Organic Matter Stability after Mechanical-Biological

Pretreatment of MSW

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Abstract

Mechanically-biologically pretreated wastes from households (MBP-wastes) still contain up to 30 % of organic substances. Biological tests (gas generation, respiration activity), however, indicate, that these materials are largely stable and non-reactive. When landfilled can the objective of waste stability be uphold despite the high content of organic? Do we have to expect release if conditions change?

It was investigated how – apparently stable – organic material of MBP-wastes can be characterized and how it behaved during a 1.5-year period of anaerobic deposition and a final re-enter of oxygen. Different parameters were used for characterization and it was found out, that cellulose – for long term degradable organic matter – and humic substances – for stable organic matter – were the most important ones. Due to their stability humic substances represent a sink for carbon and nitrogen. Although stable under constant anaerobic landfill conditions, in case of re-entering of oxygen degradation of organic matter and formation of humic substances continued.

1. INTRODUCTION

A major goal of waste treatment before deposition is reduction and stabilization of the remaining organic matter in order to minimize emission potential to a harmless level. Mechanical-biological pretreatment (MBP) is one measure to reach this goal, yet, these wastes still contain about 30 % of organic substances. However, biological tests show, that these MBP-wastes are largely stable and non-reactive leading to at least 90 % reduction of emissions compared to untreated wastes (Binner *et al*. 1999). It is an obvious question, if this organic content is long term stable.

For the characterization of stable organic substances in MBP-wastes parallels to soil organic matter might be helpful. According to soil analysis roughly 2/3 of the organic matter consist of amorphous humic substances, which are subdivided into humic acids, fulvic acids and residual humin. Depending upon the type of soil the content of organic matter varies between 1 and 5 %. MBP-wastes consist of a several times higher amount of organic matter and a different ratio of humic substances to other organic material. The formation of humic substances is, apart from degradation processes, one of the major biochemical pathways during waste composting. Particularly during the active decomposition phase a strong increase of humic substances could be observed with biowastes and rest wastes (Grassinger 1998; Heiß-Ziegler 2000; Zach and Schwanninger 1999). Further analysis of MBP-materials show that the majority of long–term degradable organic matter consists of cellulose. Consequently, for the characterization of stability of MBP-wastes these two parameters – cellulose for long term degradability and humic substances for stable organic matter – were predominantly focussed. Two different MBP-materials – one was already stable (according to the suggestions for MBP-output products from BINNER *et al*. 1999) and the other one was still reactive – were observed during a 1.5-year period of landfill-like conditions in so-called landfill simulation reactors. Partly, material was aerated after app. 60 weeks. Results should give answers to following questions:

1. How do long-term degradable organic substances behave under landfill like conditions?

2. How does stable organic matter (humic substances) behave under landfill like conditions?

3. How do long-term degradable organic substances and stable organic matter behave when aerobic conditions re-enter?

2. MATERIAL AND METHODS

As input materials for the landfill simulation tests two different MBP-wastes (both mixed with sewage sludge) were used. Materials were treated in two different treatment plants (Siggerwiesen and Oberpullendorf) and had a different degree of stabilization. App. 100 kg of material 1 (Siggerwiesen) were ground to a particle size < 20 mm. In adapted laboratory boxes material was aerated and decomposed under controlled conditions. After 8 weeks of decomposition – when stability criteria were reached – aeration was stopped and the material was put into a landfill simulation reactor (LSR), where leaching processes, degradation and humification were measured under defined boundary conditions. Material 2 was directly taken from the Oberpullendorf pretreatment plant after 5 weeks of decomposition and put into a LSR without any further treatment. Previously, separation of metals, bulk materials, plastics, adding of sewage sludge and sieving < 25 mm were done at the plant.

During the LSR-test leachate was recirculated periodically. Landfill gas was trapped in bags and the quantity was measured. Investigation temperature was 35°C. Sampling was carried out irregularly depending on the status of the degradation process. To prevent oxygen diffusion solid samples were taken out of the LSR by flushing the reactor surface wit N_2. Samples were analyzed for ignition loss, TOC and total nitrogen. Furthermore analyses of substance groups were carried out according to a method from Van Soest (1963) to determine easy degradable materials, cellulose and non degradable materials in feeding stuff. Yet, in most cases only cellulose was determined. Crude fat was determined according to the Soxhlet method at the beginning and at the end of the investigation period.

