THE BIODEGRADATION OF PLASTICS USING BIOLAN PIKAKOMPOSTORI 220 COMPOSTER AND BY OXITOP BOD_7 MEASUREMENTS

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Tässä opinnäytetyössä tutkittiin neljän eri muovityypin biohajoavuutta. Muovit toimitti Plastiroll, joka on johtava pakkaus- ja muovintuottaja Suomessa. Yrityksessä haluttiin testata heidän prototyyppi-muoviensa biohajoavuutta. Opinnäytetyön kirjoittaja osallistui hankkeeseen vuonna 2012. Environmental Engineering – koulutusohjelman koulutuspäällikkö Eeva-Liisa Viskari järjesti tapaamisen Plastiroll-yhtiön teknisen myynnin hallinnossa työskentelevän Jouni Soipion kanssa.

Kompostissa testattiin maatalousmuovia, Bioskaa sekä muovityyppejä 505 ja 506, ja näiden testitulosten perusteella Jouni Soipio valitsi muovityypit 505 ja 506 jatkotestausten kohteeksi. Nämä kaksi muovia testattiin Oxitop-järjestelmällä, jotta olisi saatu selville niiden biokemiallinen hapenkulutus. Tehtiin kolme testisarjaa, joissa jokaisessa oli yhdeksän näytettä joista kolme 505 muovista, kolme 506 muovista ja kolme kontrollinäytettä. Muovia käytettiin 1 g yhtä näytettä kohden.

Tulokset osoittivat, että kaikki muovit hajosivat kompostointitesteissä kahdeksassa viikossa. 506-muovi hajosi jo neljässä viikossa. Lisätestejä varten valituista muoviprototyypeistä 505 ja 506 tehtyjen testien tulokset osoittivat, että 505-muovin keskimääräinen BOD7-arvo oli 72,5 mg /l, kun taas 506:lla se oli vain 11,9 mg/l ja kontrolliarvo oli 5 mg/l. Kaikki muovi ei ollut hajonnut yhden viikon aikana.

Selvisi, että muovi 505 on enemmän biologisesti hajoava kuin muovi 506. Myös 506 on osittain biohajoava, vaikka sen BOD7-arvo oli paljon pienempi kuin 505:llä, mutta sen arvot olivat silti keskimäärin yli kaksi kertaa suuremmat kuin kontrollinäytteellä. Testejä olisi jatkettava pidempään ehkä vähemmällä muovimäärällä, jotta saataisiin kokonaisvaltainen arvio biohajoavuuden laajuudesta.

Asiasanat: biohajoava, muovi, komposti, biokemiallinen hapenkulutus

ABSTRACT

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In this Bachelor's thesis the biodegradability of four different plastic types was examined. The plastics were provided by Plastiroll, a leading packaging and plastic producer in Finland, as they wished to test the biodegradability of their prototype plastics. The author got involved in the project in 2012, when the head of the degree programme in Environmental Engineering, Eeva-Liisa Viskari, introduced the author to Jouni Soipio, who works in the technical sales section of Plastiroll.

Four plastic types: mulch, Bioska, 505 and 506, were tested in composting conditions. On the basis of the results obtained, two plastic types, 505 and 506, were selected by Jouni Soipio for further testing. These two plastics were tested with the Oxitop system in order to evaluate the biochemical oxygen demand for a time period of seven days. Three test sets were made, in which there were nine test samples: three 505 plastic, three 506 plastic and three blank with no plastics for control purposes. 1g of plastic was used per test sample.

The results showed that all of the plastics in the composting environment degraded in eight weeks, one of them already in four weeks. The further evaluation of the two selected plastic prototypes: 505 and 506, showed that the average BOD_7 value of the 505 plastic was 72,5 mg/l, whereas 506 only had 11,9 mg/l and the blank value was 5 mg/l. All of the plastics had not degraded in one week.

The results show that the 505 plastic is more biodegradable than 506, but the 506 plastic is also biodegradable to some extent. Even though the BOD7 value for 506 was much lower than that for the 505, it still had components that did biodegrade for the BOD_7 value was more than double that of the controls. The tests should be continued for a longer time period, but maybe using smaller amounts of plastic in order to evaluate the full extent of the biodegradability.

Key words: biodegradable, plastic, compost, biochemical oxygen demand

CONTENTS

GLOSSARY

BOD	Biochemical oxygen demand
BOD_7	Biochemical oxygen demand for seven days
COD	Chemical oxygen demand
DO	Diluted oxygen
HCl	Hydrochloric acid
$KMnO_4$	Potassium permanganate
OHS	Occupational health and safety
TAMK	Tampereen ammattikorkeakoulu

1 INTRODUCTION

In this final thesis the biodegradability of four plastics is evaluated with composting and furthermore two of these are tested with Oxitop measuring heads and Oxitop Controller OC110 in order to find out if there is actual biodegrading or if the plastics just disintegrate into smaller pieces. The thesis is done for Plastiroll which is one of the leading packaging, plastic and biodegradable plastic producers in Finland.

2 THEORY

This part is for the theory and introduction on the composting, biodegradable plastics, biochemical oxygen demand, chemical oxygen demand and the Oxitop system. Additionally there will be occupational health and safety information concerning the different hazards of the chemicals and substances used.

2.1 Composting

This part will introduce a bit of the history and the basic concepts of composting. The internal processes in a composting environment are also examined though roughly and their functions in the decomposition and degradation of biodegradable matter are looked through. Also different stages are explained and how the microbes, bacteria and fungi work together to disintegrate the biodegradable matter.

2.1.1 Basic info and history

The origin of the name composting comes from the Latin name *composium* which means mixture. This is rather basic, however accurate, description of what compost is for it is a mixture of organic matter, carbon-nitrogen balance, microorganisms, heat, oxygen and moisture that work together in order to mineralize or otherwise degrade the organic matter into smaller substances. Composting is the human way to simulate the natural biodegrading, but if managed well the mineralization in compost will be faster (Diaz, Bertoldi, Bidlingmaier & Stentiford 2007, 26).

The scarcity of resources and need for waste management were the things that made composting possible. The composting by humans is in fact only few thousand years old practice. The necessity and usefulness of composting was realized in ancient Sumeria, when urban settlements began to rise. There the organic waste was stored into pits and used in the agricultural fields later as a fertilizer. Also other early civilizations in like India and China knew the usefulness of composting (Diaz, Bertoldi, Bidlingmaier & Stentiford 2007, 7; Insam, Riddech, Klammer 2002, Preface)

After the Industrial Revolution the amount and variety of waste has increased. Therefore also the waste management practices have changed quite radically. When in ancient times, most if not all of the waste was organic nowadays; plastics, metals, inorganic chemicals and many others are produced alongside with the organic waste. This has resulted into the building of huge landfills where all, no matter whether organic or not, waste is dumped. Even though much of the organic matter could be composted to form nutrient rich soil, the fertilizers are instead produced chemically. However, as the prices of fertilizers rise and the sources for inorganic fertilizer components run scarce the composting is becoming more appealing option for sustaining the agriculture (Yrjönen 2012).

As an example the Huussi Ry project project where author worked in 2011 summer. In Kaloko region, Zambia, composting dry toilets is used to separate the urine from the feces. The urine is distilled with water and used as fertilizer in the fields whereas the dry matter is composted for a year and then used as nutrient rich soil enhancer. This is one of the many ways to educate and encourage people for composting and sustainability (Huussi ry 2011).

2.1.2 The stages in composting

Composting has fundamentally four different stages that have different function in the biodegrading process. There is one mesophilic phase when the compost begins to heat up, thermophilic phase where the temperature is the highest, another mesophilic phase when it is cooling down and the maturation phase. In this part all of the phases and their functions in the composting process are examined (Diaz, Bertoldi, Bidlingmaier & Stentiford 2007, 32-34).

As mentioned the first or starting phase, is the mesophilic phase where the temperature of the compost is between 25 to 40˚C. During this phase the primary decomposers; fungi, bacteria and actinobacteria start chopping the easily degradable material such as proteins and sugars into smaller pieces. In this stage the possible worms, millipedes and other mesophauna starts to increase, but their effect compared to the work of the primary decomposers is non-significant (Diaz et al. 2007, 32).

As the amount of life in the compost increase so does the temperature, due to the rise in the cell respiration, which leads to the next phase. In the thermophilic phase the temperature of the compost has risen to be between 35 and 65˚C. The higher temperature has made the conditions for mesophilic organisms worse and they start to die off, giving way to the thermophilic ones that thrive in these conditions. During this phase the rest of the sugars and proteins are consumed and broken by the new fauna. This stage is also important for the hygiene of the compost, for all the larvae and pathogens are destroyed by the high temperature and antibiotics that the actinobacteria produces ((Diaz et al. 2007, 32).

The decomposition in the compost increases until 62˚C is reached, and in this experiment the temperature of the compost was kept in between 55 and 60˚C. If the thermophilic phase reaches over 65˚C the microorganisms are destroyed. Therefore it is essential that the compost is turned regularly and that temperature is observed so there would be optimal conditions for the thermophilic microorganisms. The turning of the compost is important for other reason too, because the temperature and oxygen levels are not equal in all the parts of the compost. In order to the organic matter to be broken equally, turning is necessary (Diaz et al. 2007, 32-33).

The second mesophiliac stage, the third stage of the process begins when the thermophilic organisms in the have broken down all that they can and start to die of starvation. This is the reason that this phase is also called as a cooling phase for the temperature begins to decrease. The organisms differ from the ones in the first mesophilic phase for the proteins and sugars that were used by the organisms then are now broken down. In fact this is the time when bacteria and fungi begin to break the harder substances to digest like starch and cellulose (Diaz et al. 2007, 34).

End of the composting process is the maturation stage. The amount of fungi increases in the mixture, whereas the bacterial communities decrease. The sugars, proteins, starch, cellulose have been broken, the mixture has hygienic due to the actinobacteria and there are not biodegrading compounds like lignin-humus forming. At this point the biological matter has turned into most useful, nutrient rich soil that can be used by gardeners and farmers in maintaining the nutrient balance in the soil (Diaz et al. 2007, 34).

2.2 Biodegradable plastics

Plastics are part of our everyday life. They are long chained polymers that can be easily molded into different forms, they are flexibe, strong, or soft if needed and the variety of uses for them is almost unlimited. They are also difficult or energy consuming to recycle or get rid of, and if released to nature they might cause severe and long lasting damage to the environment (Yrjönen, 2012).

One of the examples of this being the so called Great Pacific Garbage Patch, which is located between the States and Asia in the North Pacific Gyre. It is a place in the ocean where there is much more inorganic polymers from plastics that there should be. The size of the Patch is not clear as it is invisible for the satellites, but it is estimated to be huge. The problems are that animals that devour these plastic might choke or get slowly poisoned to death. Also on top of floating plastic it is possible for some animals to migrate to other parts of the world which might harm the original ecosystem (Yrjönen, 2012).

Since 1980s US solid waste crisis, which was triggered the concern on the amount of waste produced and dumped to the landfills and their effect on the future of the environment, there has been a growing market for more ecological waste, one of these innovations was biodegradable plastics (Andrady 2003, 158). Even though they seem to be a miracle cure for the growing plastic problem the fact is that as long as the oil prizes are low enough to maintain the lower prize of conventional plastic industry the biodegradable plastics will probably not be the market leader in plastic industry.

There are various definitions on what is considered as biodegradable plastic depending on who gives it; a company with their own agenda, environmentalist, environmental agency, scientist or anyone. In my opinion the best definition would be that when exposed to the right conditions the chemical and physical structure of the plastic undergoes several changes that lead to the complete mineralization or carbon dioxide formation so that there is no other residue left More so this change has to be possible in natural or composting environment where the natural biodegrading by fungi, bacteria and other microorganisms rule. The time in which this will happen should take in a compost system between weeks and months (Andrady 2003, 359).

2.3 Biochemical oxygen demand

Biochemical oxygen demand or BOD is used to test the organic oxidizable matter in water sample. It is the defined as the oxygen consumption by bacteria when they break down decomposable organic matter in aerobic conditions. The test can be used to determine the organic pollutant stage of the water to the environment. If the BOD value of water is too high it can cause severe eutrophication and in the worst case dead zones, where the oxygen levels are so low that most of the aquatic life has died (Sawyer, McCarty, & Parkin 2003, 604)

The BOD is usually tested in 5 day period, for it has been noticed that 70 to 80 percent of the total value has been reached in that time period. The wastewater samples are usually too rich in organic matter so they need to be diluted for the test. The other reason why the samples need to be diluted is that the DO, dissolved oxygen in the water has a limit of 8mg/l. If the samples have too much organic matter then the oxygen will be depleted and the test won't be completed. One of the testing methods for this is the Oxitop system, which was used in this final thesis (WTW 2008, 2; Sawyer et al. 2003, 605)

2.4 Chemical oxygen demand

Chemical oxygen demand or COD is used quite like the BOD to test the organic matter in water. The difference is however that during COD all organic matter, also lignin will be oxidized. This leads to higher values than in the BOD test (Sawyer et al. 2003, 625)

When testing chemical oxygen demand only three hours are needed, whereas in BOD it was 5 days. This is because high oxidizing agents are used to convert all the organic matter that can be oxidized. The test used in this final thesis was done by titration of the sample with potassium permanganate. The COD value was used to determine the range for the Oxitop BOD test (Sawyer et al. 2003, 625-626; WTW 2008, 2).

2.5 Occupational health and safety

One important thing that has to be considered is the occupational health and safety, for there are various chemicals and substances used in this final thesis which might have harmful effects if not handled properly. Therefore in this section the substances and their ill effects will be gone through. Furthermore lab coat, goggles and gloves should be used always when handling these substances. Also hands should be always washed after leaving the labs. The individual OHS rules that are applied in the lab should be followed and everyone working in the lab should be acquainted with the OHS rules of the specific location.

First of all there is the composting material. The organic matter was obtained from the school kitchen’s bio waste containers. The hazard with this is that there might be many pathogens that have been transmitted via mouth or the hands that touched the food, so it is essential to have gloves on when handling with it and not to swallow it.

