



Project no. 038644
Bio-Norm II

Pre-normative research on solid bio-fuels for improved European standards
SPECIFIC TARGETED RESEARCH OR INNOVATION PROJECT
PRIORITY [6-1] – Sustainable energy systems



Report on the first round of sampling and testing, on the patterns of variability found in the measured properties

Deliverable D.I.10

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CTI – Comitato Termotecnico Italiano
UNIVPM – Università Politecnica delle Marche
SLU – Swedish University of Agricultural Science

Revision 1

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RE Restricted to a group specified by the consortium (including the Commission Services).

Involved Participants

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Revisions

Version	Date	Author(s)	Change
1	05/08/2009	SLU, CTI, UNIVPM	-

1. Introduction

The aim of Task I.2, according to the initial project plan, was to investigate the variance over time of specified properties of a material in a process chain, so that plans can be developed to determine where and how frequently samples should be taken and tested.

However, the sampling instruction, *(a) samples of the final goods, and of materials at a critical control point earlier in the process, will be taken at a frequency of two samples at each point per week for ten weeks*, stated in this project plan was not applicable for this type of experiment since the final goods of the process is energy and for most materials only one sampling point was useful in practice. A revised experimental design was therefore decided as reported in D.I.9 Report on review of host-sites and on protocols for sampling and testing. Some deviations from this revised design during the execution of the experiments were needed due to practical circumstances. These deviations are described in detail below for the various materials.

2. Revised experimental design for sampling and testing

2.1 Introduction

At two meetings in Ancona, Italy the 17th and 18th of September and in Vienna, Austria the 7th of October the results from Task I.1 were discussed in the WP I-group. From these results the sampling and testing plans for the various materials in Task I.2 were decided. In addition, the method for the statistical analyses was discussed and decided. In this first round of Task I.2 it was decided to take samples of all materials twice a week during ten weeks at the host-sites. Deviations from these sampling plans are described in detail below.

2.2 Sampling and testing plan for grape residue

As is discussed in section 1 the only possible sampling point is at the delivery of the material to the power plant and since a conveyor sampling is not available in this plant the heap sampling method is chosen. In Task I.1 it was shown that the sampling error for grape residue was more or less dependent on both the increment numbers and the number of sub-sample tests. The results also showed significant differences in variances between increment sizes and sampling methods that were contradictory for a majority of parameters. It was therefore decided to use an experimental design for grape residue of four increments with the size of 5L that were aggregated and homogenized followed by a dividing into two sub-samples that are analysed once for the parameters used in Task I.1. The dividing is performed by using the coning & quartering method to obtain a final sub-sample size of 2,5L. The sampling was carried out during five weeks instead of ten because of lack of material.

2.3 Sampling and testing plan for olive residue

Also in this case the only possible sampling point is at the delivery of the material to the power plant and since a conveyor sampling is not available the heap sampling method is chosen. As for grape residue it was shown that the sampling error for olive residue was more or less dependent on both the increment numbers and the number of sub-sample tests. The results also showed significant differences in variances between increment sizes and sampling methods that were contradictory for a majority of parameters. It was therefore decided to use an experimental design for olive residue of four increments with the size of 5L that were aggregated and homogenized followed by a dividing into two sub-samples that are analysed once for the parameters used in Task I.1. The dividing is performed by using the riffle box method to obtain a final sub-sample size of 2,5L. Since there is no continuous stream of olive residues arriving at the power plant, the decision was to sample 10 lorry loads from one shipment during five weeks instead of ten.

2.4 Sampling and testing plan for bark

The sampling point of choice for the bark fuel was from the tipped heap at the delivery to the power plant. From the results in Task I.1 it was shown that the sampling error for bark was more or less dependent on both the increment numbers and the number of sub-sample tests. An increment number of four and a number of sub-sample tests of two were found suitable for bark in the experimental design in the first round of Task I.2. An increment size of 5L was used and the increments were aggregated and homogenized before the general sample was divided by coning & quartering to two sub-samples with a size of about 2,5L. The sub-samples were then analysed once for the parameters used in Task I.1. Only 19 lorry loads were analysed since the company producing the bark was just able to deliver one lorry load one of the weeks.

2.5 Sampling and testing plan for wood chips

The sampling point chosen for wood chips was from the falling stream after the stem wood chipper. The reason for this was that the results from Task I.1 showed a significant bias between the sampling methods for particle size distribution and that the sampling from the falling stream was suggested to give a more accurate result for this parameter. In Task I.1 it was also shown that the sampling error for wood chips was determined almost only by the variation between the increments. The increment number chosen in the sampling of wood chips in Task I.2 was four. The increments of 2L each were aggregated, homogenized and divided by using the riffle box to two sub-samples of 4L on which one analysis of the parameters used in Task I.1 was performed. To make the comparison with the results in Task I.1 easy, the chosen numbers of increments and sub-samples were the same as in Task I.1, despite the fact that the sub-sample variation was negligible compared to the increment and the batch variation. The sampling of wood chips was performed during two weeks instead of ten as was decided in the preliminary design. The reason was that, due to technical problem at the plant, the experiments with wood chips in Task I.2 were delayed by more than 6 months and we wanted to complete the first round before the summer vacation. However, since the variation in wood chips to a large extent depends on the size and the type of stem wood and that these properties are more or less randomly distributed in the raw material, the results from this investigation should be representative for the material under study. Only 16 samples were collected since the plant was shut down before the last 4 samplings were finished.

2.6 Sampling and testing plan for pellets (6mm diameter)

It was necessary to change the host site for sampling of 6mm pellet in Task I.2. All production of 6mm pellet in the new host site (G.L.M. Ecowood) is packed in bags. Therefore the sampling is carried out by random selection of four pellet bags of 15kg from the production line. Each bag is first divided to an increment size of about 2,5kg by using the riffle box method. The four increments are then aggregated and homogenized and finally divided by use of the riffle box to two sub-samples of about 2,5kg each. The sub-samples are analysed once for the parameters used in Task I.1.

2.7 Sampling and testing plan for pellets (8mm diameter)

The sampling of 8mm pellets was carried out from a 2 tonnes pellet heap that had been stored for 3-4 weeks instead of sampling from newly produced pellets. The size of the heap corresponds to about 2-3 weeks of production. The reason was that the pellet plant got a large order of 6mm pellets until October, which would result in an additional delay of the project. The experimental design was similar to the one in Task I.1, except that the heap was divided into 20 sections from which four increments of 2,5L each were sampled. The increments were aggregated, homogenized and divided by a riffle box to two sub-samples of 2,5 L. Each sub-sample was then further divided

into two parts, where one part was used for the mechanical durability analysis, while the other part was used for moisture and ash analyses.

2.8 Method for statistical analyses

The aim of Bionorm II, WP I, Task I.2 was to investigate the variance over time of specified properties of a material in a process chain. A suitable statistical method for the evaluation of long term variation is the Shewhart control chart. In this method the values from the analyses of a fuel parameter are collected over a long period of time. From these values the average \hat{y} and the standard deviation s are calculated. A chart is then constructed where the individual values are plotted in time order and where the average \hat{y} together with $\pm 1s$ and $\pm 2s$ are shown in the chart as control lines (see figure 1 below).

The feature with the Shewhart chart is that you easily get a measure of the long term variation in the data. In addition, it indicates how much variation about the average \hat{y} that can be expected to occur by chance and if you have any outliers or trends in the data.

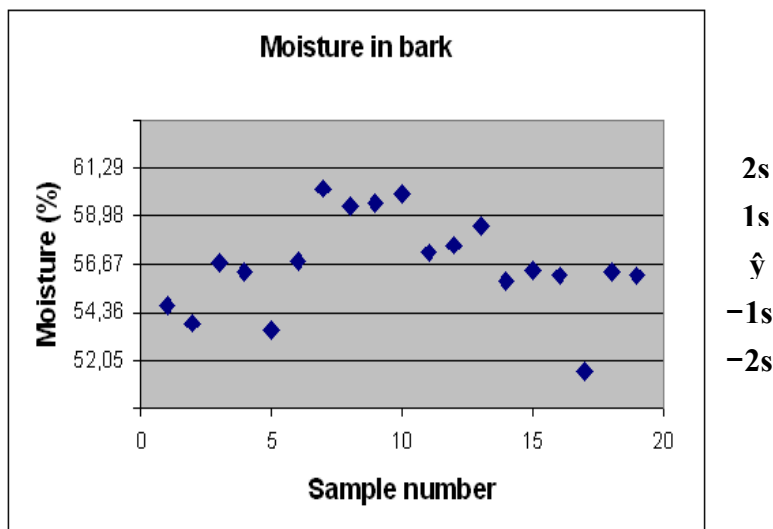


Figure 1 Example of a Shewhart control chart

In addition, a comparison of the corresponding total standard deviations in Task I.1 and Task I.2 was performed by using a significance test of variances (F-distribution). If no significant differences between the variances are found, the results may be considered as representative for the material under study and can, for example, be used for the calculation of the number of increments or sub-sample tests necessary to obtain a certain level of uncertainty in the analytical result.