Humic substances were determined according to a method of Danneberg and Schaffer (1974). The authors prescribe a 4-step extraction of an air-dried sample with 0,1 M $Na_4P_2O_7$-solution. According to the color of the extracted sample results lead to the relative parameter "optical density" for fulvic acids and humic acids. A quantitative determination of humic acids was carried out by precipitation with concentrated HCl and – after washing – redissolving the precipitate with 0,1 M $Na_4P_2O_7$. The solution was measured by a spectrophotometer at 400 nm. Calibration was done by a humic acid standard (Fluka No. 53680).

Leachate was taken from the bottom of the reactor and was analyzed for several parameters, among others TOC and the content of humic acids. Gas was collected in gas-bags and analyzed volumetrically.

3. RESULTS AND DISCUSSION

3.1 Gas generation

As expected the well pretreated material Siggerwiesen (material 1) showed hardly reactivity in the landfill simulation test, after 80 weeks only 20.9 Nl/kg DS (**d**ry **s**ubstance) of landfill gas could be measured (Figure 1). Contrary to material 1 the material Oberpullendorf (material 2) was still highly reactive showing an intensive gas generation within the first 13 weeks of investigation. Afterwards gas generation hardly increased and after 80 weeks approximately 130 Nl/kg DS could be measured.
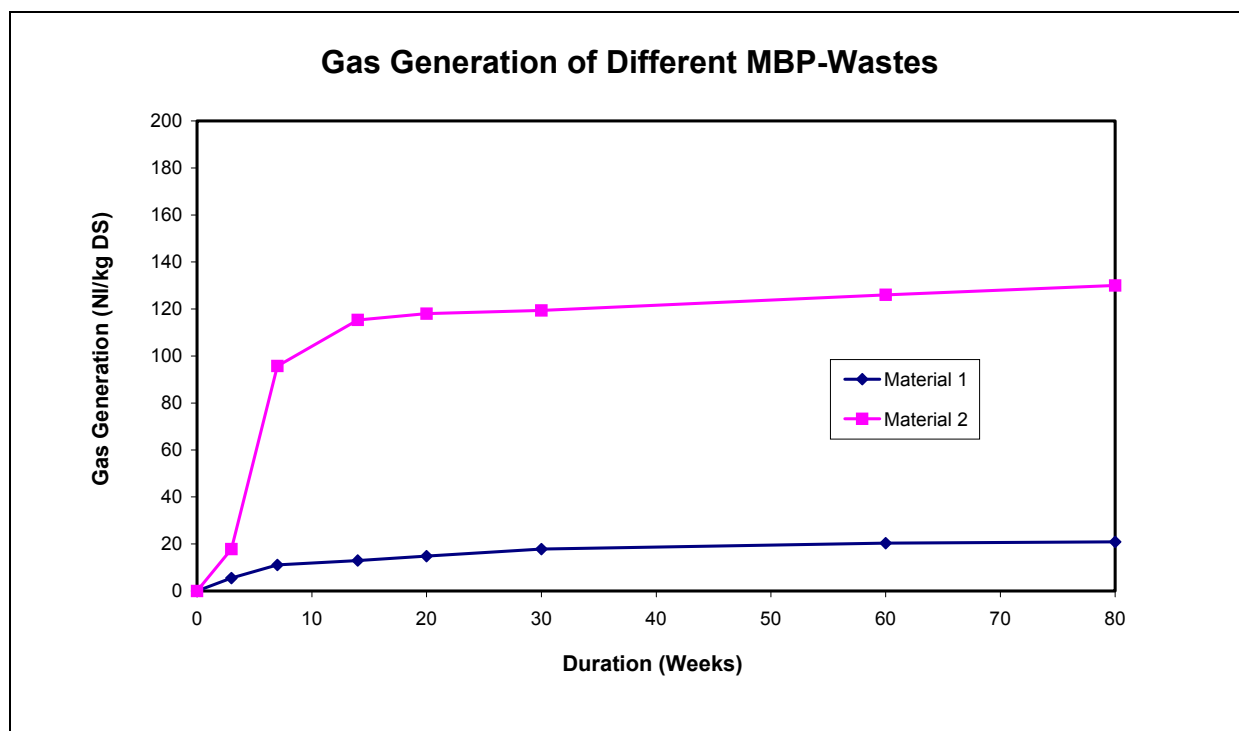
Gas Generation of Different MBP-Wastes