Then there is the sludge from Viinikanlahti wastewater plant. This has to be handled with gloves on, and hands always must be washed afterwards, for all the viruses and bacteria like E. coli, that are in the municipal wastewater might cause ill effects on one’s health if swallowed. While going to the wastewater plant it was brought to the author’s that one of the summer workers had spent 2 weeks in the hospital because of diarrhea, so the threat is real (Yrjönen 2012).

Always when handling acids one has to have protective clothing, gloves and goggles. HCl, oxalic acid and sulphuric acid are all corrosive in high concentration and if in small concentration they still can cause skin damage and irritation. When swallowed these substances might cause severe damage to the respiratory system. When handling acids, especially strong ones, it should always be done under the hood (Hanhi 2009).

At last there is the potassium permanganate. This substance is irritating to the skin so protective clothing and gloves should be used. Other effect which is more annoying is that when contact with skin it will color it to purple, which is difficult to wash off (Hanhi 2009).

Furthermore in this thesis there some of the substances were boiled, in the chemical oxygen demand testing phase. This should always be done under the hood because the different chemical fumes might cause harmful effects from simple dizziness, to severe respiratory damage or even death (Hanhi 2009).

3 METHODS

This section describes the Composting experiment and BOD_7 experiments. The section is divided into two separate parts. The first one describes in detail the composting experiment, what preparations were made to make the composter to work at its best capacity and how the samples were prepared and measured. The other part is the testing of BOD_7 with the Oxitop measuring heads; there the different measures, like the dilution water and plastic sample preparations are described. Also the possible problems in the starting the measurements and how to start them with the Oxitop controller are discussed.

3.1 Composting experiment

This part describes the plastic composting experiment, the preparations that were needed and how the different samples were tested. It also shows the different tools that were used in the experiment and how the different test materials were labeled before entering the testing phase.

3.1.1 The preparation of the Biolan Pikakompostori 220

In this experiment four different types of plastics are composted in Biolan Pikakompostori (quick composter) 220 in order to find out how fast they degrade (picture 1). First before putting the plastics into the composter the temperature in there had to be risen over 60 Celsius. This is so that the biological material is efficiently degrading and so that there will not be great fluctuation in the temperature. This was achieved by filling the composter with bio waste from the school cafeteria, and also by adding woodchips that would bind some of the moisture in order to make the process more efficient (picture 2.). The compost was turned twice a week until the temperature had risen between 55 and 60 Celsius (Diaz et al. 2007, 32-33).

PICTURE 1. Biolan Pikakompostori 220 (Photo: Samu Asikainen 2012)

PICTURE 2. The food waste from school (Photo: Samu Asikainen 2012)

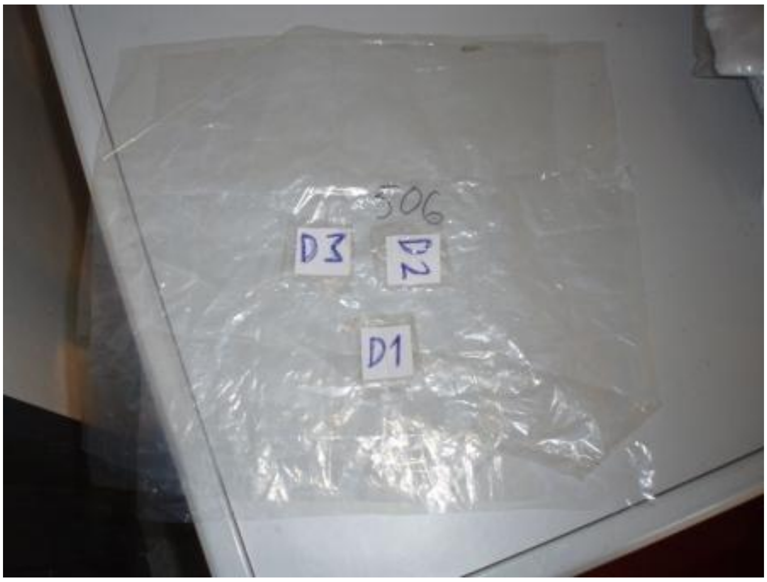
3.1.2 Preparation of the plastic samples

After about two weeks the composter was ready for use as the temperature had risen to approximately 60 degrees of Celsius. As the composter was ready the next step was to prepare the samples. The samples were cut to roughly 30 cm times 30 cm squares so that there would be three for the each four samples a there were four different samples there was 12 pieces of plastic in total. These plastic sheets were then individually weighed with the Presica XT 220A Analytical Balance and then they were place in a laundry bag and each sample was given its own code (picture 7; picture 8). The code for Mulch plastic was A, Bioska B, 505 C and 506 D. Each sample was also given a number so that the progress of individual samples could be followed, like A1, A2, A3 and so on (picture 3; picture 4; picture 5; picture 6.).

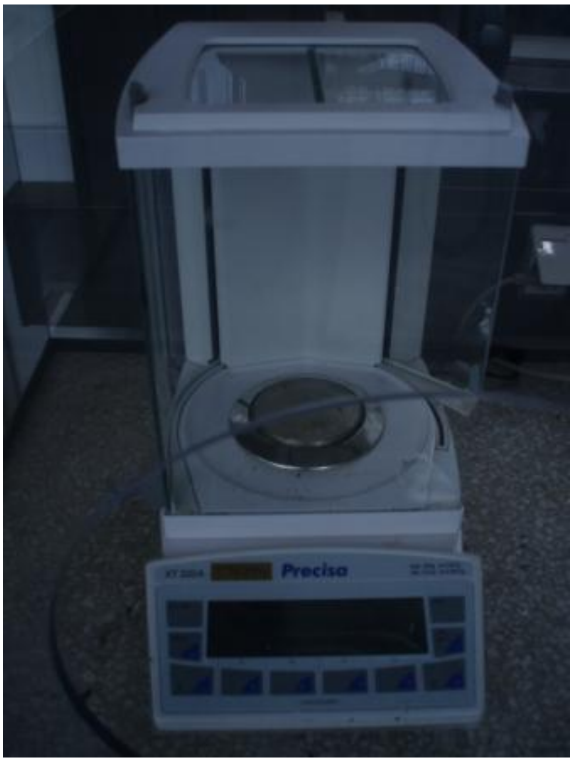
PICTURE 3. Labeling of the black mulch plastic composts samples (Photo: Samu Asikainen 2012)

PICTURE 4. Labeling of the Bioska plastic composts samples (Photo: Samu Asikainen 2012)

PICTURE 5. Labeling of the 505 plastic composts samples (Photo: Samu Asikainen 2012)



PICTURE 6. Labeling of the 506 plastic composts samples (Photo: Samu Asikainen 2012)



PICTURE 7. Precisa XT 220A Analytical Balance (Photo: Samu Asikainen 2012)

PICTURE 8. The laundry bags and their labeling (Photo: Samu Asikainen 2012)

3.1.3 The compost experiment with the plastics

After the initial preparation of labeling and weighing, one of each sample was placed on a different level of the compost. The A1, B1, C1 and D1 were placed near the surface, the second series in the middle and the third series in near the bottom of the composter. This is because the conditions in the compost system are not equal and in order to get a most accurate average on how the decomposition rate. Then they were let to be there for 2 weeks after which the bags were rinsed with water in order to get rid of excess biodegradable material and hang to dry overnight.

As the samples were dry photos were taken and the plastic matter that had not broken small enough to escape through the holes in the bags was measured with analytical balance. This was done in order to find out how much the bags had lost weight during the two week period. The compost was mixed though roughly, the plastic samples were put back to the bags and the bags were sealed and placed back to the composter for next two weeks. The procedure was repeated until there were no plastics left in the laundry bags.

3.2 BOD_7 measurement with the Oxitop system

In the Oxitop tests only the BOD_7 values for 505 and 506 plastics were measured. The tests with the Oxitop system required a lot more stages than the composting experiment. This part describes in detail the different phases of the tests and their preparation, including the preparation of the plastics, dilution water and the things that had to be done with the Oxitop controller to start the actual BOD measurements.

3.2.1 Preparation of buffer and saline solutions

When using the municipal wastewater, as in this test the wastewater from Viinikanlahti wastewater treatment plant, it is necessary to prepare buffer and three saline solutions. This is in order to have nutrients that the municipal sewage water might lack, so that the microorganisms have optimum environment to survive and to produce results that can be repeated. The measurements with Oxitop can be only done when these solutions are prepared and added to the sample in right proportions, in order to give the sample right nutrient balance. In this part the preparation of the buffer and saline solutions is explained (WTW 2000, 1-2).

Preparation of the phosphate buffer solution, pH 7.2

The task of a buffer solution is to keep the pH of a sample in the same level. Buffer solutions can even with small concentrations keep the pH at stable value, in this case pH 7.2. This section describes the preparation of the buffer solution (WTW_{31} 2000, 1).

There are four different substances that were diluted in water to make this buffer solution. The samples were measured with Precisa XT 220A Analytical Balance (picture 7). The values were following according to the WTW Application report O2 500231; 8,5g of potassium hydrogen phosphate (KH_2PO_4), 21,75g of dipotassium hydrogen phosphate (K_2HPO_4), 33,4g of disodium hydrogen phosphate heptahydrate ($Na_2HPO_4{\cdot}7H_2O$) and 1,7g of ammonium chloride (NH_4Cl). As there was no dipotassium hydrogen phosphate available, instead 28,50g of dipotassium hydrogen phosphate trihydrate ($K_2HPO_4{\cdot}3\ H_2O$) was used. These substances were mixed in approximately 500ml of water and finally diluted to 1000ml using a 1000ml volumetric flask (WTW_{31} 2000, 1).

Preparation of the saline solutions

As stated previously there are three different saline solutions to be prepared, which task are to give the sample sufficient nutrients in order for the microorganisms to survive. This section describes the preparation of these solutions (WTW_{31} 2000, 1-2).

Magnesium sulfate heptahydrate, 22,5 g/l solution

22,5 g of magnesium sulfate heptahydrate ($MgSO_4 \cdot 7H_2O$) was mixed in approximately 500ml of water and finally diluted to 1000ml using a 1000ml volumetric flask (WTW_{31} 2000, 2).

Calcium chloride, 27.5 g/l solution

36.4g of calcium chloride dehydrate ($CaCl_2 \cdot 2H_2O$) was mixed in approximately 500ml of water and finally diluted to 1000ml using a 1000ml volumetric flask. Also, if available, 27.5g of water-free calcium chloride ($CaCl_2$) could have been used (WTW_{31} 2000, 2).

Iron (III) chloride hexahydrate, 0.25g/l solution

0.25 g of Iron (III) chloride hexahydrate ($FeCl_3 \cdot 6H_2O$) was mixed in approximately 500ml of water and finally diluted to 1000ml using a 1000ml volumetric flask (WTW_{31} 2000, 2).

3.2.2 COD test

As the four solutions were prepared it was time to continue to the next phase which was the chemical oxygen demand test of the municipal waste sample. This is necessary in order to define the approximate BOD_7 value (measuring range) for the Oxitop test as one has to define the range in which the measurements will be taken (table 1; WTW_{30} 2000, 1)

TABLE 1. The volume of the samples according to the measuring range and the amount of NTH 600 drops (WTW_{30} 2000, 1)

Volume of sample (ml)	Measuring range (mg/l)	Factor	NTH 600 (drops)
432	0 – 40	1	9
365	0 – 80	2	7
250	0 – 200	5	5
164	0 – 400	10	3
97	0 – 800	20	2
43.5	0 – 2000	50	1
22.7	0 – 4000	100	1

The COD will be determined by oxidation – reduction titration using potassium permanganate ($KMnO_4$). The basis on this test is that potassium permanganate consumption is relative to the organic and materials that can be oxidized in the wastewater sample. In this test a 50 ml burette filled with potassium permanganate 0,002 mol/l solution was used for the titration (Hanhi 2009)

Cleaning the Erlenmeyer

In order to keep the risk of contamination and to have accurate results the Erlenmeyer flask used for the sample titration had to be cleaned. The process was done under the hood as there were acids and harmful potassium permanganate used. First of all 50 ml of 0,002 M $KMnO_4$ solution was poured into the Erlenmeyer flask. Then 5 ml of H_2SO_4 solution was added and this solution was boiled for ten minutes under the hood, after which the solution was dumped into a waste vessel. When the Erlenmeyer had cooled down it was rinsed with 1 ml of concentrated hydrochloric acid. Then the HCL was poured down the sink with lot of running water. After this the flask was rinsed with distilled water (Hanhi 2009)

The $KMnO_4$ titration

The wastewater sample from Viinikanlahti was allowed to settle so that the organic matter sank to the bottom. The 50 ml of the wastewater sample was transferred into an Erlenmeyer flask and 5 ml of sulphuric acid solution was added. The sample was then placed on top of an electric plate and heated under the hood. When the sample began to boil, 20 ml of the potassium permanganate solution was added and the solution kept was boiling under the hood. At this point a 50 ml burette was filled with potassium permanganate 0,002 mol/l solution. After boiling the sample for ten minutes the sample was removed from the hotplate and 20 ml of oxalic acid was added, at this point the sample was colorless. After this the burette with the potassium permanganate was placed on top of the Erlenmeyer and the sample was titrated. The end point of the titration was when the solution turned into weakly rose-red color. At this point the amount of $KMnO_4$ used was checked and the COD value was calculated. The test was repeated three times. The results are presented in the following section (Hanhi 2009)

Calculating COD

This section describes in detail the calculations for the COD of the wastewater samples. In order to find out the COD value it was necessary to find out the mass of potassium permanganate per liter, which is defined as the COD value of the sample (Hanhi 2009)

Known values

V (wastewater sample) = 50 ml = 0.05 l

V ($KMnO_4$) = 10.5 ml = 0.0105 l

M ($KMnO_4$) = 158.034 g/mol

c ($KMnO_4$) = 0.002 mol/l

First of all it is necessary to find out the amount of mols of potassium permanganate that were used in the titration. As the concentration and the volume of potassium permanganate are known the following equation can be used to determine the amount of mols of potassium permanganate (1).

$$n = c \cdot V$$
$$n(\text{KMnO}_4) = 0{,}002\ mol/l \cdot 0.0105\ l \qquad (1)$$
$$n(\text{KMnO}_4) = 0{,}000021\ mol$$

Now that the amount of mols of $KMnO_4$ is known the mass of the potassium permanganate can be calculated by multiplying the molar mass of $KMnO_4$ with the amount of mols that were used (2).