3. Results

3.1 Bark

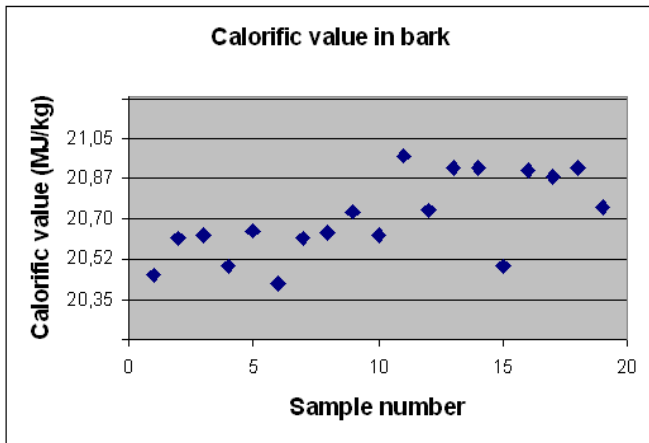
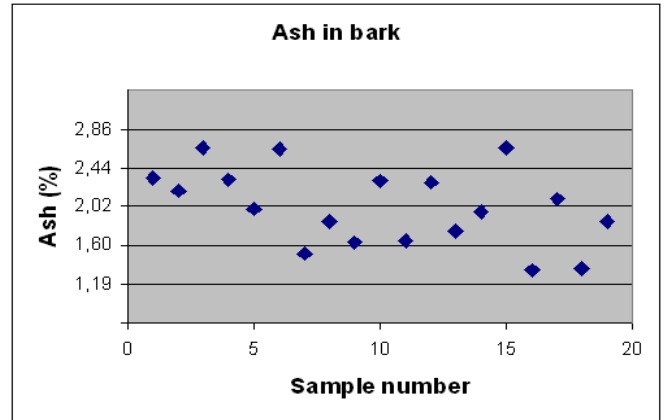
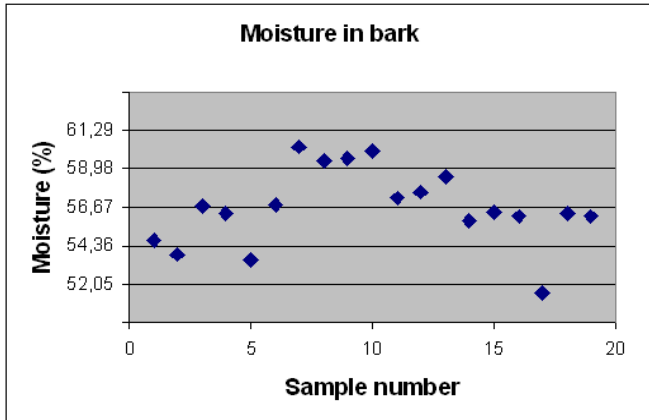


Figure 2 Variation of moisture, ash and calorific value in bark of Scots pine during ten weeks of sampling. The points represent the average of the two sub-samples.

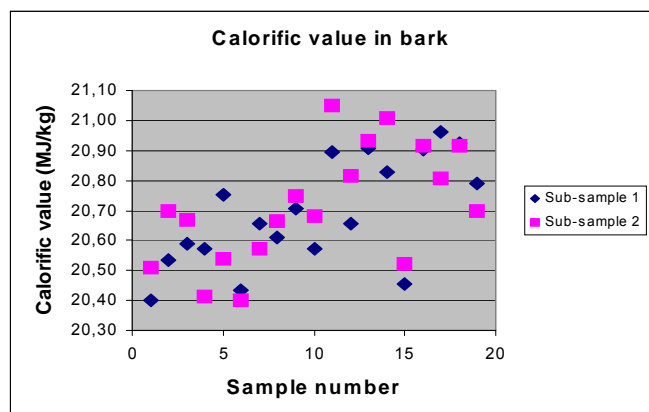
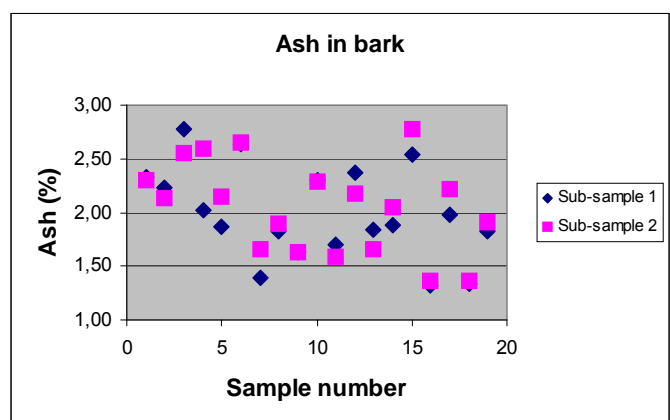
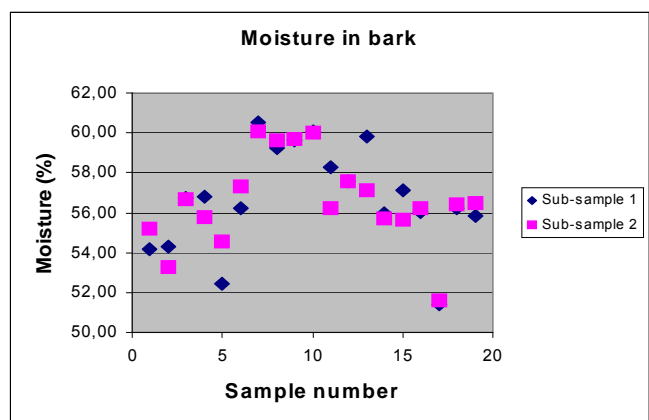


Figure 3 Individual sub-sample analyses results of moisture, ash and calorific value in bark from Scots pine.

Table 1 Comparison of total standard deviations in Task I.1 and Task I.2 of the analyses of moisture, ash and calorific value in bark from Scots pine.

Parameter	Overall std.dev. Task I.1	Overall std.dev. Task I.2	F-value overall variation	F_{crit}	Sub-sample std.dev. TaskI.1	Sub-sample std.dev. TaskI.2
Moisture	2,21	2,31	1,09	2,90	0,88	0,79
Ash	0,63	0,42	2,25	5,81	0,11	0,14
Calorific value	0,26	0,18	2,09	5,81	0,085	0,083

In figure 2 the variations of moisture, ash and calorific value in bark from Scots pine over a time period of ten weeks are shown. No outliers or trends were detected in the data except for an indication of a small rise in calorific value with time.

In figure 3 the individual subsample standard deviations for moisture, ash and calorific value in bark are shown.

In table 1 a comparison of the overall standard deviation between Task I.1 and Task I.2 are shown. The results from the F-test indicate that there is no significant difference in variation between the two investigations. In addition, the sub-sample standard deviation is presented for comparison with the overall variation. No difference in sub-sample standard deviation between the two tasks was found