Figure 1: Reaction behavior of different mechanically-biologically pretreated wastes; degradation of organic substances and gas generation in 80 weeks

3.2 Development of organic matter – ignition loss, TOC, TKN, cellulose

Results indicate, that MBP-waste from the Siggerwiesen-plant was already well stabilized, ignition loss and TOC decrease only slightly within 80 weeks (Table 1). Results vary due to material inhomogenities (high amount of plastic). Cellulose decreases to some extent. Nitrogen remains more or less constant at a value of app. 1 % DS. Fat was < 1 % and did not change significantly.

Table 1: Development of organic substances of MBP-wastes during a landfill simulation test

No.	Week	Ignition Loss (%DS)		TOC (%DS)		Cellulose (%DS)		Nitrogen (%DS)	
		Mat. 1	**Mat. 2**	**Mat. 1**	**Mat. 2**	**Mat. 1**	**Mat. 2**	**Mat. 1**	**Mat. 2**
1	Start	32.0	44.1	18.9	27.5	7.6	14.4	0.93	0.78
2	3	n.d.	42.6	n.d.	23.6	n.d.	15.1	n.d.	0.86
3	7	29.4	39.5	17.3	22.4	7.9	7.7	1.96	0.97
4	14	31.7	36.5	19.9	19.1	*10.1**	6.8	1.04	1.00
5	20	33.1	32.9	19.4	18.4	7.8	6.0	0.95	1.12
6	30	30.8	33.6	17.5	18.3	7.6	6.0	0.89	1.00
7	60	28.2	29.5	16.0	18.4	6.6	4.1	0.91	0.90
8	80	29.0	31.3	16.8	18.4	5.3	3.8	0.90	1.04

*: outlier
n.d.: not detected

For MBP-waste from the Oberpullendorf-plant ignition loss and TOC decrease clearly. Although both materials had a different characteristic, results for ignition loss and TOC were nearly equal after 80 weeks. Cellulose decreases clearly and thus contributes significantly to the gas generation. Nitrogen shows strong increase tendencies at the beginning, at the end of the investigation the content varies.

3.2.1 Degradation of cellulose

Stabilized material 1 showed only little cellulose degradation. After 80 weeks still 5.3 % of cellulose were determined, with the reactive material in LSR 2, however, a clear reduction of more than 70 % were found. For both materials the contribution of cellulose degradation to the gas generation was calculated as follows:

$$cellulose = n * glucose$$

According to following reactions and the assumption of a complete degradation:

$$C_6H_{12}O_6 \longrightarrow 3\ CH_4 + 3\ CO_2$$

are developing from:	1 mol glucose	2 x 3 mol biogas
or from:	180 g glucose	6 x 22.4 l biogas
or from:	1 g glucose	0.747 l biogas

However, 100 % of the potentially degradable cellulose are hardly transferred to biogas, at the best an efficiency of 90 % can be considered.

Table 2: Gas generation as a result of cellulose degradation

Parameter	Dimension	Material 1	Material 2
cellulose (beginning)	% DS	7.6	14.4
cellulose (end)	% DS[1]	5.1	3.1
degradation of cellulose	% DS	2.5	11.3
total degradation calculated as glucose	g/kg DS	25	113
theoretical possible gas generation	Nl/kg DS	18.7	84.4
expected gas generation (η=90 %)	Nl/kg DS	16.8	76.0
measured gas generation	Nl/kg DS	20.9	130
gas generation as a result of cellulose degradation in % of total gas generation	%	80.4	58.4

[1]: considering decomposition (related to the constant amount of ash)

To a large extent remaining gas generation potential of sufficiently pretreated MSW can be explained from cellulose reduction as shown with material 1, where more than 80 % of the gas production result from cellulose degradation. With reactive material, however, it becomes clear that also other components contribute to the gas generation. But material 2 still shows that 60 % of gas generation are from cellulose degradation. So cellulose is an important parameter for the description of remaining reactivity (Table 2).