$n = m/M$

$m = M \cdot n$

$$m(\text{KMnO}_4) = 158.034\ g/mol \cdot 0{,}000021\ mol \qquad (2)$$

$m(\text{KMnO}_4) \approx 0.00332\ g$

Now that the mass of the potassium permanganate is know it is possible to define the chemical oxygen demand. As the COD is straightly relative to the amount of potassium permanganate in the sample the concentration of potassium permanganate (mg/l) in the sample is the COD value. This is calculated by dividing the mass of potassium permanganate with the volume of the sample (3).

$c = m/V$

$$c(\text{KMnO\_4 }) = (0.00332\ g)/(0{,}05\ l) \qquad (3)$$

$c(\text{KMnO}_4) \approx 66\ mg/l$

There are three different levels that can determine the level of contamination of water in terms of COD. The first level ranges between 0 and 20 mg/l, which means that the water is drinkable. When the value is 20 – 40 mg/l the situation is alarming and in the final stage the water is not drinkable. As the value of the sample was over 40 mg/l the water was not drinkable and as it was from the municipal waste water it probably contains high pathogen content (Hanhi 2009).

3.2.3 Sample preparation

In this part the methods used to examine the BOD_7 of the plastic samples are examined. There are various steps which each will be gone through though roughly. The dilution water had to be prepared, then the sludge, which contains the microbial base for the test had to be added

Dilution water

The saline solutions that were made are needed to make the dilution water, into which the wastewater samples will be added. The task of the dilution water is to have same regulated conditions for all samples so that the results will be consistent.

There were three saline and one buffer solution prepared; Magnesium sulfate heptahydrate, 22,5 g/l, Calcium chloride, 27,5 g/l, Iron (III) chloride hexahydrate, 0,25 g/l and phosphate buffer solution, pH 7.2. 1000 ml volumetric flask was taken and 1 ml of each of these solutions was added into approximately 500 ml of water and mixed. Then the volumetric flask was filled and mixed. Four liters of dilution water was prepared this way (WTW_{31} 2000, 2).

After the dilution water had been prepared it was put into a thermostat cabinet so that the temperature of the water would be 20°C ±2°C. Then the sample, kept in the cabinet was aerated using an air pump with an aeration head for 1,5 hours, even though in the WTW Application report O2 500231 the minimum time is 1 hour. This is because the dissolved oxygen concentration meter was not working and the dissolved oxygen content of the dilution water should reach 8 mg/l, so in order to get the desired value it was better to keep the aeration going on a bit longer than suggested (WTW_{31} 2000, 2-3).

Viinikanlahti sewage sample

The municipal wastewater was left to settle so that the coarse biological material had sunk to the bottom. Then, by decanting, the clearer wastewater was moved to another container. From there 80ml was transferred to the four liters of dilution water and mixed, making the wastewater concentration of the sample 20 ml/l. When ready the sewage samples were kept in the thermostat cabinet at 20°C (WTW_{31} 2000, 2).

Plastic samples

The 505 and 506 plastic samples were cut with a pair of scissors into pieces approximately 1x1 cm so that they will be evenly distributed in the Oxitop sample bottles, nominal volume of 510 ml (WTW_{31} 2000, 1). This would make it more probable to get even results, as the magnetic stirrers would be able to mix the samples in the bottles, distributing it evenly which might not happen if the samples were bigger pieces.

Preparation of the Oxitop measuring bottles

As the doped dilution water and the plastic samples were prepared, it was time to begin with the actual BOD_7 tests. First thing to do before adding anything was to determine the range in which the tests would be made. As it was earlier stated the COD value of an undiluted sample was 66 mg/l. As the BOD_7 value is not known it is assumed to be approximately 80% of the COD, therefore 53 mg/l. As, however, the sample wastewater concentration was only 20 ml/l, the BOD value was 50 times smaller, so approximately 1,3 mg/l. Therefore to lowest measuring range of 0 – 40 mg/l was selected for this test. (WTW_{31} 2000, 2; WTW_{30} 2000, 2))

As the measuring range was known the sample bottles could then be filled with the doped solution. Volumetric pipettes were of 100, 30 and 2 ml were used to fill up the bottles to 432 ml which is the volume stated for the range 0 – 40 mg/l. Nine bottles were filled with the 20 ml/l wastewater samples. The bottles were marked following; three 505, three 506 and three blank samples. After this the 505 bottles were each added 1 g of 505 plastic, 506 bottles 1 g of 506 plastic and nothing was added to the blank sample. The idea of this is that the blank sample, which has no plastics, only the wastewater, can be used to compare whether there was any difference when the plastic samples were added. Then 9 NTH drops and one magnetic rod were added to each of the bottles. After this the Oxitop heads were screwed on the bottles tightly (WTW_{30} 2000, 1)

3.2.4 Starting the BOD_7 with the Oxitop Controller OC110

When everything else was prepared it was time to begin the measurements. This was done with the Oxitop Controller OC110. With the controller it was possible to select the measuring method and duration of the measurement, which in this case was BOD for seven days. Also the measuring range was known to be 40mg/l and after the first week experiments it had to be increased to 80mg/l for the 505 samples, because the range was not enough. This part describes how all of this is done with the Oxitop Controller. When communicating with the measuring head one had to keep the controller approximately 5 cm away from it (WTW 2006)

Checking free measuring heads

First thing to be done was to check if the measuring heads are free. The controller was turned on from the ON/OFF button, after which the GLP/TOOLS button was pressed. Then there was a list of different options to select from which SHOW FREE was selected and then RUN/ENTER button was pressed, while holding the controller close to the measuring head. If a measuring head was free then a red light blinked in the measuring head, if not the measuring head had to be released (WTW 2006)

Releasing occupied measuring heads

First of all GLP/TOOLS button was pressed. Then there was a list of different options to select from which MAINTENANCE was selected and then RUN/ENTER button was pressed. Then a new list appeared where RESET/RELEASE was selected and RUN/ENTER button was pressed while holding the controller close to the measuring head (WTW 2006)

Now the measuring head was freed. However, if controller wasn't held close enough or for some other undefined reasons it was possible that text QUERY STOPPED came. In this case CONTINUE QUERY was selected. This was done repeatedly until the measuring head was free (WTW 2006)

Setting operation mode

Now that the measuring heads were free the operation mode had to be selected. In these test the standard BOD was used. The GLP/TOOLS button was pressed and from the list SETTINGS was selected and RUN/ENTER button was pressed. From the settings menu the OPERATION MODE was selected and the RUN/ENTER button was pressed. From the menu that comes MODE was selected and RUN/ENTER was pressed. After this it was possible with the UP/DOWN ARROWS to select the BOD STANDARD and RUN/ENTER was selected (WTW 2006)

Setting measuring time

As the operation mode was selected the measuring time could be selected. In these tests seven days were used. The GLP/TOOLS button was pressed and from the list SETTINGS was selected and RUN/ENTER button was pressed. From that menu MEASURING TIME was selected and RUN/ENTER was pressed. With the UP/DOWN ARROWS the measuring time was set to seven days after which RUN/ENTER was pushed (WTW 2006)

Setting the range and starting the experiment

When the measuring heads were free, the mode and time of the measurements was selected then the measurements could begin. The COMMUNICATING WITH MEASURING HEADS was selected. Then START SAMPLE was selected and RUN/ENTER button was pressed. After this a list of different BOD ranges appeared, from which 40 mg/l was selected, or 80 mg/l for the last two sets of measurements with the 505 plastic and RUN/ENTER was pressed. The sample type, measuring range, final date were now visible and they were checked so that they are correct (WTW 2006)

Then an I.D. number was given to each individual sample so that the identification of the samples would be easier when checking the final data. I.D. NUMBER was selected, RUN/ENTER was pressed and with the UP/DOWN ARROWS the sample was numbered. The 505 plastic samples were numbered from 1 to 3, 506 from 4 to 6 and blank from 7 to 9. When the numbering was done the controller was held close to the measuring head, START was selected and RUN/ENTER was pressed. The method was repeated until all nine measuring heads had begun the measurements. The bottles were placed in a thermostat cabinet with the temperature of 20 Celsius on top of a magnetic stirrer for seven days (WTW 2006)

3.2.5 Calling up the BOD_7 data with the Oxitop Controller OC110

When seven days had passed the measurements had stopped and the data was ready for collecting. The bottles were taken out from the cabinet and put close to each other on the table. All the data was possible to be obtained simultaneously with the controller (WTW 2006).

The controller was turned on with the ON/OFF button and COMMUNICATING WITH MEASURING HEADS button was pressed. From the actions available CALL UP ALL DATA was selected and RUN/ENTER button was pressed. The controller shows how many of the measurements were called up and the procedure was repeated until all nine samples had been called up (WTW 2006)

As there was some mysterious glitch in the software that could be used for getting the data to the computer the results were copied by hand. This was done in the following manner. SAMPLE MANAGEMENT was pressed, after which EVALUATION button was pressed to see the graphical presentation of the sample. Then RUN/ENTER button was pressed and with the DOWN ARROW the sample was traced until the beginning. From there the results were copied one by one going with the UP ARROW until the end of the results (WTW 2006).

4 RESULTS

This part described the results obtained from the tests. First there is a section for the composting results, which will be presented in numerical and graphical data that is described more in detail in the sections themselves. Then there are also photos which show the amount of degradation of the plastics that has happened in the compost. Then there is the section for BOD_7 results that show the correlation between time and BOD values.

4.1 Composting results

The experiment lasted for 8 weeks and all the data obtained is presented in this section. In this section one can see the results obtained from the experiment there are also pictures that show roughly how the samples looked as the time spent in the compost increased. First there are the weights of the samples originally. From those values a mean value was calculated that was then used to see the average mass loss during the experiment. Then there is also the graphical presentation where one can see the development of the plastic degradation.

4.1.1 The numerical data

This part describes the mass loss in numerical form. There is a table for individual samples and also for the average values of all the samples combined presented as the percentage loss of mass and the actual weight loss of mass of the plastic samples during the check-ups that were made every two weeks (table 2; table 3; table 4).

TABLE 2. The average mass-% loss of the samples

Time in weeks/ Sample name	Mulch Film mass-%	Bioska mass-%	505 mass-%	506 mass-%
0	100	100	100	100
2	83,7	93,7	89,8	42
4	58,4	48,3	50,4	0
6	17,5	10,9	9,2	0
8	0	0	0	0

TABLE 3. The average mass loss of the samples

Sample name /Time in weeks	Mulch Film (g)	Bioska (g)	505 (g)	506 (g)
0	1,4049	2,5683	2,2331	2,5608
2	1,1759	2,4053	2,0051	1,0754
4	0,8211	1,2405	1,126	0
6	0,246	0,2793	0,2065	0
8	0	0	0	0

TABLE 4. The initial masses of the samples and the progress of the mass loss

time	sample	Mulch (g)	Bioska (g)	505 (g)	506 (g)
Initial	Sample 1	1,4306	2,0154	2,179	2,5812
	Sample 2	1,387	2,8022	2,2387	2,5345
	Sample3	1,397	2,8873	2,2816	2,5667
	Average	**1,404867**	**2,5683**	**2,2331**	**2,5608**
2 weeks	Sample 1	1,3168	1,8805	2,054	1,4585
	Sample 2	1,1517	2,6367	1,9008	1,5043
	Sample3	1,0592	2,6987	2,0604	0,2634
	Average	**1,1759**	**2,4053**	**2,005067**	**1,0754**
4 weeks	Sample 1	0,9065	1,143	0,9985	0
	Sample 2	0,7923	1,356	1,1246	0
	Sample3	0,7646	1,2224	1,2549	0
	Average	**0,821133**	**1,240467**	**1,126**	**0**
6 weeks	Sample 1	0,5456	0,5585	0	0
	Sample 2	0,1289	0,1404	0,4651	0
	Sample3	0,0635	0,1391	0,1544	0
	Average	**0,246**	**0,279333**	**0,2065**	**0**
8 weeks	Sample 1	0	0	0	0
	Sample 2	0	0	0	0
	Sample3	0	0	0	0
	Average	**0**	**0**	**0**	**0**

4.1.2 The graphical data

This part the results are presented in the form of scatter plots from where it is easier to see the actual weight loss that happened during the test period. There are two different graphs that are used for this. The first one shows the actual mass loss in grams during the test period. The second scatter plot shows the mass percentage loss during the test period. As the samples were measured only every two weeks the lines might not totally correspond to the real mass loss that had happened during the time periods of these two weeks (figure 1; figure 2).