3.2 Wood chips

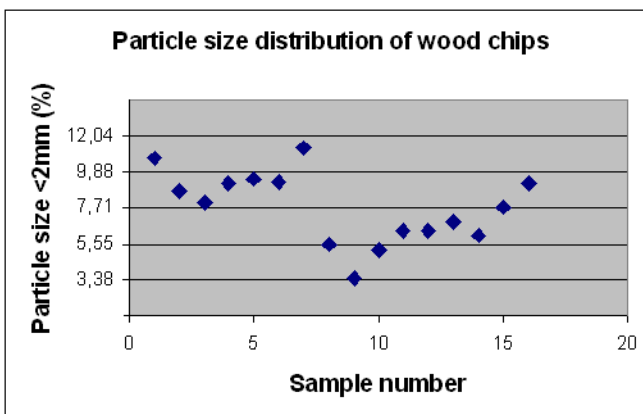
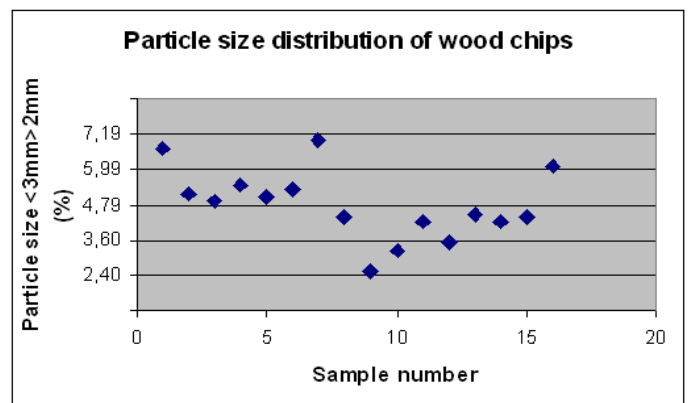
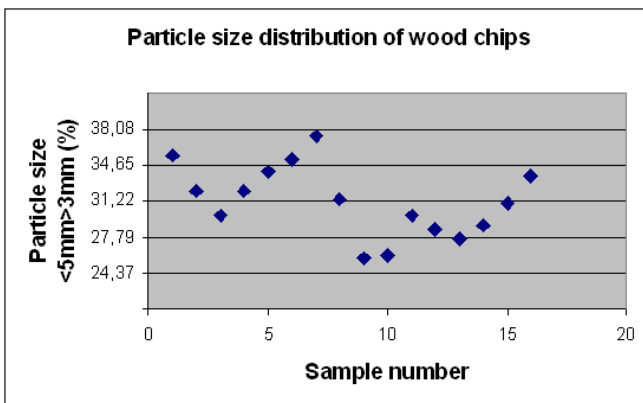
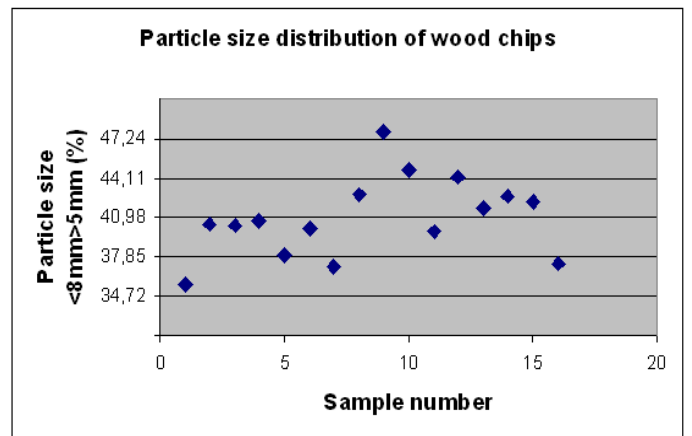
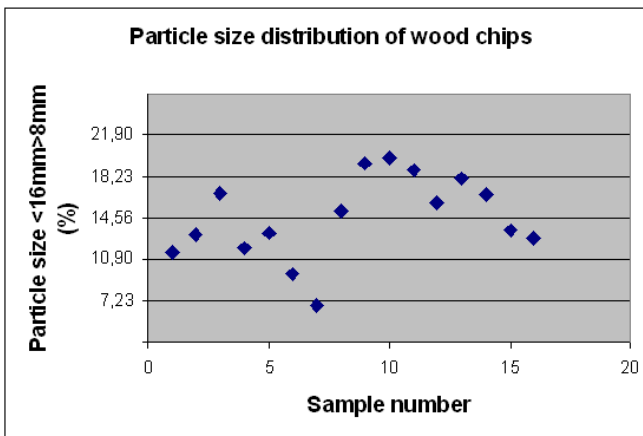
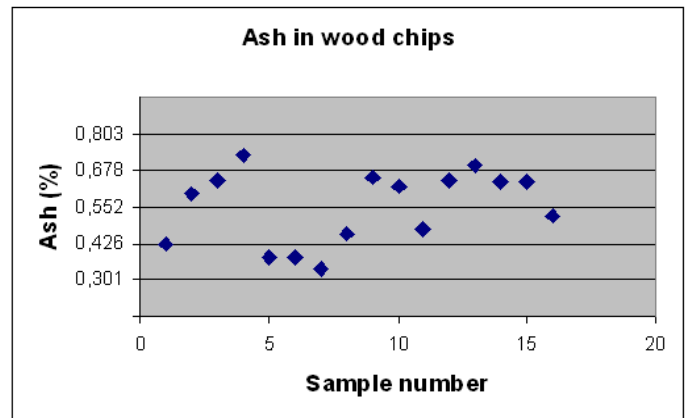
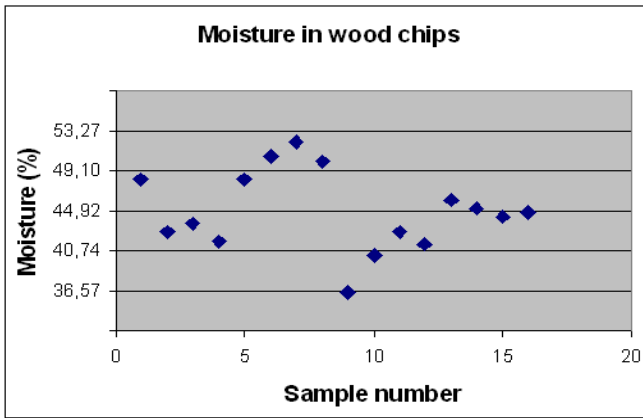


Figure 4 Variation of moisture, ash and particle size distribution in wood chips during two weeks of sampling. The points represent the average of the two sub-samples.

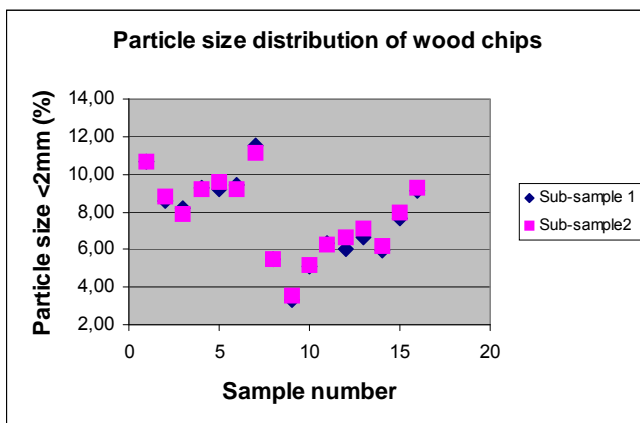
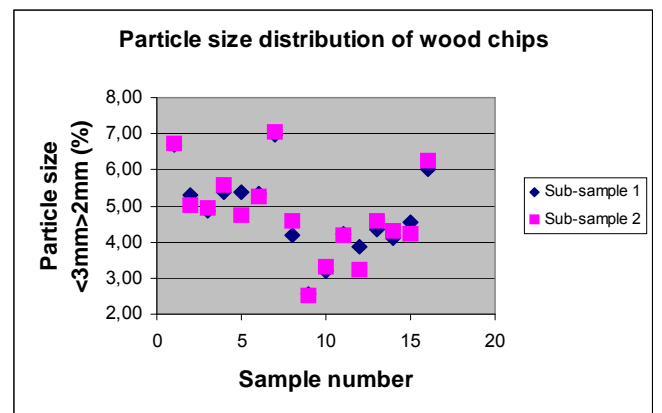
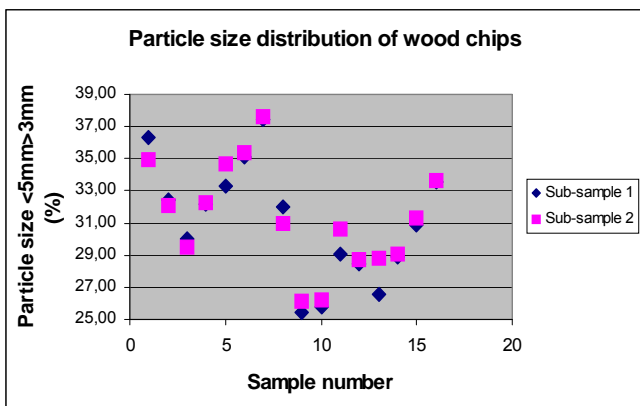
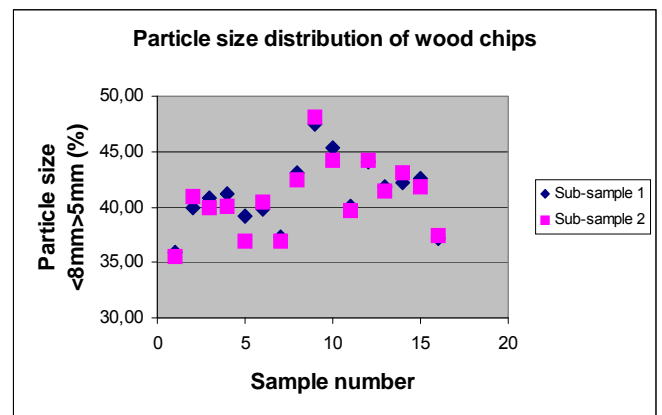
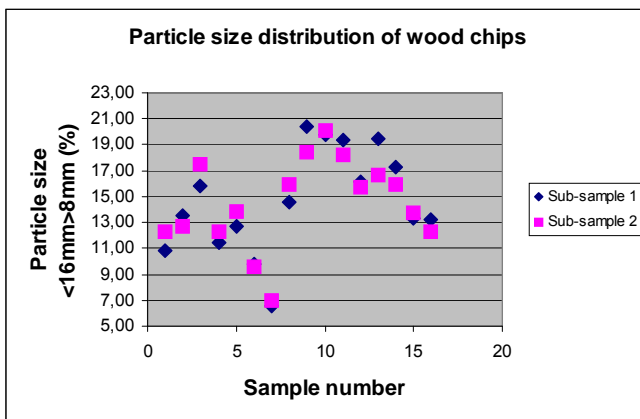
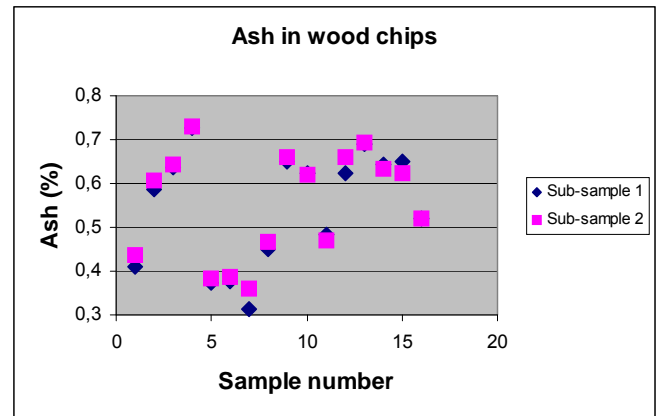
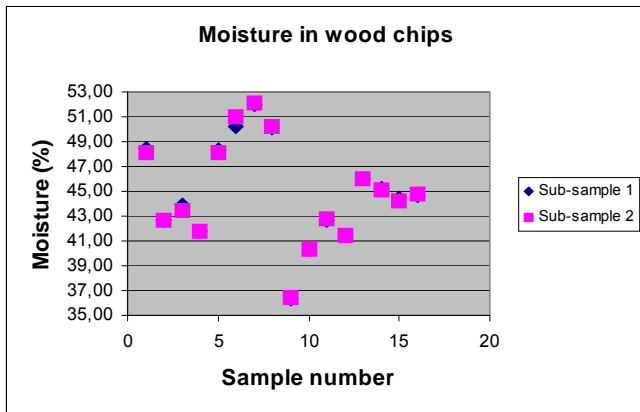