3.2.2 Substance groups according to Van Soest

Van Soest analysis were carried out from the input samples of the LSR-tests and the output samples after 80 weeks to investigate the development of easy degradable organic substances, cellulose and non degradable organic substances. This analysis provides sum parameters, that can be correlated with a specific degradational behavior. As mentioned above, cellulose seems to be the most important parameter to describe residual emission behavior (Table 3). However, still a high content of easy degradable organic substances could be detected. As both materials are non-reactive after 80 weeks this result might be ascribed to the grinding of the materials from 20 mm to < 0.5 mm for analysis. The amount of non degradable organic matter, including humic substances, lignin and plastics, remains to a large extent constant.

Table 3: Results of Van Soest analysis

Parameter	Material 1-Input (% DS)	Material 1-Output (% DS)	Material 2-Input (% DS)	Material 2-Output (% DS)
Ignition loss	32.0	27.8	44.1	25.5
Ash	68.0	68.0	55.9	55.9
Easy degradable	15.0	14.3	15.9	10.7
Cellulose	7.6	5.3	14.4	3.8
Non degradable	8.8	8.6	11.7	10.4

3.3 Development of stable organic matter

3.3.1 Humification

Figure 2 and Figure 3 show the development of humic substances during the landfill simulation test of MBP-material. Results are given in optical densities related to the content of dry organic substance at the time of reactor input. Furthermore, the amount of humic acids is given percentually (related to the dry organic substance of the reactor input).
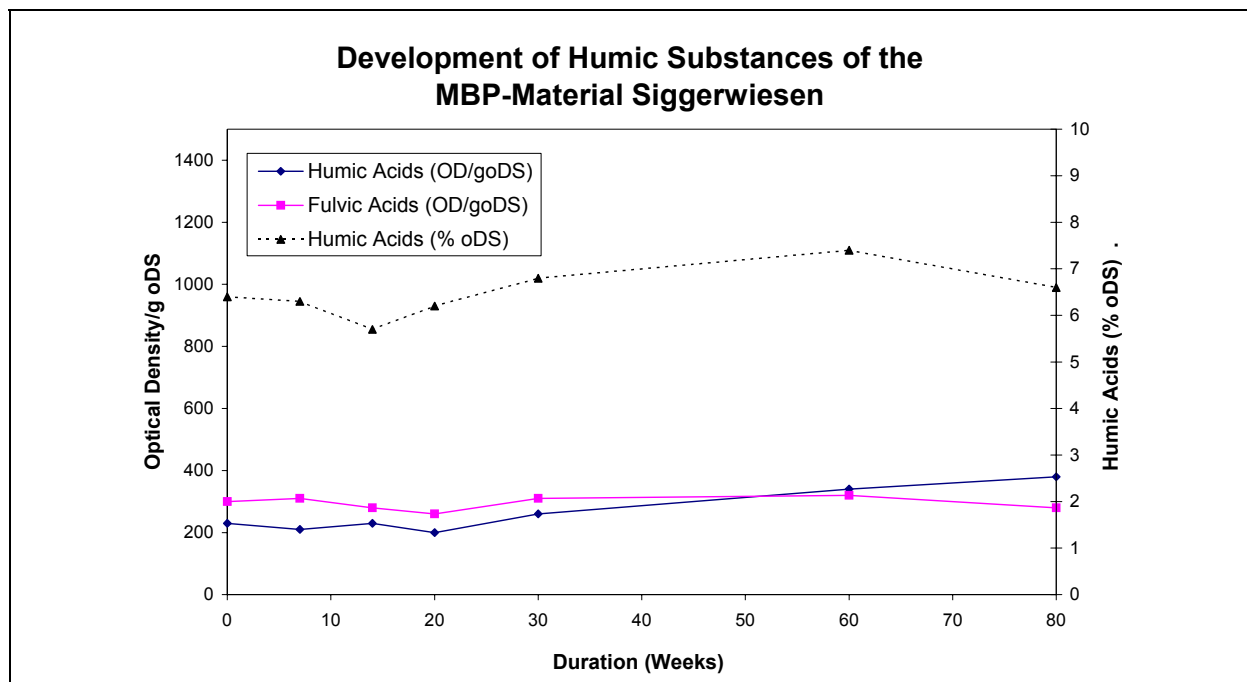

