 520–526.
5. Filip Z (1983) Beurteilung von Stabilisierungsvorgängen im deponierten Hausmüll mit der Hilfe eines Respirationstestes. *Forum Staedte-Hyg* 34: 139–143.
6. Filip Z (1995) Einfluß chemischer Kontaminanten (insbesondere Schwelmetalle) auf die Bodenmikroorganismen und ihre ökologisch bedeutenden Aktivitäten. *UWSF – Z Umweltchem Ökotox* 7: 92–102.
7. Filip Z, Berthelin J (2001) Analytical determination of microbial utilization and transformation of humic acids extracted from municipal refuse. *Fresenius J Anal Chem* 371: 675–681.
8. Filip Z, Cheshire MW, Goodman BA, McPhail DB (1985) The occurrence of copper, iron, zinc and other elements and the nature of some copper and iron complexes in humic substances from municipal refuse disposed of in a landfill. *Sci Total Environ* 44: 1–16.
9. Filip Z, Claus H, Dippel G (1998) Abbau von Huminstoffen durch Bodenmikroorganismen – eine Übersicht. *Z Pflanzenernähr Bodenk* 161: 606–612.
10. Filip Z, Dizer H, Berthelin J (1999) Bacterial toxicity testing of humic acid-like substances from a municipal refuse disposed of in a landfill. *Humic Subst Environ* 1: 15–19.
11. Filip Z, Haider K, Martin JP (1972) Influence of clay minerals on the formation of humic substances by *Epicoccum nigrum* and *Stachybotrys chartarum*. *Soil Biol Biochem* 4: 147–154.
12. Filip Z, Küster E (1979) Microbial activity and the turnover of organic matter in a municipal refuse disposed of in a landfill. *European J Appl Microbiol Biotechnol* 7: 371–379.
13. Filip Z, Pecher W, Berthelin J (2000) Mirobial utilization and transformation of humic acid-like substances extracted from a mixture of municipal refuse and sewage sludge disposed of in a landfill. *Environ Pollution* 109: 83–89.
14. Filip Z, Smed-Hildmann R (1988) Microbial activity in sanitary landfills – a possible source of the humic substances in groundwater? *Wat Sci Tech* 20: 55–59.
15. Fresenius W, Schneider W, Gorbach H, Poth W (1979) Analyse von Müll, Klärschlamm, Sickerwasser und Gas von Abfalldeponien. In: Collins H.-J. (ed.) *Wasser- und Stoffhaushalt in Abfalldeponien und deren Wirkung auf Gewässer*. Bericht eines interdisziplinäres Forschungsvorhaben; Müll and Abfall 11, Erich Schmidt Verlag, Berlin, 53–60.
16. Frimmel FH, Abbt-Braun G, Heumann KG, Hock B, Lüdemann HD, Spiteller M (eds) (2002) *Refractory Organic Substances in the Environment*. Wiley, Weinheim.
17. Fuentes M, Baigorri R, Gonzales-Gaitano G, Garcia-Mina JM (2007) The complementary use of 1H NMR, 13C NMR, FTIR and size exclusion chromatography to investigate the principal structural changes associated with composting of organic materials with diverse origin. *Org Geochem* 38: 2012–2023.
18. Haider K, Martin JP, Filip Z (1975) Humus biochemistry. In: Paul EA, McLaren AD (eds.) *Soil Biochemistry*, vol. 4, Dekker, New York.
19. Kerndorff H, Schnitzer M (1979) Humic and fulvic acids as indicators of soil and water pollution. *Water Air Soil Pollut* 12: 319–329.
20. Laine-Ylijoki J, Syrjä JJ, Wahlström M (2004) Biodegradability testing of the municipal solid waste reject. NT Techn Report 560, Nordic Innov. Centre, Oslo.

21. Mondini C, Sanchez-Monedero MA, Sinicco T, Leita L (2006) Evaluation of extracted organic carbon and microbial biomass as stability parameters in ligno-cellulosic waste composts. *J Environ Qual* 35: 2313–2320.
22. Montoneri E, Boffa V, Quagliotto PL, Mendichi R, Chierotti MR, Gobetto R, Medana C (2008) Humic acid-like matter isolated from green urban wastes. Part I: Structure and surfactant properties. *BioResources* 3: 123–144.
23. Montoneri E, Savarino P, Bottigliengo S, Musso G, Boffa V, Prevot AB, Fabbri D, Pramauro E (2008) Humic acid-like matter isolated from green urban wastes. Part II: Performance in chemical and environmental technologies. *BioResources* 3: 217–233.
24. Newman RH, Theng BKG, Filip Z (1987) Carbon-13 nuclear magnetic resonance spectroscopic characterisation of humic substances from municipal refuse decomposing in a landfill. *Sci Total Environ* 6: 69–84.
25. Seibel F, Heidenreich S, Frimmel FH (1996) Interaction of humic substances with polycyclic aromatic hydrocarbons (PAHs) during the biodegradation of PAHs. *ActaHydrochim Hydrobiol* 24: 260–266.
26. Spillmann P, Collins H-J (1986) Zentrale Versuchsanlage und Versuchsdurchführung. In: Spillmann P (ed.) *Wasser- und Stoffhaushalt von Abfalldeponien und deren Wirkungen auf Gewässer*, VCH, Weinheim.
27. Tang P, Zhao Y, Liu D (2008) A laboratory study on stabilization criteria of semi-aerobic landfill. *Waste Manag Res* 26: 566–572.
28. Wu L, Ma LQ (2002) Realtionship between compost stability and extractable organic carbon. *J Environ Qual* 31: 1323–1328.
29. Zhao Y, Chen Q, Huang R (2001) Monitoring and long-term prediction of refuse compositions and settlement in large-scale landfill. *Waste Manag Res* 19: 160–168.
30. Zhao Y, Song L, Huang R, Song L (2007) Recycling of aged refuse from a closed landfill. *Waste Manag Res* 25: 130–138.