Figure 5 Individual sub-sample analyses results of moisture, ash and particle size distribution in wood chips.

Table 2 Comparison of total standard deviation in Task I.1 and Task I.2 of the analyses of moisture, ash and particle size distribution in wood chips.

Parameter	Overall std.dev. Task I.1	Overall std.dev. Task I.2	F-value overall variation	F_{crit}	Sub-sample std.dev. TaskI.1	Sub-sample std.dev. TaskI.2
Moisture	2,53	4,18	2,73	5,86	0,25	0,18
Ash	0,16	0,13	1,51	3,06	0,022	0,013
Particle size <16mm>8mm	3,03	3,67	1,47	5,86	1,57	0,89
Particle size <8mm>5mm	2,02	3,13	2,40	5,86	1,02	0,63
Particle size <5mm>3mm	3,22	3,43	1,13	5,86	1,10	0,66
Particle size <3mm>2mm	0,45	1,20	7,11	5,86	0,26	0,21
Particle size <2mm	1,16	2,16	3,47	5,86	0,49	0,20

In figure 4 the variations of moisture, ash and particle size distribution in wood chips over a time period of two weeks are shown. No outliers or trends were detected for moisture and ash content. An indication of a grouping between the first seven samples compared to the last nine was observed for particle size distribution, especially for the smallest size.

In figure 5 the individual subsample standard deviations for moisture, ash and particle size distribution in wood chips are shown. The sub-sample variation is very small and contributes almost nothing to the overall standard deviation of all parameters.

In table 2 a comparison of the overall standard deviation between Task I.1 and Task I.2 are shown. The results from the F-test indicate that there is no significant difference in variation between the two investigations except for particle size <3mm>2mm. The reason is the low standard deviation in Task I.1 compared to the other particle sizes. In addition, the sub-sample standard deviation is presented for comparison with the overall variation. Only small deviations between the two tasks are shown.

3.3 Pellets (8mm)

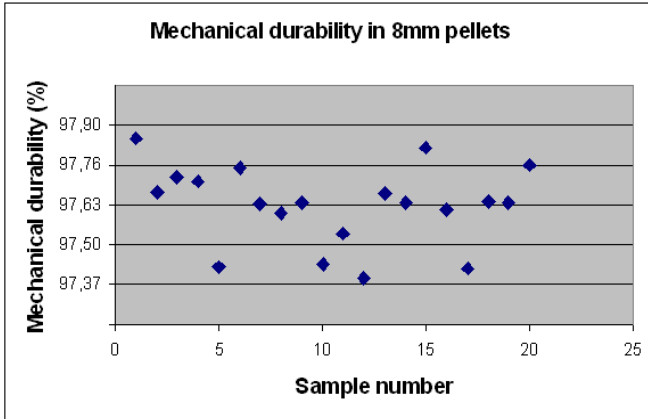
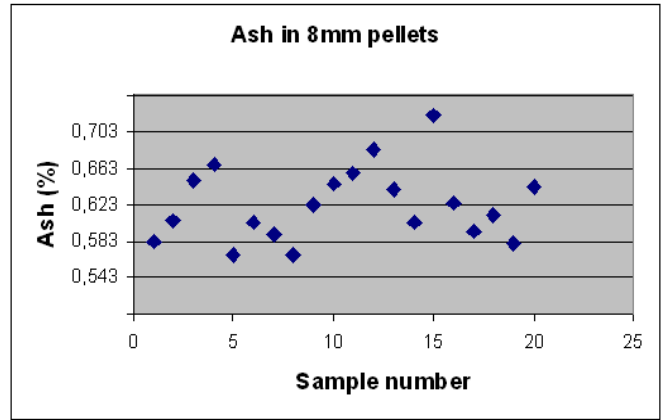
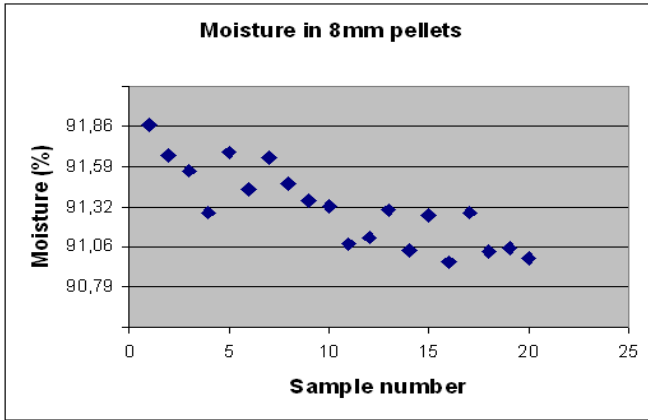


Figure 6 Variation of moisture, ash and mechanical durability in 8mm pellets during two weeks of sampling. The points represent the average of the two sub-samples.

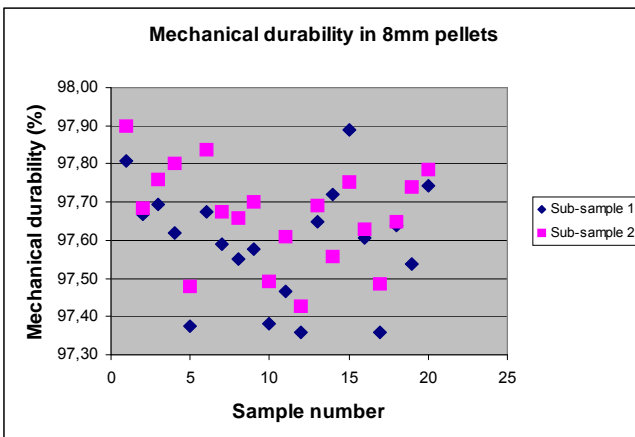
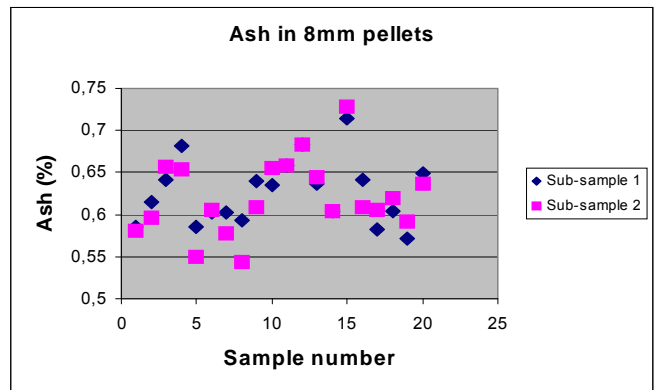
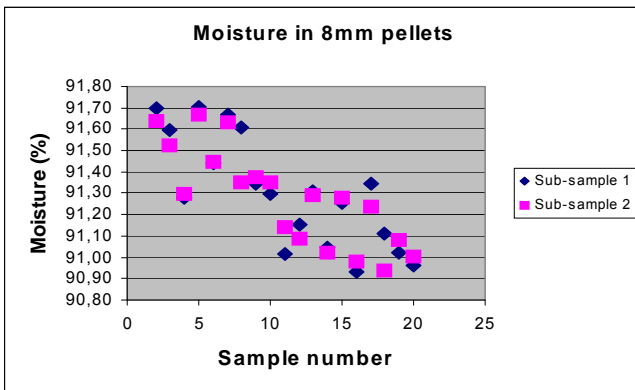


Figure 7 Individual sub-sample analyses results of moisture, ash and mechanical durability in 8mm pellets.

Table 3 Comparison of total standard deviations in Task I.1 and Task I.2 of the analyses of moisture, ash and mechanical durability in 8mm pellets.