Figure 2: Development of humic substances of material 1
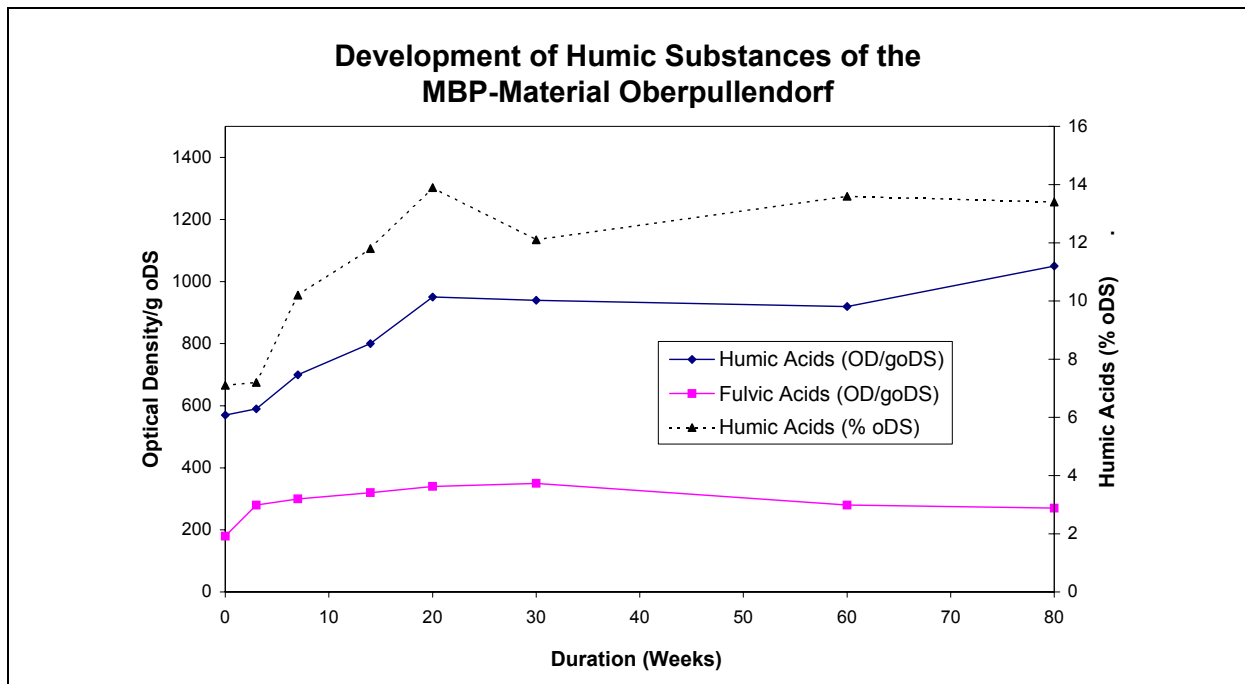
Figure 3:   Development of humic substances of material 2

Already the amount of humic substances of the input material 1 – after 8 weeks of aerobic pretreatment – must be classified quite small. Compared to investigations of other MBP-wastes amounts up to three times higher were found (Zach and Schwanninger 1999; Heiß-Ziegler 2000). Optical densities for fulvic acids and humic acids remain more or less constant. The quantitative determination of humic acids underlines this result partly, showing an increase from week 20 – 60 but finally the amount decreases again. A significant increase of humic substances, especially humic acids, could be observed in material 2. However, this increase does not prove to be linear and indicates a specific dynamics of increase and decrease. At the beginning of the anaerobic phase app. 3 % of the total dry substance were classified humic acids, after 80 weeks 4.2 % - related to the input sample - were found. The last value corresponds to 13.4 % of humic acids in the organic dry substance. The strongest increase of humic acids was found in the most active gas generation phase. The presence of intermediate degradation products obviously contributes to the humification. Towards the end of the active gas generation phase a decrease of the humic acids was observed. Similar development was also discovered by Heiß-Ziegler (2000).