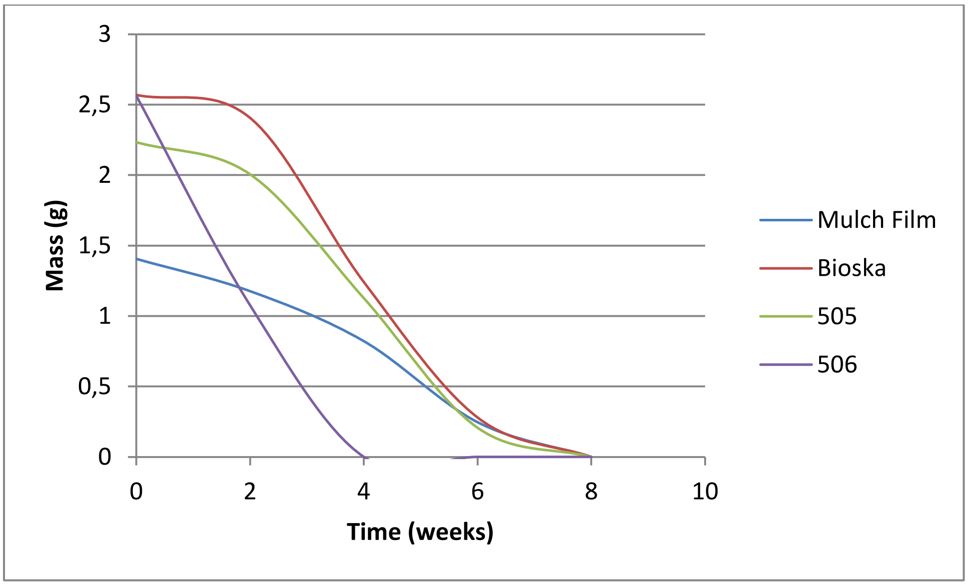


FIGURE 1. The average mass loss of the samples

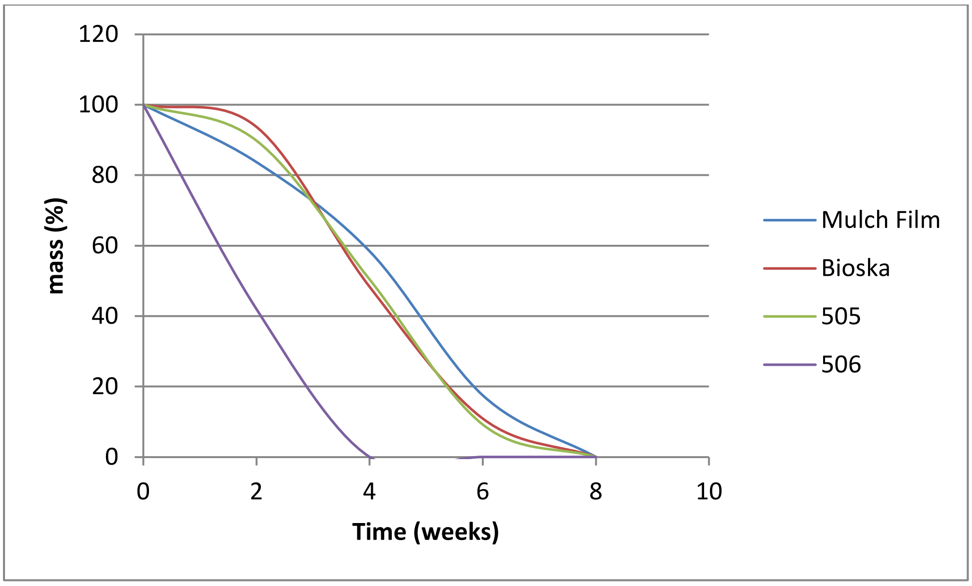


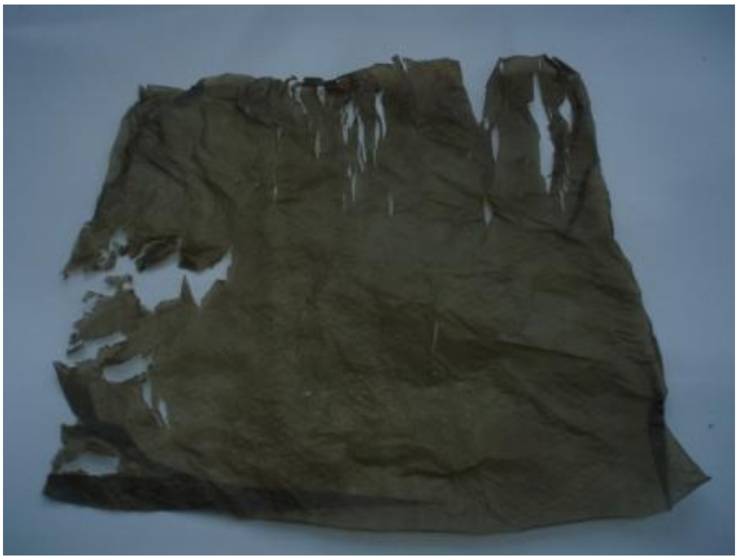
FIGURE 2. The average mass-% loss of the samples

4.1.3 The photos

In this section one can see the development of the plastics as they spent more time in the composter. The samples were photographed every two weeks. The photographs show clearly the transformation which the plastic sheet went through during the eight week testing period. There are no pictures of the samples from the week eight for all the samples had deranged into so small pieces that they were able to escape the holes in the laundry bags.

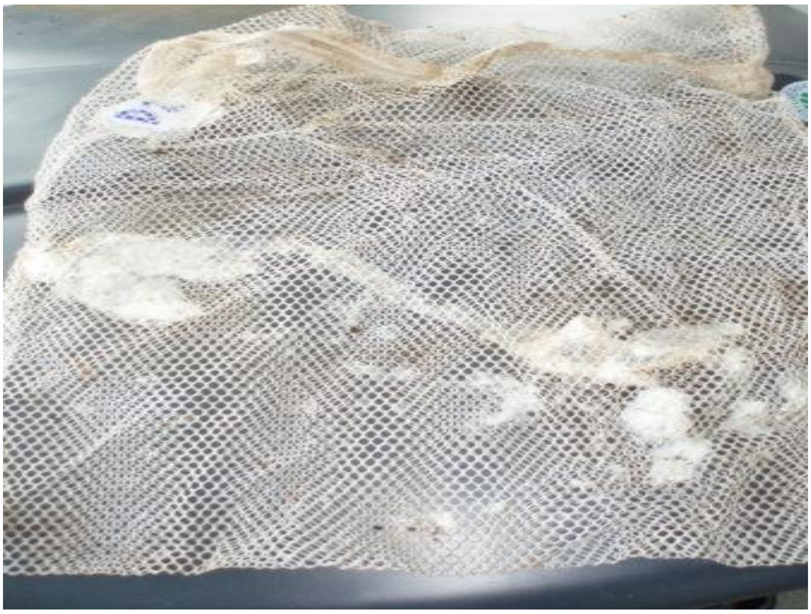
After 2 weeks of composting there were already visual changes in the plastic samples. The 505 had degraded the least, whereas Bioska and mulch film had already holes and tears in them (picture 9; picture 10; picture 11). The most drastic change was in the 506 plastic that had already turned into small flakes (picture 12).

PICTURE 9. The Mulch film (A1) after 2 weeks of composting (Photo: Samu Asikainen 2012)



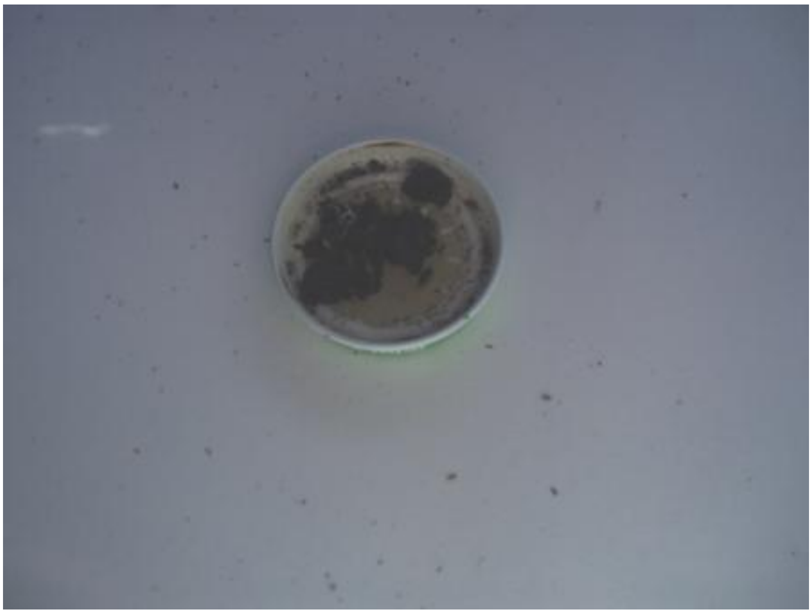
PICTURE 10. The Bioska (B1) after 2 weeks of composting (Photo: Samu Asikainen 2012)

PICTURE 11. The 505 (C2) after 2 weeks of composting (Photo: Samu Asikainen 2012)



PICTURE 12. the 506 (D2) after 2 weeks of composting (Photo: Samu Asikainen 2012)

After 4 weeks of composting all of the samples had degraded to flakes. The 506 plastic had fully degraded and therefore there is no photo of it in here. The photos for the mulch film, Bioska and 505 plastic sheets show that all of the samples had visually changed and clearly lost mass (picture 13; picture 14; picture 15). The samples were in size already so small that they could be fitted into a small lid as it can be seen from the pictures.

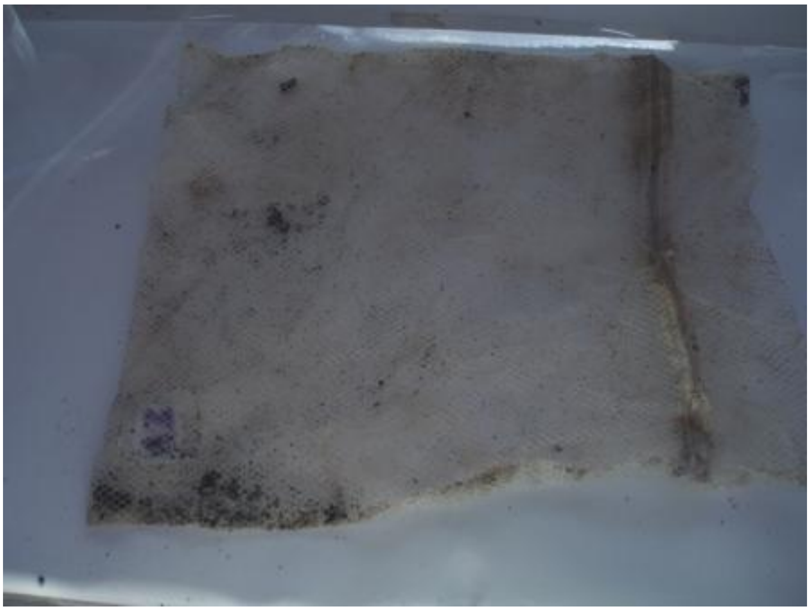


PICTURE 13. The mulch film (A2) after 4 weeks of composting (Photo: Samu Asikainen 2012)

PICTURE 14. The Bioska (B3) after 4 weeks of composting (Photo: Samu Asikainen 2012)

PICTURE 15. The 505 (C3) after 4 weeks of composting (Photo: Samu Asikainen 2012)

After 6 weeks all the samples had almost fully degraded there were only small flakes left of the samples (picture 16; picture 17; picture 18). Visually it was difficult to determine which part of the flakes was dried soil and which was plastic, especially with the darker mulch film (picture 16). When the samples were touched by hand they crumbled into even smaller flakes.



PICTURE 16. The mulch film (A3) after 6 weeks of composting (Photo: Samu Asikainen 2012)

PICTURE 17. The Bioska (B2) after 6 weeks of composting (Photo: Samu Asikainen 2012)

PICTURE 18. The 505 (C1) after 6 weeks of composting (Photo: Samu Asikainen 2012)

4.2 BOD_7 results

In this section the results obtained from the Oxitop BOD_7 tests are shown. There are different graphs from which the first three show the variation in BOD of the between all the same samples (figure 3; figure 4; figure 5). There is one only for the results from blank sample, one for 505 and one for 506 plastics. Then there is the graph that shows the BOD development of all the samples, so that one can see the difference between the blank, 505 and 506 samples (figure 6).

There are also table that shows the average BOD_7 values and comparison of blank, 505 and 506 samples. The measuring range of 40 mg/l for all the three of the first set of 505 samples was exceeded; therefore the measuring range for 505 plastic samples was increased in the second and third measuring sets to 80 mg/l (table 5).

The following figure shows the development of BOD values for blank samples during the 168 hour period. The first set of samples is marked as red, the second as blue and the third as green (figure 3).

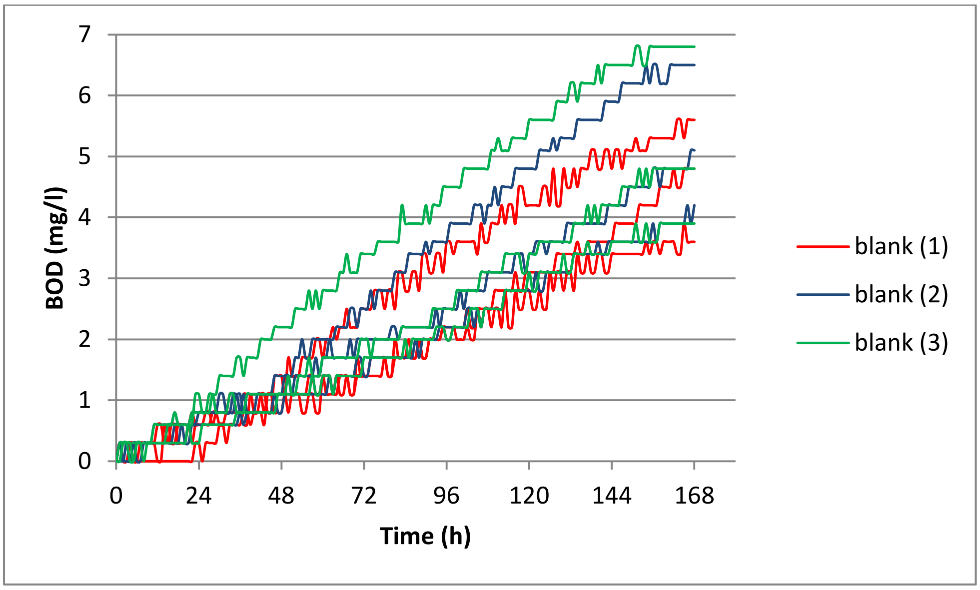


FIGURE 3. the first (red), the second (blue) and the third (green) test sets of blank BOD_7 samples

The following figure shows the development of BOD values for 505 plastic samples during the 168 hour period. The first set of samples is marked as red, the second as blue and the third as green (figure 4).