Parameter	Overall std.dev. Task I.1	Overall std.dev. Task I.2	F-value overall variation	F_{crit}	Sub-sample std.dev. TaskI.1	Sub-sample std.dev. TaskI.2
Moisture	0,71	0,27	6,91	2,90	0,084	0,063
Ash	0,068	0,040	2,89	2,90	0,017	0,016
Mechanical durability	0,24	0,13	3,41	2,90	0,068	0,081

In figure 6 the variations of moisture, ash and mechanical durability in 8mm pellets in the pellet heap are shown. No outliers or trends were detected for ash content and mechanical durability. A small decrease in moisture content with sample number was found.

In figure 7 the individual subsample standard deviations for moisture, ash and mechanical durability in 8mm pellets are shown.

In table 3 a comparison of the overall standard deviation between Task I.1 and Task I.2 are shown. The results from the F-test indicate that there is a significant difference in variation between the two investigations for moisture content and mechanical durability. In addition, the sub-sample standard deviation is presented for comparison with the overall variation. No significant difference between the sub-sample standard deviations of the two tasks was found.

3.4 Pellets (6mm)

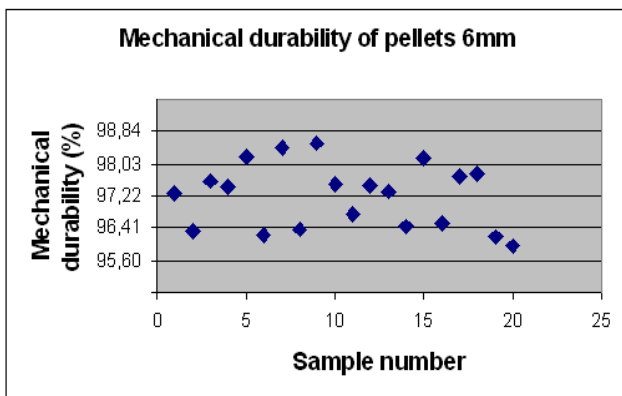
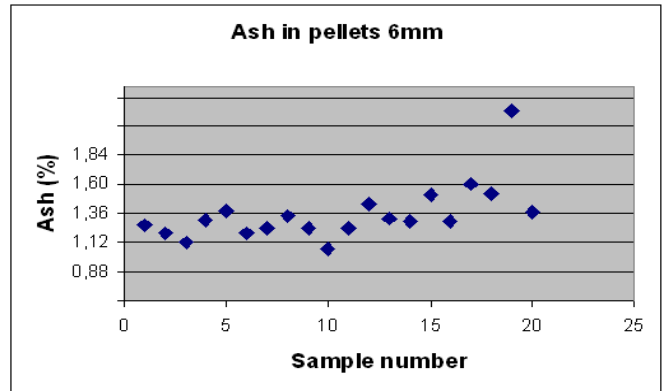
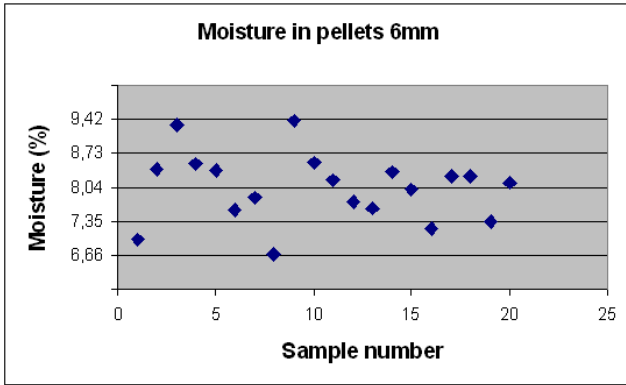


Figure 8 Variation of moisture, ash and mechanical durability in 6mm pellets during ??? weeks of sampling. The points represent the average of the two sub-samples.

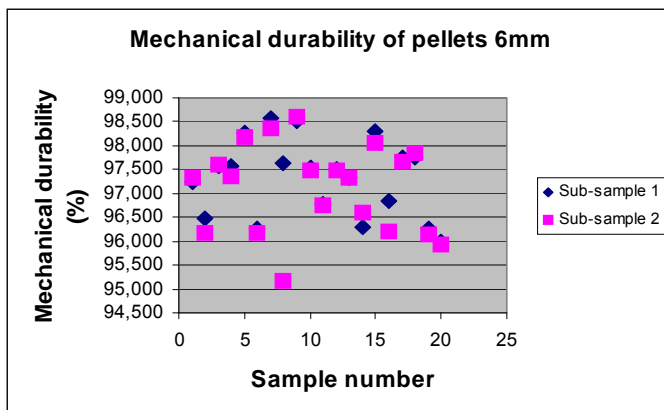
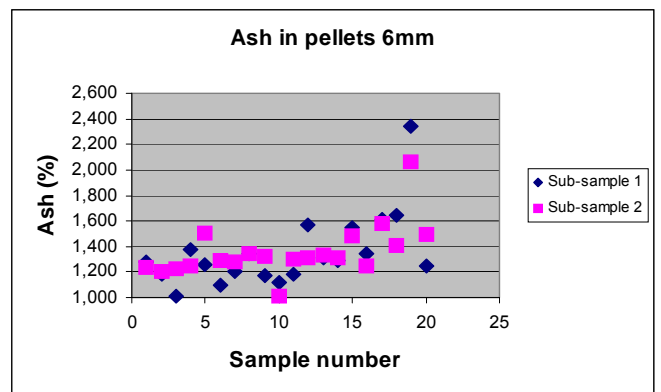
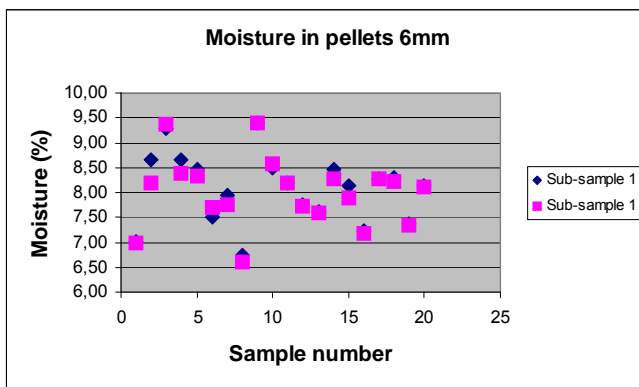


Figure 9 Individual sub-sample analyses results of moisture, ash and mechanical durability in 6mm pellets.

Table 4 Comparison of total standard deviations in Task I.1 and Task I.2 of the analyses of moisture, ash and mechanical durability in 6mm pellets.