Investigations show that stability and formation of humic substances depends on the residual reactional behavior and humic substances can be built up under anaerobic conditions.

3.3.2   Elementary analysis of humic acids

To evaluate their ability of C- and N-fixation some of the humic acids were analyzed for their elementary composition. Results are given in table 4. The carbon-content of humic acids remains to a large extent constant, tendencies of decrease might, however, be indicated. Results for carbon can be compared with literature data for compost humic acids as well as for soil humic acids (Filip 1993; Haider 1996; Scheffer and Schachtschabel 1998). Nitrogen content varies between 5.3 and 6.4 % which is higher than usually found in humic acids from soil. Chen *et al*. (1996) point out, that the N-content of humic acids from composts tends to be higher than the one in soil. This might result from a higher N-offer in waste materials at the begin of decomposition.

Table 4: Elementary analysis of humic acids of MBP-wastes

Sample	Age	C (%)	N (%)	S (%)
LSR 1:				
Humic acid sample No.1	input	52.0	6.2	1.2
Humic acid sample No.7	60 weeks	51.4	5.3	1.7
Humic acid sample No.8	80 weeks	n.a.		
LSR 2:				
Humic acid sample No.1	input	53.7	5.5	1.4
Humic acid sample No.7	60 weeks	52.4	6.4	2.0
Humic acid sample No.8	80 weeks	49.6	5.9	n.a.

n.a.: not analyzed

3.4   Leachate

Leachate was recirculated periodically. In both materials, TOC rises only weakly after the intensive gas generation. Material 2 shows – after a low start – a very intensive TOC degradation during the first weeks, finally, TOC is four times higher than in material 1 (Figure 4). Dissolved humic acids decrease for both materials at the beginning of the gas generation. For material 2, which has a higher amount of organics and a lower amount of plastics, a significant stronger increase than for material 1 could be detected around week 10. For material 2 a final concentration of 2,700 mg/l was analyzed, whereas material 1 shows only about 100 mg/l. Based on the amount of carbon in humic acids these concentrations represent 5 % of the leachate TOC in material 1 and about 30 % in material 2.
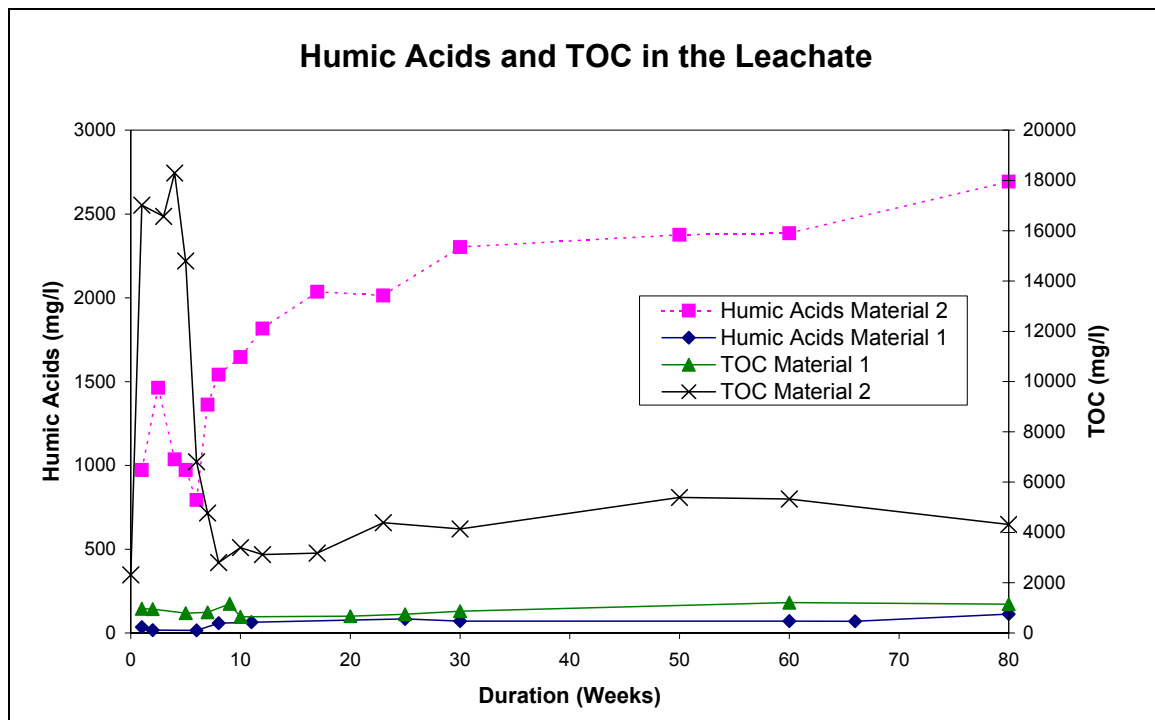