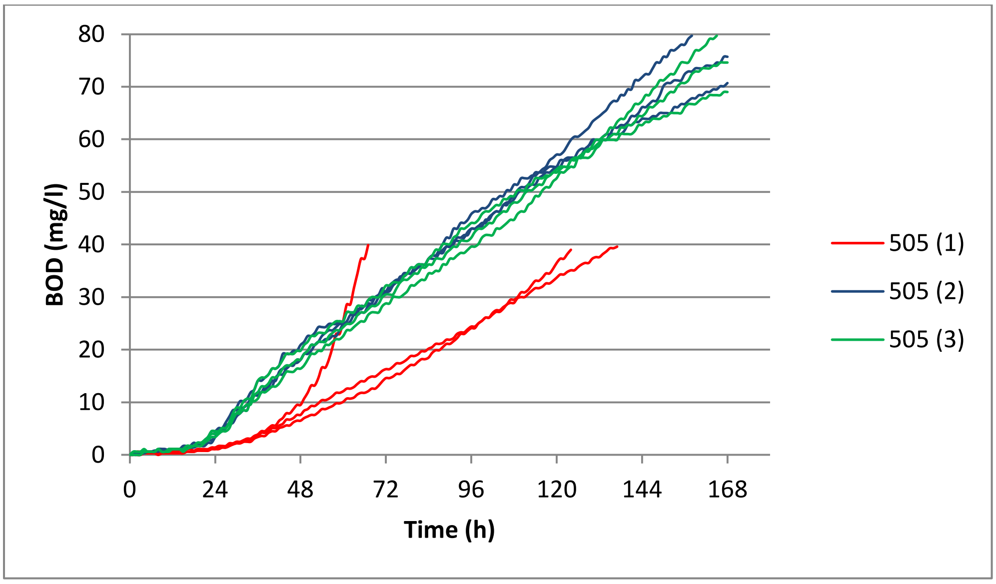


FIGURE 4. the first (red), the second (blue) and the third (green) test sets of 505 plastic BOD_7 samples

The following figure shows the development of BOD values for 506 plastic samples during the 168 hour period. The first set of samples is marked as red, the second as blue and the third as green (figure 5).

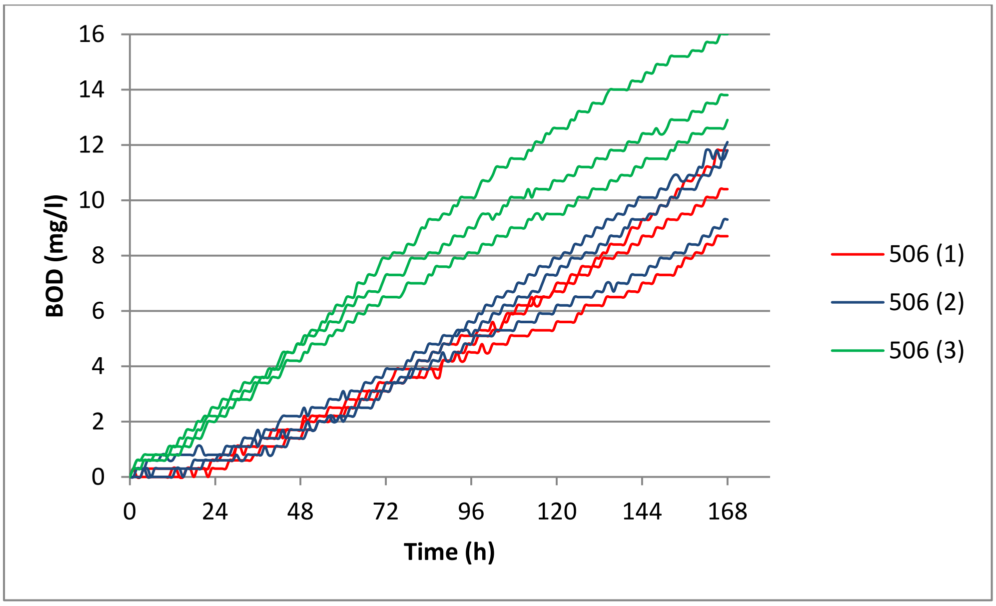


FIGURE 5. the first (red), the second (blue) and the third (green) test sets of 506 plastic BOD_7 samples

In order to compare visually the development of BOD values of blank, 505 and 506 samples the following was formed. In this figure one can see the BOD increase versus time in the blank samples as blue lines, 505 samples as purple lines, and 506 as pink lines (figure 6).

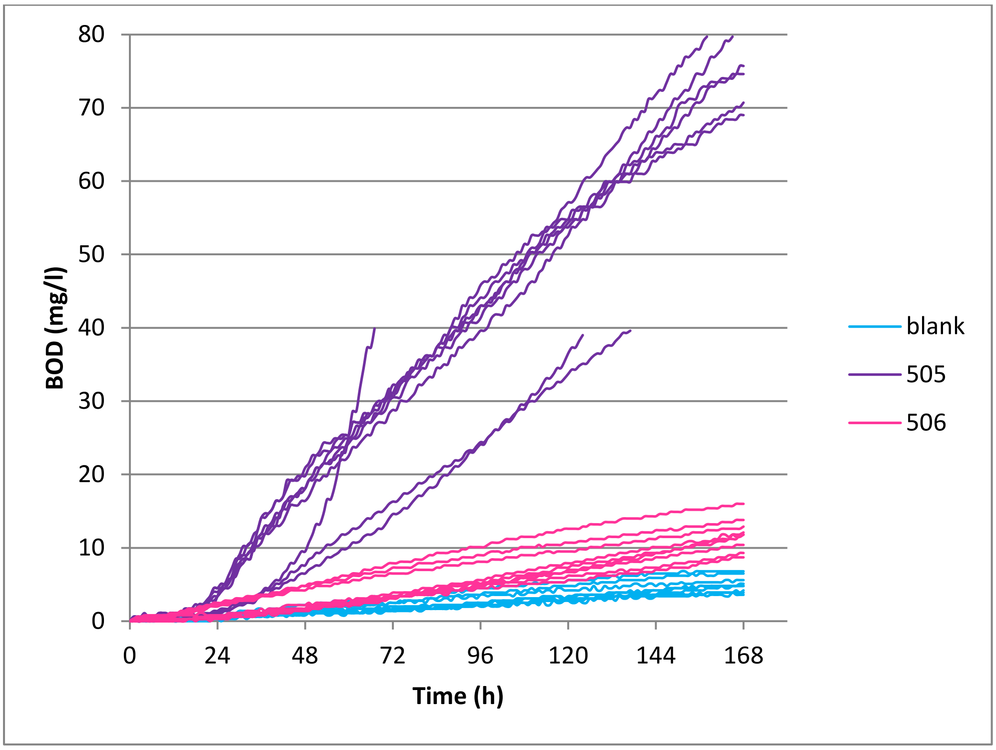


FIGURE 6. The comparison of BOD_7 results of all blank, 505 and 506 plastic Oxitop samples

The following table shows the development of BOD every 24 hours, until seven days, 168 hours was reached (table 5). In five of the 505 samples the time limit of 168 hours was not reached, but the BOD values went over the measuring range. This was taken into consideration and when the value went over the range it was no longer calculated to the average value. This means that the average of 505 for the 0 hours was taken from all the nine samples, whereas only four samples were used to calculate the final average BOD value after seven days.

TABLE 5. The average BOD increase of blank, 505 and 506 samples every 24 hours

Time (h)	BOD $blank_{average}$ (mg/l)	BOD $505_{average}$ (mg/l)	BOD $506_{average}$ (mg/l)
0	0	0	0
24	0,7	3	1,1
48	1,2	15	2,7
72	2,0	26,9	4,7
96	2,8	38,2	6,3
120	3,7	49,7	8,2
144	4,4	66	10
168	5,0	72,5	11,9

Additionally, when the bottles were taken out from the thermal cabinet and examined, there were no visible changes in the structure of the plastics. When the 505 plastic was touched with hands one could feel a slimy layer on top of the plastic, this was not the case with the 506 samples.

5 CONCLUSIONS AND DISCUSSION

The composting results showed that all the plastic samples, mulch, Bioska, 505 and 506 all degraded during an eight week time period. One of the plastics however proved to degrade faster than the others. The 506 plastic samples turned fast into small flakes and after four weeks in the compost the flakes had turned so small that they penetrated the holes of the laundry bags and disappeared to the compost. The other plastic samples also had turned into flakes by fourth week, but were still too big to fall through the holes of the laundry bags and it took them yet another four weeks to be totally invisible in the laundry bags.

As the results were presented to Jouni Soipio the Plastiroll contact for this final thesis, he was surprised that the 506 plastic had gone faster than the 505 plastic. This is because the 505 plastic is supposed to be biodegradable and the 506 not. The degradation of the 506 samples into smaller flaky pieces however made it possible for the samples to escape the laundry bag faster than with the 505 samples.

Puzzled by these results it was decided that the Oxitop BOD tests, that would define if the matter biodegrades or just degrades into smaller pieces by some other chemical reaction, were decided to be done with 505 and 506 plastic samples. The BOD_7 tests showed that the BOD was a lot higher in 505 than in 506 samples. During the seven day period the 505 samples produced an average value of 72,5 mg/l, whereas 506 samples were able to produce only 11,9 mg/l (table 5). This shows that there was a lot more biodegradable matter in the 505 plastics than what there was in 506. The 506 samples are also partially biodegradable for the blank or control samples where only 5 mg/l was produced.

Even though there is variance in the individual results, still the trend that the samples follow is clear, 505 samples produced way higher BOD_7 than 505. In fact there is also clearly visible variance between 505 and blank results also, even though the values are quite close to each other. The fluctuation in the results can be explained by the magnetic stirrer, which didn’t mix the rods equally. In the sides of the magnetic stirrer the rods in the bottles didn’t turn as well as in the middle of it. Another reason for the variance might be that the plastics had gotten stuck together and formed bigger unities which decreased the area that the microbes could digest.

Because of these results it can be concluded that there might be some biodegradable matter in 506 plastics which is just holding the structure together and when subjected to compost or other system where microbes, bacteria and fungi will digest the biodegrading matter in the plastic. This results into the structural collapse of the plastic sheet and formation of small flaky material that will visually disappear to the surrounding environment. This matter might be either non-biodegradable or biodegradable matter that is more resistant to oxidation and therefore the degradation will be slower.

Even though it was found out that the 505 will produce higher BOD_7 value in Oxitop tests, it still remains unclear whether all the material is biodegradable in the 505 plastic and whether 506 is only partially biodegradable. This is because in the seven day experiment not all the plastics degraded. In fact visually, most of the plastics remained intact, and only by touching the 505 plastic that had been tested one could feel a slimy layer like a biofilm on top of the plastic.

In order to find out the true extent of the biodegradation the tests should be done for longer period of time. The BOD test could be done for 28 days, in which there might already be more visible changes on the plastics. However the problem is that the dissolved oxygen levels in the Oxitop bottles might run so low that the microbes would not have enough oxygen for the full time. This could probably be solved by adding a smaller amount of plastic samples, like 0,2 or 0,1 grams only, but it is hard to say the amount of plastics that should be used without testing it first. Also another possibility would be to make the BOD_7 tests using the same samples. This would be done so the old liquid would be poured out from the bottles and that the bottles would be filled with new aerated dilution water that has the same amount of sludge added. This is how the oxygen levels would not be depleted and the testing would be probably more efficient.

All in all it was still found out that all four plastics degrade in the compost to smaller pieces and that the 506 has higher BOD values than 505 samples, which also contained some biodegradable matter for the values were higher than the control. It was not found out whether the plastic samples were fully biodegradable or not. Suggestions for improvement are additional testing as mentioned earlier and bigger test sets.

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(*) The sources will be differentiated in the text so that the Application report O2 500230 will be marked as WTW_{30} and the Application report O2 500231 will be WTW_{31}

APPENDICES

Appendix 1. The BOD_7 results for blank samples

The sample set is marked in brackets, so the ones in the first testing se has number one, the second number 2 and the third number three.

time (h)	blank (1)	blank (1)	blank (1)	blank (2)	blank (2)	blank (2)	blank (3)	blank (3)	blank (3)
0	0,00	0,00	0,00	0	0	0	0	0	0
1	0,30	0,30	0,30	0	0,3	0,3	0	0	0,3
2	0,00	0,00	0,30	0	0	0,3	0,3	0,3	0,3
3	0,00	0,00	0,30	0	0,3	0,3	0,3	0,3	0,3
4	0,00	0,30	0,30	0	0	0,3	0	0,3	0,3
5	0,00	0,30	0,00	0,3	0,3	0,3	0	0	0,3
6	0,00	0,30	0,00	0,3	0	0,3	0,3	0,3	0,3
7	0,00	0,30	0,30	0,3	0	0,3	0,3	0,3	0,3
8	0,00	0,30	0,30	0,3	0,3	0,3	0	0,3	0,3
9	0,00	0,30	0,30	0,3	0,3	0,3	0,3	0,3	0,3
10	0,00	0,30	0,30	0,3	0,3	0,3	0,3	0,3	0,3
11	0,00	0,30	0,30	0,3	0,3	0,6	0,3	0,3	0,6
12	0,00	0,60	0,00	0,3	0,3	0,6	0,3	0,3	0,6
13	0,00	0,60	0,00	0,3	0,3	0,6	0,3	0,3	0,6
14	0,00	0,30	0,60	0,3	0,3	0,6	0,3	0,3	0,6
15	0,00	0,60	0,30	0,3	0,3	0,6	0,3	0,6	0,6
16	0,00	0,30	0,60	0,3	0,3	0,6	0,3	0,6	0,6
17	0,00	0,30	0,60	0,3	0,6	0,8	0,3	0,6	0,8
18	0,00	0,60	0,30	0,3	0,6	0,6	0,3	0,6	0,6
19	0,00	0,60	0,30	0,6	0,6	0,6	0,3	0,6	0,6
20	0,00	0,60	0,30	0,3	0,6	0,6	0,3	0,6	0,6
21	0,00	0,60	0,60	0,3	0,6	0,6	0,6	0,6	0,6
22	0,00	0,80	0,30	0,6	0,6	0,8	0,3	0,6	0,8
23	0,30	0,60	0,60	0,6	0,6	0,8	0,3	1,1	0,8
24	0,30	0,60	0,60	0,6	0,8	0,8	0,3	1,1	0,8
25	0,00	0,60	0,60	0,6	0,8	0,8	0,6	0,8	0,8
26	0,30	0,80	0,60	0,6	0,8	0,8	0,6	0,8	0,8
27	0,30	0,80	0,60	0,6	0,8	0,8	0,6	0,8	1,1
28	0,30	0,60	0,80	0,6	0,8	0,8	0,6	1,1	1,1
29	0,30	0,80	0,80	0,6	0,8	0,8	0,6	0,8	1,1
30	0,60	0,80	0,60	0,6	1,1	0,8	0,6	0,8	1,4
31	0,60	0,80	0,60	0,6	1,1	0,8	0,6	0,8	1,4
32	0,30	0,80	0,80	0,6	0,8	0,8	0,6	0,8	1,4
33	0,60	1,10	0,80	0,6	0,8	0,8	0,6	1,1	1,4
34	0,60	1,10	0,80	0,6	1,1	0,8	0,6	1,1	1,4
35	0,60	0,80	0,80	0,6	1,1	1,1	0,8	0,8	1,7
36	0,60	0,80	0,80	0,8	1,1	0,8	0,8	0,8	1,7