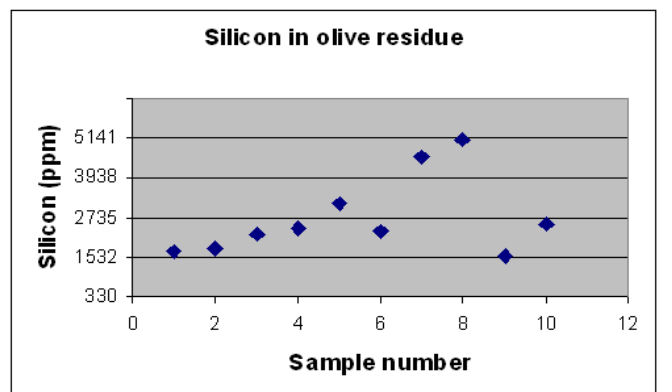
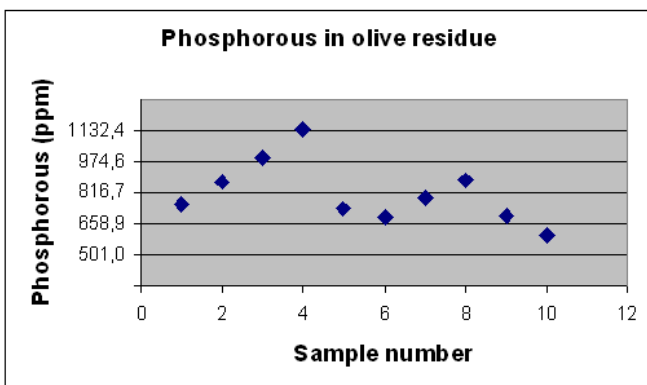
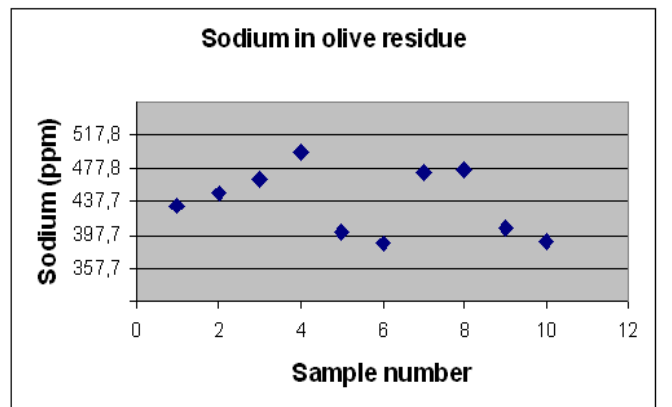
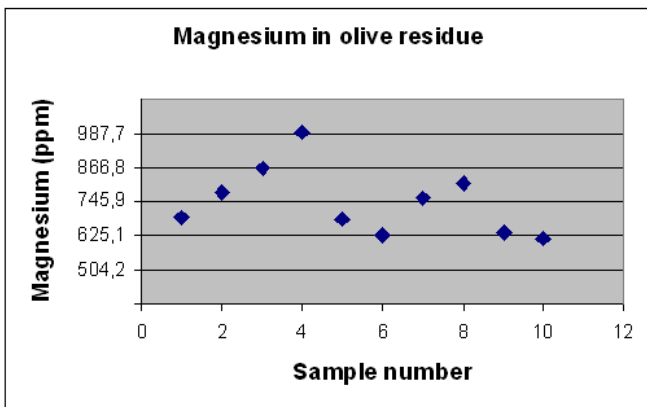
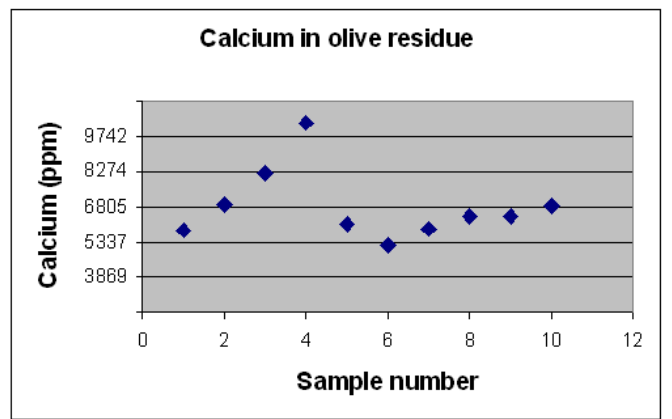
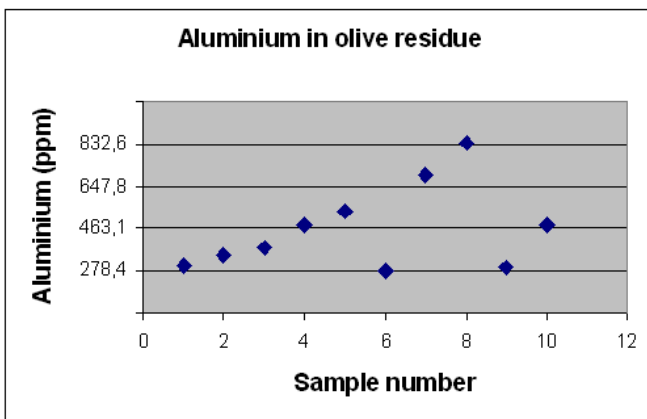
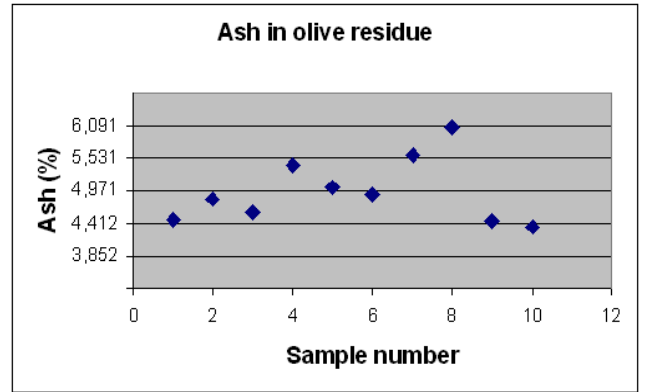
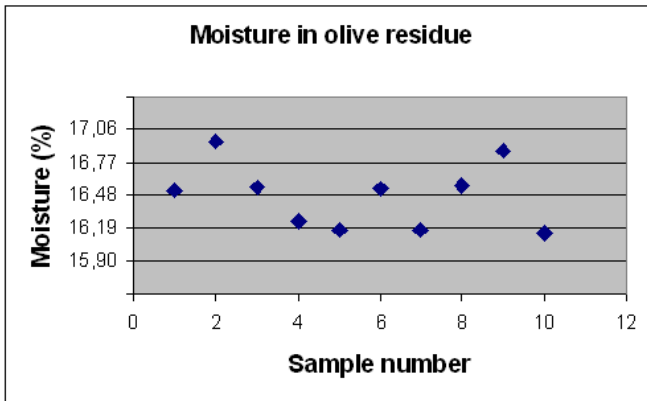
Parameter	Overall std.dev. Task I.1	Overall std.dev. Task I.2	F-value overall variation	F_{crit}	Sub-sample std.dev. TaskI.1	Sub-sample std.dev. TaskI.2
Moisture	0,087	0,69	62,9	5,81	0,14	0,12
Ash	0,040	0,24	36,0	5,81	0,089	0,11
Mechanical durability	0,030	0,81	729	5,81	0,026	0,42

In figure 8 the variations of moisture, ash and mechanical durability in 6mm pellets are shown. No outliers or trends were detected except for ash content where a suspected outlier was found according to Dixon's outlier test.

In figure 9 the individual subsample standard deviations for moisture, ash and mechanical durability in 6mm pellets are shown.

In table 4 a comparison of the overall standard deviation between Task I.1 and Task I.2 are shown. The results from the F-test indicate that there is a large, significant difference in variation between the two investigations for all three parameters. In addition, the sub-sample standard deviation is presented for comparison with the overall variation. No significant difference between the sub-sample standard deviations of the two tasks was found.

3.5 Olive residue



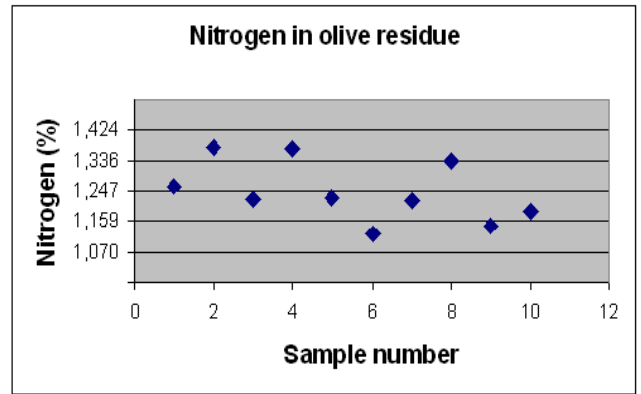
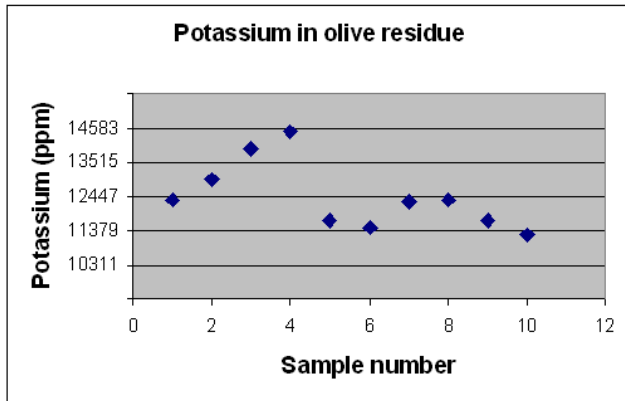
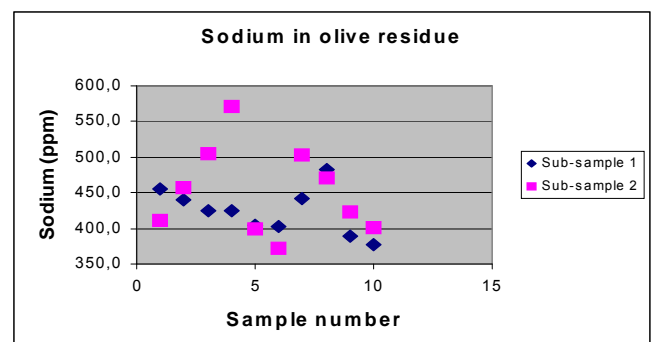
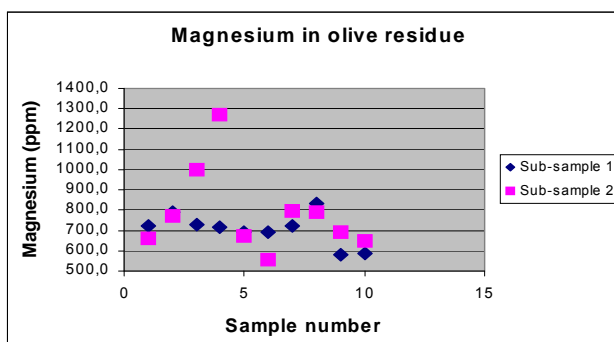
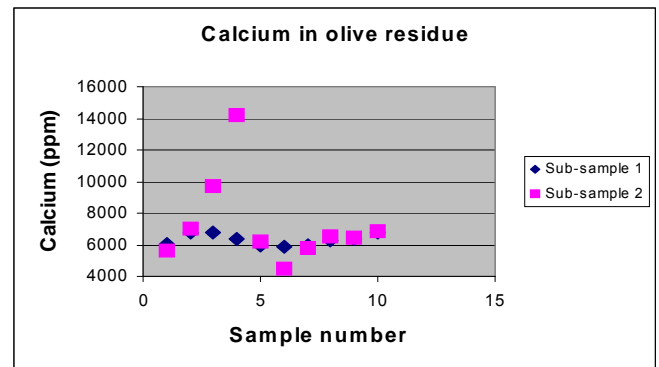
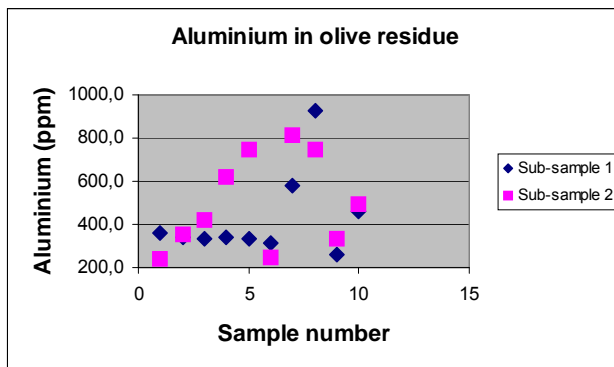
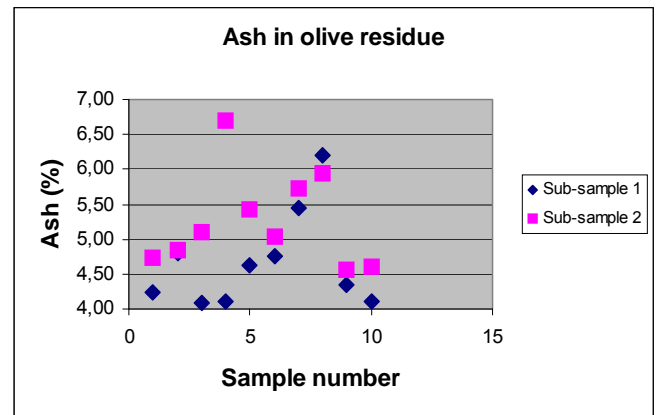
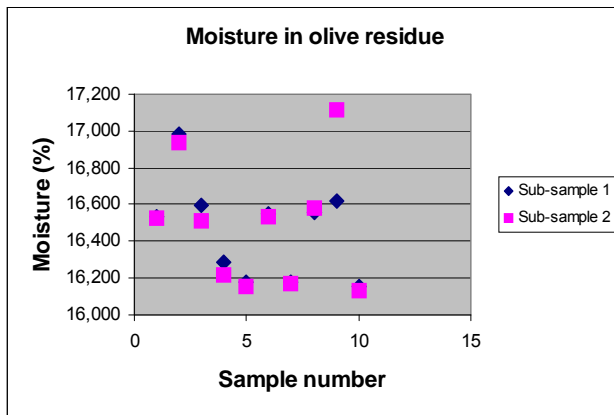