Figure 4:   Humic acids and TOC in the leachate of both materials

3.5 Influence of aerobic conditions

To investigate the influence of changing environmental conditions representative amounts of materials were taken out of the LSR's after termination of gas generation and exposed to aerobic conditions. After 8 and 16 weeks of aeration samples were taken and analyzed for ignition loss, TOC, N and humic substances.
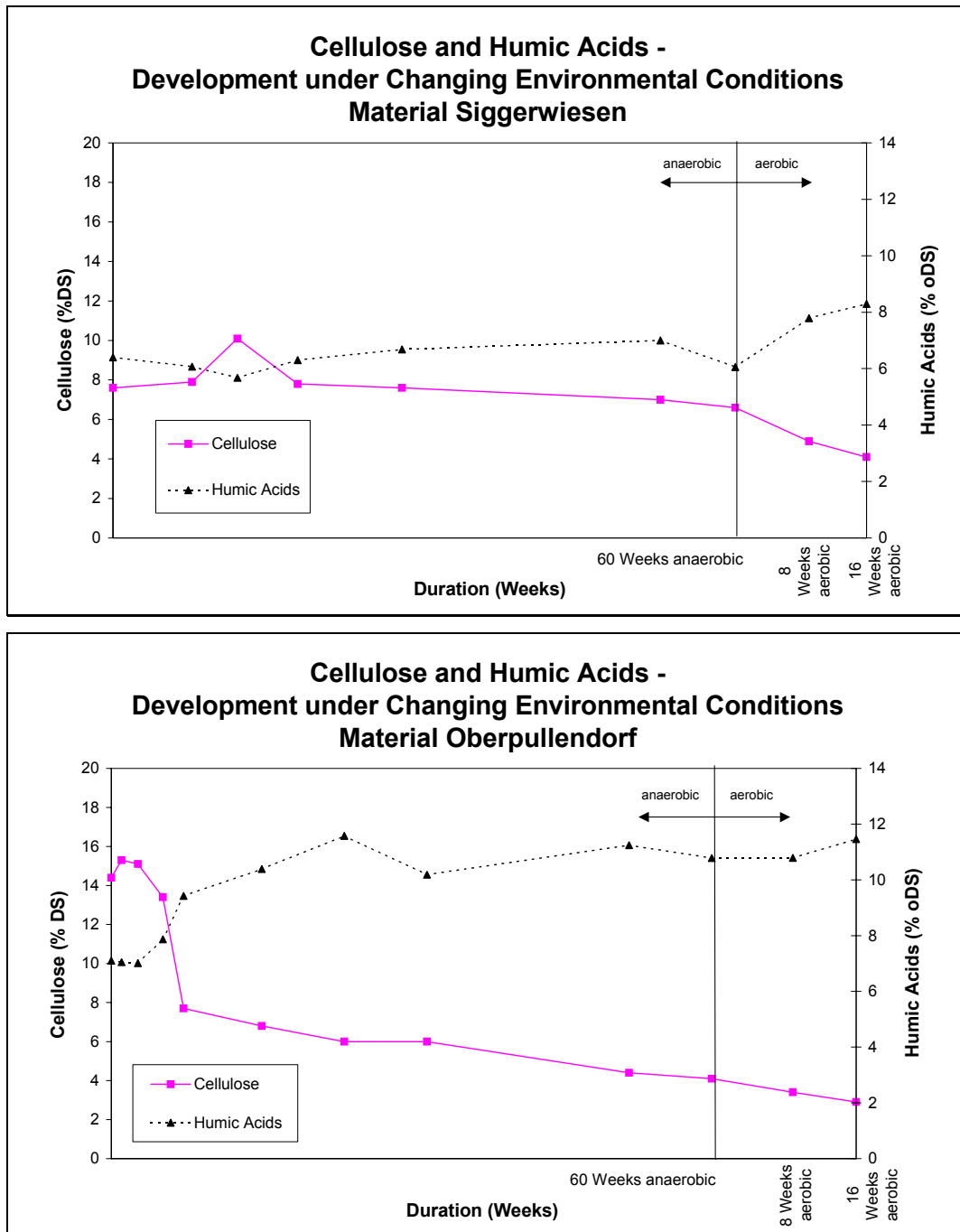