37	0,80	1,10	0,60	0,6	0,8	1,1	0,8	0,8	1,4
38	0,80	1,10	0,60	0,8	1,1	0,8	0,8	1,1	1,7
39	0,60	1,10	1,10	0,8	1,1	0,8	0,8	1,1	1,7
40	0,80	1,10	0,80	0,8	1,1	0,8	0,8	1,1	1,7
41	0,80	1,10	0,80	0,8	1,1	1,1	0,8	1,1	1,7
42	0,80	1,10	1,10	0,8	1,1	1,1	0,8	1,1	2
43	0,60	0,80	1,10	0,8	1,1	1,1	0,8	1,1	2
44	1,10	1,10	0,80	0,8	1,1	1,1	0,8	1,1	2
45	1,10	1,10	0,80	0,8	1,1	1,1	0,8	1,1	2
46	0,80	1,10	1,40	1,1	1,1	1,4	0,8	1,1	2,2
47	0,80	1,10	1,40	0,8	1,1	1,4	1,1	1,1	2,2
48	0,80	1,10	1,40	0,8	1,1	1,4	1,1	1,1	2,2
49	1,10	1,10	1,10	1,1	1,4	1,4	1,1	1,1	2,2
50	0,80	1,10	1,70	1,1	1,4	1,4	1,1	1,4	2,2
51	1,10	1,10	1,40	1,1	1,1	1,4	1,1	1,1	2,2
52	1,10	1,10	1,40	1,1	1,4	1,7	1,1	1,1	2,5
53	1,10	1,10	1,40	1,1	1,4	1,7	1,1	1,4	2,5
54	0,80	1,10	1,70	1,1	1,4	2	1,1	1,4	2,5
55	0,80	1,10	1,70	1,1	1,4	1,7	1,1	1,4	2,5
56	1,10	1,40	1,70	1,1	1,4	1,7	1,1	1,7	2,8
57	1,10	1,40	1,70	1,1	1,4	2	1,4	1,4	2,5
58	0,80	1,10	2,00	1,1	1,7	2	1,1	1,4	2,8
59	0,80	1,10	2,00	1,1	1,4	2	1,1	1,4	2,5
60	1,40	1,40	1,70	1,1	1,7	2	1,4	1,7	2,8
61	1,10	1,40	2,00	1,1	1,7	2	1,4	1,7	2,8
62	1,10	1,40	2,00	1,4	2	2	1,4	1,7	2,8
63	1,10	1,10	2,20	1,1	1,7	2	1,1	1,7	2,8
64	1,10	1,40	2,00	1,4	1,7	2,2	1,4	1,7	2,8
65	1,40	1,10	2,20	1,4	1,7	2,2	1,4	1,7	3,1
66	1,40	1,10	2,20	1,4	1,7	2,2	1,4	1,7	3,1
67	1,40	1,40	2,50	1,4	1,7	2,2	1,4	1,7	3,4
68	1,10	1,10	2,20	1,4	2	2,5	1,4	1,7	3,1
69	1,10	1,10	2,20	1,4	1,7	2,5	1,4	1,7	3,1
70	1,70	1,40	2,20	1,7	2	2,2	1,4	1,7	3,1
71	1,40	1,40	2,50	1,7	2	2,5	1,4	2	3,4
72	1,40	1,40	2,50	1,4	2	2,5	1,7	2	3,4
73	1,40	1,40	2,50	1,4	2	2,5	1,7	2	3,4
74	1,70	1,40	2,50	1,7	2	2,8	1,7	1,7	3,4
75	1,70	1,40	2,80	1,7	2	2,5	1,7	2	3,4
76	1,70	1,40	2,80	1,7	2	2,8	1,7	2	3,6
77	1,70	1,40	2,80	1,7	2	2,8	1,7	2	3,6
78	1,70	1,70	2,50	1,7	2	2,8	1,7	2	3,6
79	1,40	1,40	2,80	1,7	2	2,8	1,7	2	3,6
80	1,40	1,40	2,80	1,7	2,2	2,8	1,7	2	3,6
81	2,00	1,70	2,50	1,7	2,2	3,1	1,7	2	3,6
82	1,70	1,70	3,10	1,7	2	3,1	1,7	2	3,6

83	1,70	1,70	3,10	1,7	2,2	3,1	1,7	2,2	4,2
84	1,70	1,70	2,80	1,7	2,2	3,1	2	2,2	3,9
85	2,00	1,70	2,80	1,7	2,2	3,4	1,7	2,2	3,9
86	1,70	1,70	3,10	1,7	2,2	3,4	2	2,2	3,9
87	1,70	1,70	3,10	2	2,2	3,4	2	2,2	3,9
88	2,00	2,00	2,80	1,7	2,2	3,4	2	2,2	3,9
89	1,70	1,70	3,40	2	2,2	3,4	2	2,2	3,9
90	1,70	1,70	3,40	2	2,2	3,6	2	2,2	4,2
91	2,00	2,00	3,10	2	2,2	3,4	2	2,2	3,9
92	2,00	2,00	3,10	2	2,2	3,6	2	2,5	4,2
93	2,00	2,00	3,40	2	2,5	3,6	2,2	2,5	4,2
94	2,00	2,00	3,40	2,2	2,2	3,6	2,2	2,5	4,2
95	2,20	2,20	3,10	2,2	2,5	3,6	2,2	2,5	4,5
96	2,00	2,20	3,60	2,2	2,5	3,6	2	2,5	4,5
97	2,00	2,20	3,60	2,2	2,5	3,9	2	2,5	4,5
98	2,20	2,20	3,40	2,2	2,5	3,9	2,2	2,5	4,5
99	2,00	2,20	3,60	2,2	2,5	3,9	2,2	2,8	4,5
100	2,00	2,20	3,60	2,2	2,8	3,9	2,2	2,8	4,5
101	2,00	2,20	3,60	2,2	2,5	3,9	2,2	2,8	4,8
102	2,20	2,50	3,60	2,5	2,8	3,9	2,2	2,8	4,8
103	2,00	2,20	3,60	2,5	2,8	3,9	2,5	2,8	4,8
104	2,00	2,20	3,60	2,2	2,8	4,2	2,5	2,8	4,8
105	2,50	2,50	3,40	2,5	2,8	4,2	2,5	2,8	4,8
106	2,20	2,50	3,90	2,2	2,8	4,2	2,2	3,1	4,8
107	2,50	2,50	3,60	2,5	2,8	3,9	2,5	3,1	4,8
108	2,50	2,50	3,60	2,5	3,1	4,2	2,5	3,1	4,8
109	2,20	2,50	3,90	2,5	3,1	4,2	2,5	3,1	5,1
110	2,50	2,80	3,90	2,5	3,1	4,5	2,5	3,1	5,1
111	2,50	2,80	3,90	2,5	3,1	4,2	2,5	3,1	5,3
112	2,20	2,80	4,20	2,5	3,1	4,5	2,5	3,1	5,1
113	2,80	2,80	3,90	2,8	3,1	4,5	2,8	3,4	5,1
114	2,20	2,80	4,20	2,8	3,1	4,5	2,8	3,4	5,1
115	2,20	2,80	4,20	2,8	3,1	4,5	2,8	3,4	5,3
116	2,80	3,10	3,90	2,8	3,4	4,8	2,8	3,4	5,3
117	2,50	2,80	4,50	2,8	3,4	4,8	2,8	3,4	5,3
118	2,50	2,80	4,50	2,8	3,4	4,8	2,8	3,1	5,3
119	2,80	3,10	4,20	2,8	3,1	4,8	2,8	3,1	5,3
120	2,80	3,10	4,20	2,8	3,4	4,8	3,1	3,4	5,6
121	2,50	3,10	4,20	2,8	3,4	4,8	2,8	3,4	5,6
122	2,50	3,10	4,20	3,1	3,6	4,8	2,8	3,4	5,6
123	2,80	3,10	4,20	2,8	3,6	5,1	3,1	3,6	5,6
124	2,50	3,10	4,50	2,8	3,6	5,1	3,1	3,6	5,6
125	2,50	3,10	4,50	3,1	3,4	5,1	3,1	3,6	5,6
126	3,10	3,10	4,20	3,1	3,6	5,1	3,1	3,6	5,6
127	2,80	3,10	4,80	3,1	3,6	5,3	3,1	3,6	5,6
128	3,10	3,40	4,20	3,1	3,6	5,1	3,1	3,6	5,9

129	3,10	3,40	4,20	3,1	3,6	5,3	3,1	3,6	5,9
130	2,80	3,40	4,80	3,1	3,6	5,3	3,4	3,6	5,9
131	3,10	3,40	4,50	3,1	3,9	5,3	3,1	3,6	5,9
132	3,10	3,40	4,50	3,1	3,9	5,3	3,1	3,6	6,2
133	2,80	3,40	4,80	3,4	3,9	5,3	3,4	3,9	6,2
134	3,40	3,60	4,50	3,4	3,9	5,6	3,4	3,9	5,9
135	3,10	3,40	4,80	3,4	3,9	5,6	3,4	3,9	6,2
136	3,10	3,40	4,80	3,4	3,9	5,6	3,4	3,9	6,2
137	3,40	3,60	4,80	3,4	3,9	5,6	3,6	4,2	6,2
138	3,10	3,60	5,10	3,4	3,9	5,6	3,4	3,9	6,2
139	3,10	3,60	5,10	3,4	3,9	5,6	3,4	4,2	6,2
140	3,40	3,60	4,80	3,6	3,9	5,6	3,4	3,9	6,5
141	3,40	3,60	4,80	3,4	3,9	5,6	3,4	4,2	6,2
142	3,10	3,60	5,10	3,4	3,9	5,9	3,4	4,2	6,5
143	3,10	3,60	5,10	3,6	4,2	5,9	3,4	4,2	6,5
144	3,40	3,60	4,80	3,6	4,2	5,9	3,6	4,2	6,5
145	3,40	3,90	5,10	3,6	4,2	5,9	3,6	4,2	6,5
146	3,40	3,90	5,10	3,6	4,2	5,9	3,6	4,2	6,5
147	3,40	3,90	4,80	3,6	4,2	6,2	3,6	4,5	6,5
148	3,40	3,90	5,10	3,6	4,2	6,2	3,6	4,5	6,5
149	3,40	3,90	5,10	3,6	4,5	6,2	3,6	4,5	6,5
150	3,40	3,90	5,10	3,6	4,5	6,2	3,6	4,5	6,5
151	3,40	3,90	5,30	3,6	4,5	6,2	3,9	4,5	6,8
152	3,40	4,20	5,10	3,6	4,5	6,2	3,6	4,8	6,8
153	3,40	4,20	5,10	3,6	4,5	6,2	3,6	4,5	6,5
154	3,60	4,20	5,10	3,6	4,5	6,5	3,9	4,8	6,5
155	3,40	4,20	5,30	3,6	4,5	6,2	3,6	4,5	6,8
156	3,60	4,20	5,30	3,9	4,8	6,5	3,6	4,8	6,8
157	3,60	4,20	5,30	3,6	4,8	6,5	3,6	4,8	6,8
158	3,40	4,50	5,30	3,9	4,5	6,2	3,9	4,8	6,8
159	3,60	4,50	5,30	3,9	4,8	6,2	3,9	4,8	6,8
160	3,60	4,50	5,30	3,9	4,8	6,2	3,9	4,8	6,8
161	3,60	4,50	5,30	3,9	4,8	6,5	3,9	4,8	6,8
162	3,60	4,80	5,30	3,9	4,8	6,5	3,9	4,8	6,8
163	3,40	4,50	5,60	3,9	4,8	6,5	3,9	4,8	6,8
164	3,40	4,50	5,60	3,9	4,8	6,5	3,9	4,8	6,8
165	3,90	4,80	5,30	3,9	4,8	6,5	3,9	4,8	6,8
166	3,60	4,80	5,60	4,2	4,8	6,5	3,9	4,8	6,8
167	3,60	4,80	5,60	3,9	5,1	6,5	3,9	4,8	6,8
168	3,60	4,80	5,60	4,2	5,1	6,5	3,9	4,8	6,8

Appendix 2. The BOD_7 results for 505 samples

The sample set is marked in brackets, so the ones in the first testing se has number one, the second number 2 and the third number three.