Figure 10 Variation of moisture, ash and 8 major elements in olive residue during 5 weeks of sampling. The points represent the average of the two sub-samples.



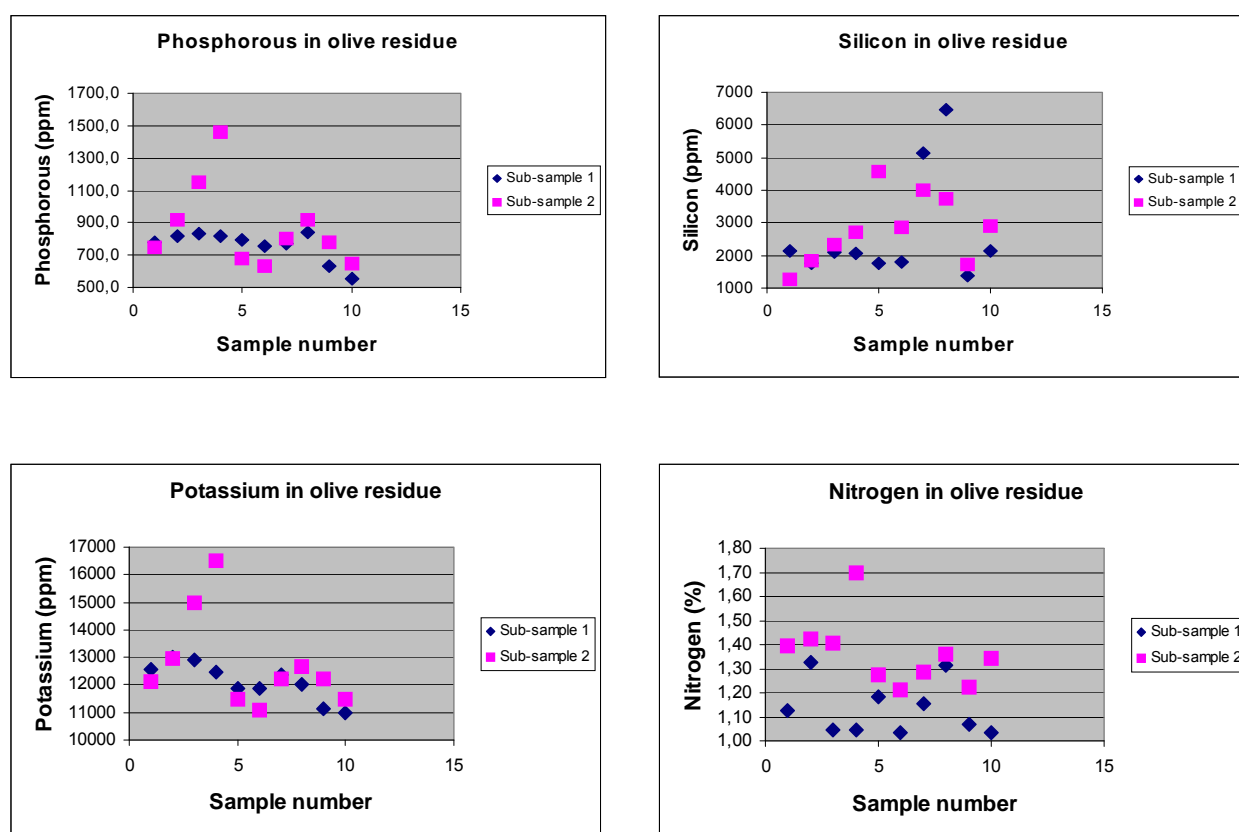


Figure 11 Individual sub-sample analyses results of moisture, ash and 8 major elements in olive residue.

Table 5 Comparison of total standard deviation in Task I.1 and Task I.2 of the analyses of moisture, ash and 8 major elements in olive residue.