Figure 5:   Development of cellulose and humic acids under aerobic conditions of both materials

Figure 5 shows the results for cellulose and humic acids of the LSR materials after 60 weeks of anaerobic conditions, followed by 8 and 16 weeks of aeration. It is clearly recognizable

that mineralization starts again. Cellulose decreases stronger compared to the parallel-running anaerobic LSR's (Table 1). The humic acid content remains stable with increasing tendencies in material 2.

4. CONCLUSIONS

The behavior of organic substances of two different mechanically-biologically pretreated wastes was examined under landfill-like conditions. Special focus was put on the development of stable organic matter, expressed by the parameter humic substances. By means of different analysis quality and quantity of the stable organic matter was studied. Investigations show that organic matter of MBP-wastes changes under landfill-like conditions, depending on the degree of stabilization. MBP-waste, which is already stable, remains to a large extent stable in the anaerobic landfill environment. Only negligible emissions were detected which were less than 10 % compared to untreated waste. The gas path represents the main discharge of organic substances whereas emissions in the leachate are negligible. Humic acids represent a major component in the leachate.

Ignition loss and thus TOC decrease, Binner *et al.* (1998) found a correlation between gas generating potential and ignition loss of MBP wastes showing that a "zero-gas generation" would correspond to an ignition loss of approximately 29 % DS. This value was analyzed in both materials after about 1.5 years of landfill simulation. The most converted and degraded organic component is cellulose which contributes to 60 - 80 % to the remaining gas generation potential.

A part of the gasification can be explained by degradation of easy degradable organic substances. This sum parameter includes proteins, easy soluble carbohydrates, partly fats and fulvic acids. But even in stabilized materials still about 10 – 15 % are determined to be easy degradable, although no considerable reduction could be recognized. As both materials are non-reactive at the end of the LSR-tests this result might be ascribed to the grinding of the materials from 20 mm to < 0.5 mm for analysis. So less stable organic material which is protected from degradation by sorption, integration or inclusion into organic or inorganic particles could be set free. Also hydrophobic protective mechanisms or formation of micelles can include organic material and reduce availability. Soil science speaks about centuries, when meaning availability from enclosed organic substances (Haider 1998).

Formation of humic substances by means of mechanical-biological pretreatment leads to a fixation and immobilization of carbon and nitrogen. The investigation of the MBP-materials showed that humic substances are in dependence on the reactivity of the deposited material either stable or can be built up. This underlines their sink-function for carbon and nitrogen. Still reactive MBP-material shows an increase of humic substances. A total amount of humic acids, which are a part of the humic substance system, of about 13 % of organic matter were analyzed in this material.

About 30 % of the total organic carbon are bound in humic substances and are to a large extent stable. Equally, a high amount of nitrogen could be found in humic substances of MBP-wastes. It might be concluded that humification can have a positive effect on nitrogen release, leading to retention or a "slow release effect". Compared with soil humic acids a tendency of increased nitrogen fixation could be observed.

Investigation of changing environmental conditions show that mineralization continues under aerobic conditions, showing a clear degradation of cellulose. Even the humic substance system changes, showing an increase of fulvic and humic acids. It can be assumed, that "left-over" degradational products from the anaerobic degradation are further mineralized or humified. These first investigations show quite clearly that with a modification of the environ-

mental conditions the forecast of the long-term behavior of organic containing wastes, which is – so far - based on constant anaerobic landfill conditions, has to be reconsidered. Sudden change of the environment may lead to increasing degradational processes and release of organic substances either in gas or leachate. Further investigations are necessary.

5. LITERATURE

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