time (h)	505 (1)	505 (1)	505 (1)	505 (2)	505 (2)	505 (2)	505 (3)	505 (3)	505 (3)
0	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0
1	0,3	0,0	0,3	0,3	0,0	0,3	0,0	0,6	0,6
2	0,6	0,3	0,0	0,3	0,0	0,3	0,0	0,6	0,6
3	0,6	0,3	0,0	0,6	0,3	0,3	0,0	0,6	0,6
4	0,6	0,3	0,3	0,6	0,3	0,6	0,6	1,1	0,6
5	0,6	0,3	0,3	0,6	0,6	0,6	0,6	0,6	0,6
6	0,6	0,3	0,3	0,6	0,6	0,6	0,6	0,6	0,6
7	0,6	0,3	0,3	0,8	0,6	0,8	0,6	0,6	0,6
8	0,6	0,3	0,0	0,8	1,1	0,6	1,1	1,1	1,1
9	0,6	0,3	0,3	1,1	1,1	1,1	0,6	0,6	0,6
10	0,6	0,3	0,3	1,1	0,6	0,8	0,6	0,6	0,6
11	0,6	0,3	0,3	0,8	1,1	1,1	0,6	1,1	1,1
12	0,6	0,3	0,3	1,1	1,1	1,1	1,1	1,1	1,1
13	0,6	0,3	0,3	1,1	1,1	1,1	1,1	1,1	1,1
14	0,8	0,3	0,3	1,1	1,1	1,1	1,1	1,1	1,1
15	0,6	0,3	0,3	1,1	1,7	1,1	0,6	1,1	1,1
16	1,1	0,6	0,6	1,4	1,7	1,1	1,1	1,7	1,7
17	1,1	0,6	0,6	1,4	1,7	1,7	1,4	1,7	1,7
18	0,8	0,6	0,6	1,4	1,7	2,3	1,7	1,7	1,7
19	1,1	0,8	0,8	1,7	1,7	2,0	1,7	2,3	2,3
20	1,1	0,8	0,8	1,7	2,3	2,0	1,7	2,3	2,3
21	1,1	0,8	0,8	1,7	2,3	2,8	2,3	2,3	2,8
22	1,1	0,8	0,8	2,3	2,8	3,4	2,8	3,4	3,4
23	1,4	1,1	1,1	2,3	2,8	4,5	3,4	4,5	4,0
24	1,4	1,1	1,1	3,4	3,4	4,5	3,4	4,5	4,0
25	1,7	1,4	1,1	4,5	4,5	5,1	4,0	4,5	4,5
26	1,7	1,4	1,4	4,5	4,5	5,1	4,5	5,1	5,1
27	1,7	1,4	1,4	5,6	5,1	6,2	4,5	5,1	5,1
28	2,2	1,7	1,7	5,9	6,2	7,3	5,1	6,2	6,2
29	2,2	2,0	2,0	6,1	7,9	8,5	6,8	7,9	7,3
30	2,5	2,2	2,2	7,3	9,0	8,5	7,9	9,0	7,9
31	2,5	2,2	2,2	7,9	10,2	9,0	8,5	9,0	7,9
32	2,8	2,5	2,5	8,5	10,2	9,0	8,5	10,2	9,0
33	3,1	2,5	2,8	8,5	10,7	9,6	8,5	10,7	9,6
34	3,1	2,5	2,8	10,7	11,9	10,7	10,2	10,7	9,6
35	3,6	3,1	3,4	11,3	12,4	11,3	10,2	12,4	11,3
36	3,9	3,4	3,6	11,9	14,1	11,3	10,7	14,1	11,9
37	4,5	3,6	4,2	11,9	14,1	11,9	11,9	14,7	13,0
38	4,5	3,6	4,2	13,0	14,7	12,4	11,9	14,7	13,0
39	5,1	4,2	4,5	13,0	15,3	13,0	12,4	15,3	13,6
40	5,6	4,5	5,1	14,1	16,4	13,0	13,0	16,4	14,7

41	5,6	4,5	5,1	14,1	16,4	14,7	13,0	16,4	14,7
42	6,5	5,1	5,6	15,8	17,0	15,3	13,6	17,0	15,3
43	7,0	5,3	5,9	16,4	19,2	15,3	14,7	18,1	16,4
44	7,9	5,6	6,7	16,4	19,2	16,4	15,8	19,2	17,0
45	7,9	5,6	6,7	17,0	19,2	17,0	15,8	19,2	17,0
46	8,7	6,2	7,0	17,5	19,8	17,0	15,8	19,2	17,5
47	9,5	6,5	7,6	17,5	19,8	18,1	16,4	19,8	18,1
48	9,5	6,5	7,6	18,1	20,9	18,1	16,4	19,8	18,1
49	10,7	7,0	8,4	19,2	21,5	19,2	17,0	20,9	19,2
50	11,8	7,3	8,7	19,2	22,6	19,8	18,1	21,5	19,8
51	13,2	7,6	9,3	19,8	22,6	20,9	19,2	22,6	20,9
52	13,2	7,6	9,3	20,9	23,2	20,9	19,2	22,6	20,9
53	14,6	8,1	9,8	21,5	24,3	21,5	19,8	23,2	21,5
54	16,6	8,7	10,4	21,5	24,3	22,6	19,8	23,2	21,5
55	16,6	8,7	10,4	22,0	24,3	23,2	20,9	23,2	21,5
56	18,2	9,0	10,7	22,0	24,9	23,7	20,9	24,3	22,6
57	20,5	9,3	11,2	22,6	24,9	23,7	21,5	24,9	23,2
58	23,0	9,8	11,8	22,6	24,9	24,3	22,0	25,4	23,7
59	23,0	9,8	11,8	23,7	25,4	24,9	22,0	25,4	23,7
60	25,5	10,1	12,1	24,9	25,4	24,9	22,6	25,4	24,3
61	28,6	10,7	12,6	24,9	27,1	25,4	23,7	27,1	24,9
62	28,6	10,7	12,6	25,4	27,1	26,6	23,7	27,1	24,9
63	31,7	10,9	12,9	26,6	27,1	26,6	24,3	27,1	25,4
64	34,5	11,5	13,5	26,6	27,1	27,7	24,9	28,3	26,6
65	37,3	11,8	14,0	27,1	28,3	27,7	25,4	28,3	27,1
66	37,3	11,8	14,0	27,1	28,3	28,3	25,4	28,3	27,1
67	39,9	12,1	14,6	28,3	29,4	28,8	26,6	29,4	27,7
68		12,6	14,9	28,3	29,4	28,8	27,1	30,0	28,3
69		12,6	14,9	28,8	30,0	30,0	27,1	30,0	28,3
70		13,2	15,4	30,0	30,0	30,5	27,1	30,0	28,8
71		14,0	16,0	30,5	31,1	31,7	28,3	31,1	30,0
72		14,6	16,3	31,1	31,1	30,5	28,8	32,2	30,5
73		14,6	16,3	31,1	32,2	31,7	28,8	32,2	30,5
74		14,9	16,8	32,2	32,8	32,8	30,0	32,8	30,5
75		15,4	17,4	32,8	32,8	33,3	30,0	32,8	31,7
76		15,4	17,4	33,3	33,9	33,3	30,0	32,8	32,8
77		16,0	17,7	34,5	33,9	33,9	30,5	33,9	33,3
78		16,6	18,2	34,5	34,5	34,5	31,1	34,5	33,3
79		17,1	18,8	34,5	35,6	34,5	32,2	35,6	33,9
80		17,1	18,8	35,0	35,6	35,6	32,2	35,6	34,5
81		17,7	19,1	35,6	36,2	35,6	32,8	36,2	34,5
82		18,2	19,7	36,2	36,2	36,2	33,3	36,2	35,6
83		18,2	19,7	36,2	36,2	36,2	33,3	36,2	35,6
84		18,5	20,2	37,3	37,3	37,3	34,5	37,3	36,2
85		19,4	20,5	37,9	37,9	37,3	34,5	37,9	36,2
86		19,9	21,1	37,9	37,9	37,3	35,0	39,0	37,3

87		19,9	21,1	38,4	39,0	38,4	35,0	39,0	37,3
88		20,5	21,3	38,4	40,1	39,0	36,2	40,1	37,3
89		21,1	21,9	39,6	41,3	39,6	36,2	40,1	38,4
90		21,1	21,9	39,6	41,3	39,6	37,3	40,1	39,0
91		21,6	22,2	40,1	43,0	40,7	37,3	41,3	39,6
92		22,2	23,0	41,3	43,0	40,7	37,9	41,8	39,6
93		23,0	23,3	41,3	44,1	40,7	38,4	43,0	40,7
94		23,0	23,3	41,8	44,1	41,3	38,4	43,0	40,7
95		23,6	23,9	41,8	44,7	42,4	39,0	43,5	40,7
96		24,1	24,4	43,0	45,8	43,0	39,6	44,1	41,3
97		24,1	24,4	43,0	46,3	43,0	39,6	44,1	42,4
98		25,0	25,0	43,5	46,3	43,5	40,1	44,7	43,0
99		25,5	25,5	43,5	46,9	44,1	41,3	45,8	43,0
100		26,1	26,1	44,7	46,9	44,1	41,8	46,3	43,5
101		26,1	26,1	44,7	47,5	45,2	41,8	46,3	44,1
102		26,7	27,0	45,8	48,6	45,8	41,8	46,9	44,1
103		27,2	27,5	46,3	48,6	46,3	43,0	47,5	45,2
104		27,2	27,5	46,3	49,2	46,3	43,0	47,5	45,8
105		27,8	28,1	47,5	49,2	47,5	43,5	48,6	46,3
106		28,6	28,6	47,5	50,3	48,0	44,1	48,6	46,3
107		28,9	29,5	48,6	50,3	48,0	44,7	49,2	47,5
108		28,9	29,5	49,2	51,4	48,6	44,7	49,2	48,0
109		29,8	30,0	50,3	51,4	49,7	45,8	50,3	48,0
110		30,0	30,9	50,9	52,6	50,3	46,3	50,3	48,6
111		30,0	30,9	50,9	52,6	50,3	46,3	50,3	49,7
112		30,6	31,4	51,4	52,6	50,9	47,5	51,4	50,3
113		31,2	32,3	52,6	53,1	51,4	48,0	51,4	50,3
114		31,7	33,1	53,7	53,1	51,4	49,2	52,6	50,9
115		31,7	33,1	53,7	53,7	52,6	49,2	52,6	51,4
116		32,0	33,7	54,3	53,7	53,1	50,3	52,6	51,4
117		32,6	34,5	54,8	54,3	53,7	50,9	53,1	52,6
118		32,6	34,5	56,0	54,8	53,7	50,9	53,1	53,1
119		33,1	35,4	56,5	54,8	54,3	52,0	53,7	53,7
120		33,7	36,5	57,1	54,8	54,8	52,6	54,3	53,7
121		34,3	37,3	57,1	56,0	54,8	53,7	54,8	54,3
122		34,3	37,3	57,7	56,0	56,0	53,7	54,8	54,8
123		34,8	38,2	58,8	56,0	56,5	54,3	54,8	54,8
124		35,1	39,0	59,9	56,5	56,5	54,8	56,0	56,0
125		35,1		60,5	56,5	56,5	54,8	56,0	56,5
126		35,7		60,5	56,5	57,7	56,5	56,5	56,5
127		36,2		61,0	57,1	58,2	57,1	56,5	56,5
128		36,5		61,6	58,2	58,2	57,7	56,5	57,7
129		36,5		62,2	58,8	58,8	57,7	56,5	58,2
130		37,3		63,3	59,9	59,4	58,8	57,1	58,2
131		37,6		63,9	59,9	59,9	59,9	58,2	58,8
132		37,6		64,4	59,9	59,9	59,9	58,8	59,4

133		38,2		65,0	59,9	60,5	60,5	59,9	59,9
134		38,7		65,6	59,9	61,0	61,0	59,9	59,9
135		39,3		66,7	61,0	61,0	62,2	59,9	60,5
136		39,3		67,3	61,0	62,2	62,2	59,9	61,0
137		39,6		67,3	61,0	62,2	63,3	59,9	61,0
138				68,4	61,0	62,7	63,9	61,0	62,2
139				68,4	61,6	62,7	63,9	61,0	62,2
140				69,5	62,7	63,3	65,0	61,0	62,7
141				69,5	62,7	64,4	65,6	61,0	62,7
142				71,2	63,3	64,4	66,7	61,6	63,3
143				71,2	63,3	65,0	66,7	62,7	64,4
144				71,8	63,9	66,1	67,3	62,7	64,4
145				72,4	63,9	66,1	68,4	63,3	65,0
146				72,4	63,9	66,7	68,4	63,3	66,1
147				73,5	64,4	67,3	69,5	63,9	66,1
148				74,6	64,4	67,3	70,1	63,9	66,7
149				74,6	65,0	68,4	71,2	63,9	67,3
150				75,7	65,0	70,1	71,2	64,4	67,3
151				75,7	65,0	70,7	71,8	64,4	68,4
152				76,9	65,0	70,7	72,4	65,0	69,0
153				76,9	66,1	71,2	72,4	65,0	69,0
154				77,4	66,1	71,2	73,5	65,0	70,1
155				78,0	66,7	71,2	74,6	65,0	70,7
156				78,0	66,7	72,4	74,6	66,1	70,7
157				79,1	67,3	72,9	74,6	66,7	71,2
158				79,7	67,8	72,9	75,7	66,7	72,4
159					67,8	73,5	76,9	66,7	72,9
160					68,4	73,5	76,9	67,3	72,9
161					68,4	73,5	77,4	67,8	73,5
162					69,0	74,0	78,0	67,8	73,5
163					69,0	74,0	79,1	68,4	73,5
164					69,5	74,0	79,1	68,4	74,0
165					69,5	74,6	79,7	68,4	74,0
166					70,1	74,6		68,4	74,6
167					70,1	75,7		69,0	74,6
168					70,7	75,7		69,0	74,6

Appendix 3. The BOD_7 results for 506 samples

The sample set is marked in brackets, so the ones in the first testing se has number one, the second number 2 and the third number three.

time (h)	506 (1)	506 (1)	506 (1)	506 (2)	506 (2)	506 (2)	506 (3)	506 (3)	506 (3)
0	0,00	0,00	0,00	0	0	0,00	0	0	0
1	0,30	0,00	0,30	0	0	0,30	0,3	0,3	0,3
2	0,00	0,00	0,30	0,3	0	0,30	0,6	0,6	0,3
3	0,00	0,00	0,30	0,3	0	0,30	0,6	0,6	0,3
4	0,30	0,00	0,30	0,3	0,3	0,30	0,8	0,6	0,6
5	0,00	0,00	0,30	0,6	0	0,30	0,8	0,6	0,6
6	0,00	0,00	0,30	0,6	0	0,00	0,8	0,6	0,6
7	0,00	0,00	0,30	0,6	0	0,30	0,8	0,8	0,6
8	0,00	0,00	0,30	0,6	0	0,30	0,8	0,8	0,6
9	0,00	0,00	0,30	0,8	0,00	0,30	0,8	0,8	0,6
10	0,00	0,00	0,30	0,8	0,00	0,30	0,8	0,8	0,6
11	0,00	0,00	0,30	0,6	0,00	0,30	1,1	0,8	0,8
12	0,00	0,30	0,30	0,6	0,00	0,30	1,1	1,1	0,8
13	0,00	0,30	0,30	0,8	0,30	0,30	1,1	1,1	0,8
14	0,00	0,00	0,00	0,8	0,30	0,30	1,4	1,1	0,8
15	0,00	0,00	0,00	0,8	0,00	0,30	1,4	1,1	1,1
16	0,30	0,30	0,30	0,8	0,30	0,30	1,7	1,4	1,1
17	0,30	0,30	0,30	0,8	0,30	0,30	1,7	1,4	1,1
18	0,00	0,30	0,30	0,8	0,60	0,30	1,7	1,4	1,4
19	0,30	0,30	0,30	1,1	0,60	0,30	2	1,7	1,4
20	0,30	0,30	0,30	1,1	0,60	0,30	2	1,7	1,4
21	0,30	0,30	0,30	0,8	0,60	0,60	2,2	2	1,7
22	0,00	0,30	0,30	0,8	0,60	0,60	2,2	2,2	2
23	0,30	0,60	0,60	0,8	0,60	0,60	2,5	2,2	2
24	0,30	0,60	0,60	0,8	0,60	0,60	2,5	2,2	2
25	0,30	0,60	0,60	0,8	0,80	0,60	2,5	2,2	2,2
26	0,30	0,80	0,60	0,8	0,80	0,60	2,8	2,5	2,2
27	0,30	0,80	0,60	1,1	0,80	0,60	2,8	2,5	2,2
28	0,60	0,80	0,60	1,1	0,80	0,60	2,8	2,8	2,5
29	0,60	0,80	0,60	1,1	1,10	0,60	3,1	2,8	2,5
30	0,60	1,10	1,10	1,1	1,10	0,80	3,1	2,8	2,8
31	0,60	1,10	1,10	1,1	1,10	0,60	3,1	2,8	2,8
32	0,60	1,10	0,80	1,1	1,40	0,60	3,4	3,1	2,8
33	0,60	1,10	1,10	1,1	1,40	0,80	3,4	3,1	2,8
34	0,60	1,10	1,10	1,1	1,40	0,80	3,4	3,1	2,8
35	0,80	1,10	1,10	1,4	1,40	0,80	3,6	3,4	3,1
36	0,80	1,10	1,10	1,1	1,70	0,80	3,6	3,4	3,4
37	1,10	1,40	1,40	1,4	1,40	0,80	3,6	3,6	3,4
38	1,10	1,40	1,40	1,4	1,70	1,10	3,6	3,6	3,4
39	1,10	1,40	1,40	1,4	1,70	0,80	3,9	3,6	3,4
40	1,10	1,70	1,40	1,4	1,70	0,80	3,9	3,9	3,6

41	1,10	1,70	1,40	1,4	1,70	1,10	3,9	3,9	3,6
42	1,10	1,70	1,70	1,4	2,00	1,10	4,2	3,9	3,6
43	1,10	1,70	1,40	1,7	2,20	1,10	4,5	4,2	3,9
44	1,40	1,70	1,70	1,4	2,20	1,10	4,5	4,5	4,2
45	1,40	1,70	1,70	1,7	2,20	1,40	4,5	4,5	4,2
46	1,40	1,70	1,70	1,7	2,20	1,40	4,5	4,5	4,2
47	1,40	1,70	1,70	1,7	2,20	1,40	4,8	4,8	4,2
48	1,40	1,70	1,70	1,7	2,20	1,40	4,8	4,8	4,2
49	1,70	2,20	2,00	1,7	2,50	1,40	5,1	4,8	4,5
50	1,70	2,00	2,00	2	2,20	1,70	5,1	5,1	4,5
51	1,70	2,00	2,20	1,7	2,50	1,70	5,3	5,1	4,8
52	1,70	2,00	2,20	1,7	2,50	1,70	5,3	5,1	4,8
53	2,00	2,20	2,20	2	2,50	2,00	5,3	5,3	4,8
54	2,00	2,20	2,20	2	2,50	2,00	5,6	5,3	4,8
55	2,00	2,20	2,20	2	2,50	2,00	5,6	5,3	4,8
56	2,00	2,50	2,20	2,2	2,80	2,20	5,9	5,6	5,1
57	2,20	2,50	2,20	2,2	2,80	2,00	5,9	5,6	5,1
58	2,20	2,50	2,20	2	2,80	2,00	6,2	5,6	5,3
59	2,20	2,50	2,20	2,2	2,80	2,20	6,2	5,6	5,3
60	2,20	2,50	2,50	2	3,10	2,20	6,2	5,9	5,3
61	2,50	2,80	2,50	2,2	2,80	2,20	6,5	6,2	5,6
62	2,50	2,80	2,50	2,2	3,10	2,50	6,5	6,2	5,6
63	2,50	2,80	2,50	2,2	3,10	2,50	6,5	6,2	5,6
64	2,50	2,80	2,80	2,5	3,10	2,50	7	6,5	5,9
65	2,80	3,10	2,80	2,5	3,10	2,80	7	6,5	5,9
66	2,80	3,10	2,80	2,5	3,40	2,80	7	6,5	5,9
67	3,10	3,10	2,80	2,5	3,40	2,80	7,3	6,7	6,2
68	3,10	3,10	2,80	2,5	3,40	3,10	7,3	6,7	6,2
69	3,10	3,10	2,80	2,80	3,60	3,10	7,3	6,7	6,2
70	3,40	3,40	3,10	2,80	3,60	3,10	7,6	6,7	6,2
71	3,40	3,40	3,10	3,10	3,60	3,10	7,9	7	6,5
72	3,40	3,40	3,10	3,10	3,90	3,40	7,9	7,3	6,5
73	3,40	3,40	3,10	3,10	3,90	3,40	7,9	7,3	6,5
74	3,60	3,40	3,40	3,40	3,90	3,40	8,1	7,3	6,5
75	3,90	3,40	3,40	3,40	3,90	3,40	8,1	7,3	6,5
76	3,90	3,40	3,40	3,40	3,90	3,60	8,1	7,3	6,5
77	3,90	3,40	3,40	3,40	3,90	3,60	8,1	7,3	6,7
78	3,90	3,60	3,60	3,60	4,20	3,60	8,4	7,6	7
79	3,90	3,60	3,60	3,90	4,20	3,60	8,4	7,9	7
80	3,90	3,60	3,60	3,90	4,50	3,90	8,4	7,9	7
81	4,20	3,60	3,60	4,20	4,50	3,90	8,7	7,9	7
82	4,20	3,90	3,60	4,20	4,50	3,90	9	7,9	7
83	4,20	3,90	3,60	4,20	4,50	3,90	9	7,9	7
84	4,20	3,90	3,90	4,20	4,80	3,90	9,3	8,1	7,3
85	4,50	3,90	3,90	4,50	4,80	4,20	9,3	8,1	7,3
86	4,50	3,90	3,60	4,50	4,80	4,20	9,3	8,1	7,6

87	4,50	3,90	3,60	4,50	4,80	4,20	9,3	8,1	7,6
88	4,80	4,20	4,20	4,80	5,10	4,50	9,5	8,4	7,6
89	4,80	4,20	4,20	4,80	5,10	4,20	9,5	8,4	7,6
90	4,80	4,20	4,20	4,80	5,10	4,20	9,5	8,4	7,6
91	4,80	4,20	4,20	5,10	5,10	4,50	9,8	8,7	7,9
92	4,80	4,50	4,50	5,10	5,30	4,50	9,8	8,7	7,9
93	5,10	4,20	4,50	5,30	5,30	4,50	10,1	8,7	7,9
94	5,10	4,20	4,50	5,30	5,30	4,80	10,1	8,7	7,9
95	5,10	4,50	4,80	5,30	5,60	4,80	10,1	9	8,1
96	5,10	4,50	4,80	5,10	5,60	4,80	10,1	9	8,1
97	5,10	4,50	4,80	5,30	5,60	5,10	10,1	9	8,1
98	5,30	4,50	5,10	5,30	5,90	5,10	10,4	9,3	8,1
99	5,30	4,80	5,10	5,60	5,90	5,10	10,7	9,5	8,4
100	5,30	4,50	5,10	5,60	6,20	5,10	10,7	9,5	8,4
101	5,30	4,50	5,10	5,60	6,20	5,10	10,7	9,5	8,4
102	5,60	4,80	5,30	5,90	6,20	5,10	10,9	9,3	8,4
103	5,30	4,80	5,30	5,90	6,50	5,30	11,2	9,5	8,7
104	5,30	4,80	5,30	5,90	6,50	5,30	11,2	9,5	8,7
105	5,60	4,80	5,60	6,20	6,50	5,30	11,2	9,8	8,7
106	5,90	4,80	5,60	6,20	6,70	5,30	11,2	9,8	8,7
107	5,90	5,10	5,90	6,20	6,70	5,30	11,5	10,1	9
108	5,90	5,10	5,90	6,20	6,70	5,30	11,5	10,1	9
109	6,20	5,10	5,90	6,50	7,00	5,60	11,5	10,1	9
110	6,20	5,10	5,90	6,50	7,00	5,60	11,5	10,1	9
111	6,20	5,10	5,90	6,50	7,00	5,60	11,5	10,1	9
112	6,20	5,10	6,20	6,50	7,30	5,60	11,8	10,4	9,3
113	6,20	5,30	6,50	6,70	7,30	5,60	11,8	10,1	9,3
114	6,50	5,30	6,20	6,70	7,30	5,60	12,1	10,4	9,5
115	6,50	5,30	6,20	6,70	7,60	5,90	12,1	10,4	9,5
116	6,50	5,30	6,50	7,00	7,60	5,90	12,1	10,4	9,3
117	6,50	5,30	6,50	7,30	7,60	5,90	12,4	10,4	9,5
118	6,50	5,30	6,50	7,30	7,60	5,90	12,4	10,4	9,5
119	6,70	5,30	6,70	7,30	7,90	5,90	12,6	10,7	9,5
120	6,70	5,60	7,00	7,30	7,90	6,20	12,6	10,7	9,5
121	6,70	5,60	7,00	7,60	7,90	6,20	12,6	10,7	9,5
122	6,70	5,60	7,00	7,60	8,10	6,20	12,6	10,7	9,5
123	7,00	5,60	7,00	7,60	8,10	6,20	12,6	10,9	9,8
124	7,00	5,60	7,30	7,90	8,10	6,20	12,9	10,9	9,8
125	7,00	5,60	7,30	7,90	8,40	6,50	12,9	10,9	9,8
126	7,30	5,90	7,30	7,90	8,40	6,50	13,2	11,2	10,1
127	7,30	5,90	7,60	7,90	8,40	6,50	13,2	11,2	10,1
128	7,30	6,20	7,60	8,10	8,70	6,50	13,2	11,2	10,1
129	7,30	6,20	7,60	8,10	8,70	6,50	13,2	11,2	10,1
130	7,60	6,20	7,60	8,10	8,70	6,50	13,5	11,2	10,4
131	7,60	6,20	7,90	8,10	9,00	6,70	13,5	11,5	10,4
132	7,60	6,20	7,90	8,40	9,00	6,70	13,5	11,5	10,4

133	7,90	6,20	8,10	8,40	9,00	6,70	13,5	11,5	10,4
134	7,90	6,50	8,10	8,40	9,30	7,00	13,8	11,5	10,4
135	7,90	6,50	8,40	8,70	9,30	7,00	14	11,8	10,7
136	7,90	6,50	8,40	8,70	9,30	6,70	14	11,8	10,7
137	8,10	6,50	8,40	8,70	9,50	7,00	14	11,8	10,7
138	8,10	6,50	8,40	8,70	9,50	7,00	14	11,8	10,9
139	8,10	6,50	8,40	9,00	9,50	7,00	14	11,8	10,9
140	8,10	6,70	8,70	9,00	9,80	7,00	14	12,1	10,9
141	8,40	6,70	9,00	9,30	9,80	7,30	14,3	12,1	10,9
142	8,40	6,70	9,00	9,30	9,80	7,30	14,3	12,1	11,2
143	8,40	6,70	9,00	9,30	10,10	7,30	14,3	12,1	11,2
144	8,70	7,00	9,30	9,30	10,10	7,30	14,3	12,4	11,2
145	8,70	7,00	9,30	9,30	10,10	7,30	14,6	12,4	11,5
146	8,70	7,00	9,30	9,50	10,10	7,60	14,6	12,4	11,5
147	8,70	7,00	9,50	9,50	10,10	7,60	14,6	12,4	11,5
148	9,00	7,30	9,50	9,50	10,10	7,60	14,9	12,6	11,5
149	9,00	7,30	9,80	9,80	10,40	7,90	14,9	12,4	11,5
150	9,00	7,30	9,80	9,80	10,40	7,90	14,9	12,4	11,5
151	9,30	7,30	9,80	9,80	10,40	7,90	14,9	12,6	11,5
152	9,30	7,30	10,10	10,10	10,70	7,90	15,2	12,9	11,8
153	9,30	7,30	10,10	10,10	10,90	8,10	15,2	12,9	11,8
154	9,30	7,60	10,40	10,10	10,90	8,10	15,2	12,9	12,1
155	9,50	7,60	10,40	10,40	10,70	8,10	15,2	12,9	12,1
156	9,50	7,90	10,70	10,40	10,70	8,10	15,2	12,9	12,1
157	9,50	7,90	10,70	10,40	10,90	8,40	15,2	12,9	12,1
158	9,50	7,90	10,70	10,40	10,90	8,40	15,4	13,2	12,4
159	9,80	8,10	10,90	10,40	10,90	8,40	15,4	13,2	12,4
160	9,80	8,10	10,90	10,70	11,20	8,40	15,4	13,2	12,4
161	9,80	8,10	10,90	10,90	11,20	8,70	15,4	13,2	12,4
162	10,10	8,40	11,20	10,90	11,80	8,70	15,7	13,5	12,6
163	10,10	8,40	11,20	10,90	11,80	8,70	15,7	13,5	12,6
164	10,10	8,40	11,20	11,20	11,50	9,00	15,7	13,5	12,6
165	10,10	8,70	11,80	11,20	11,80	9,00	15,7	13,5	12,6
166	10,40	8,70	11,80	11,20	11,50	9,00	16	13,8	12,6
167	10,40	8,70	11,80	11,80	11,50	9,30	16	13,8	12,6
168	10,40	8,70	11,80	12,10	11,80	9,30	16	13,8	12,9