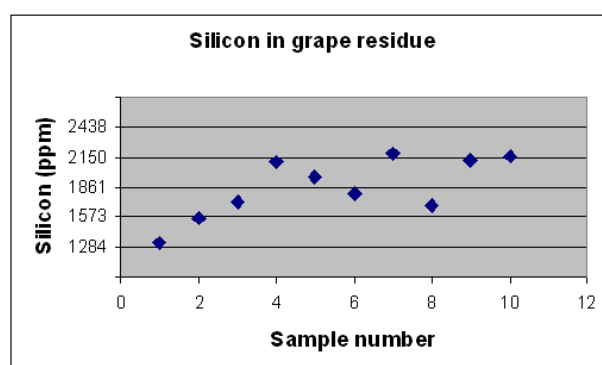
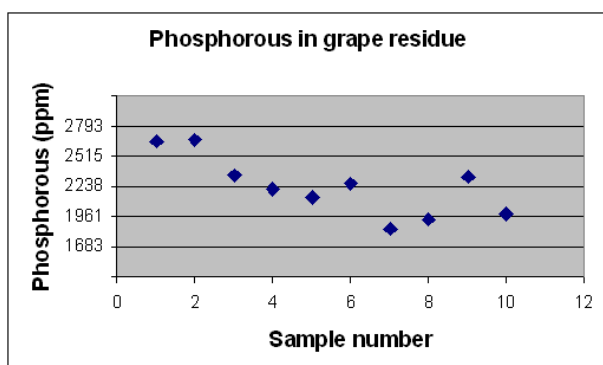
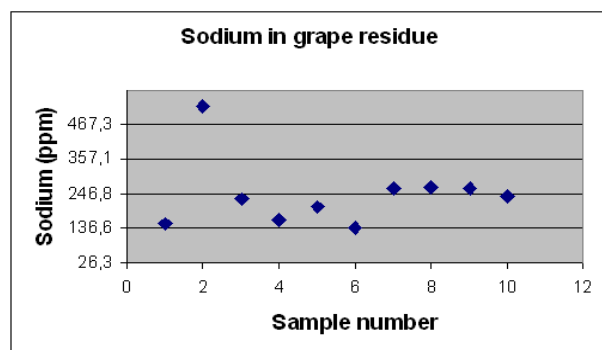
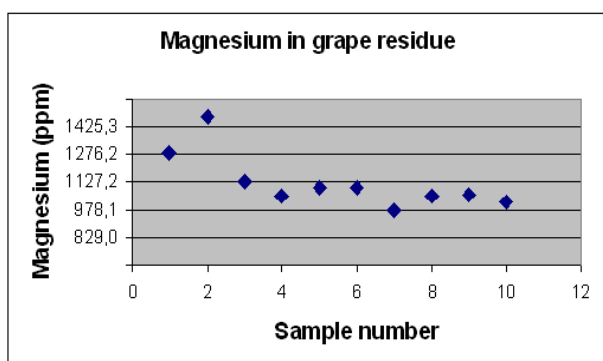
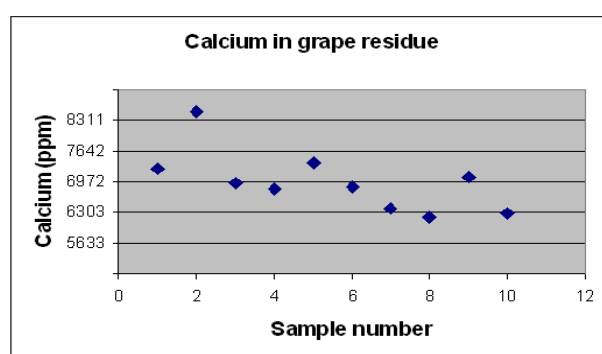
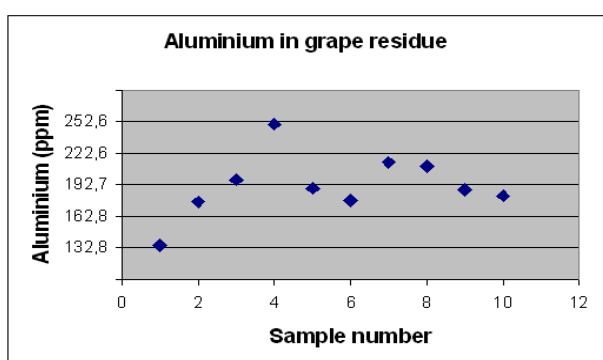
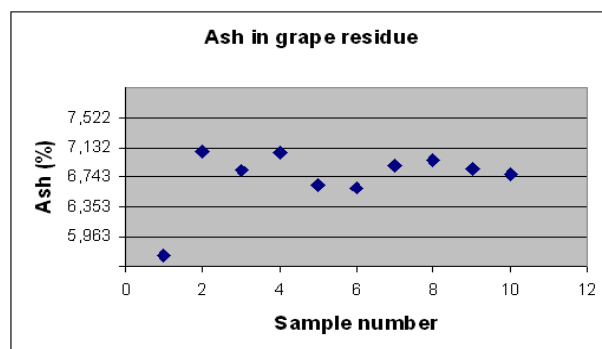
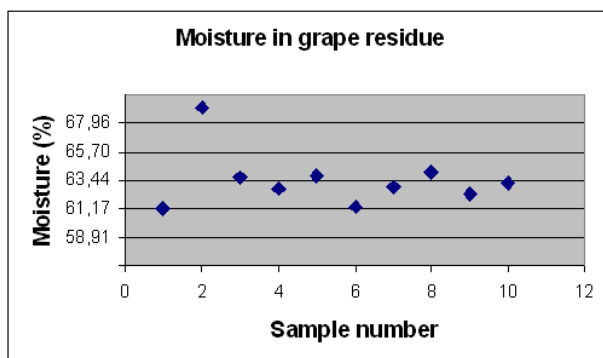
Parameter	Overall std.dev. Task I.1	Overall std.dev. Task I.2	F-value overall variation	F _{crit}	Sub-sample std.dev. Task I.1	Sub-sample std.dev. Task I.2
Moisture	0,50	0,29	2,97	3,63	0,18	0,12
Ash	0,39	0,56	2,06	6,00	0,58	0,67
Aluminium	18	185	106	6,00	143	136
Calcium	344	1468	18,2	6,00	1018	1892
Magnesium	250	121	4,27	3,63	846	147
Sodium	43	40	1,16	3,63	45,6	42,6
Phosphorous	30	158	27,7	6,00	38,7	172
Silicon	264	1203	20,8	6,00	1326	992
Potassium	526	1068	4,12	6,00	549	1081
Nitrogen	0,091	0,088	1,07	3,63	0,071	0,20

In figure 10 the variations of moisture, ash and 8 major elements in olive residue are shown. No outliers were detected. A suspicious trend for the first samples for all metallic elements was found.

In figure 11 the individual subsample standard deviations for moisture, ash and 8 major elements in olive residue are shown. A strange behaviour of sample 3 and 4 with a significantly higher result for the second sub-sample was detected.

In table 5 a comparison of the overall standard deviation between Task I.1 and Task I.2 are shown. The results from the F-test indicate that there is a significant difference in variation between the two investigations for half of the parameters. In addition, the sub-sample standard deviation is presented for comparison with the overall variation. No significant difference between the sub-sample standard deviations of the two tasks was found except for magnesium, phosphorous and nitrogen.

3.6 Grape residue



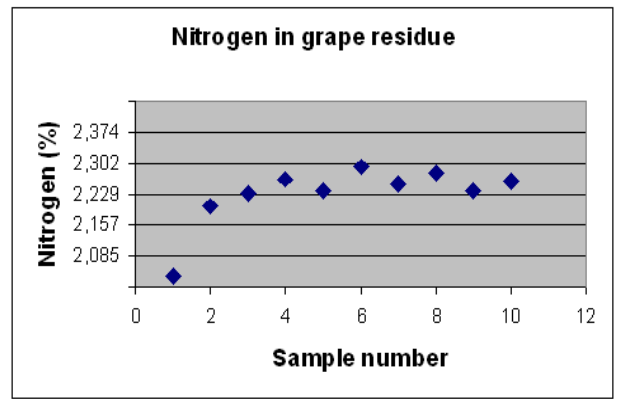
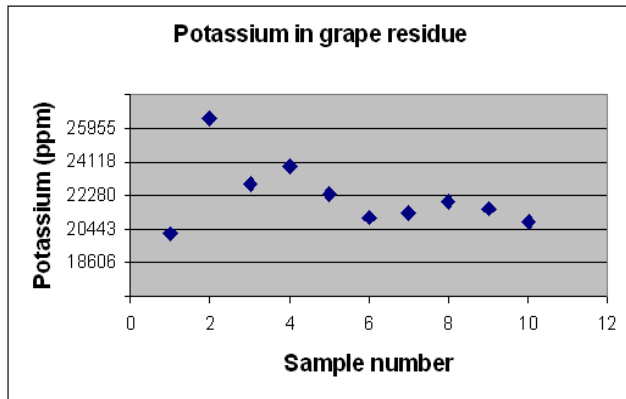
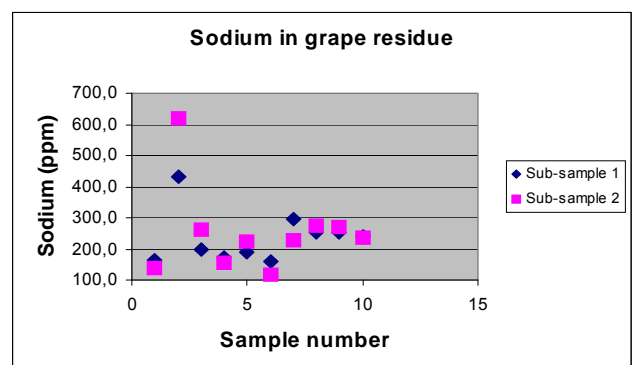
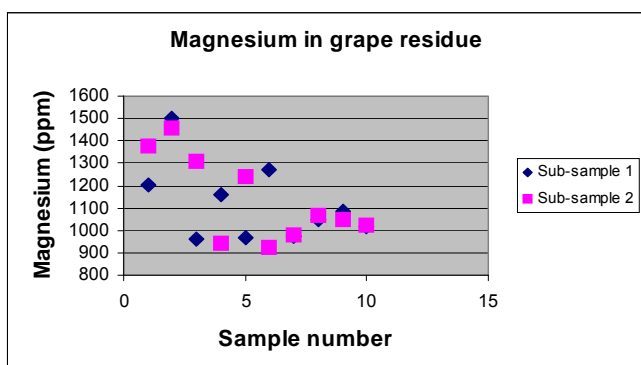
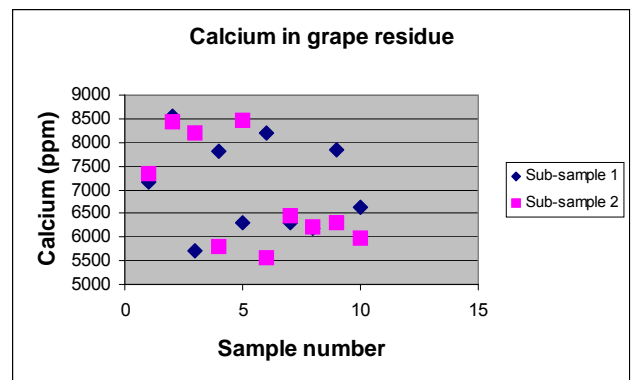
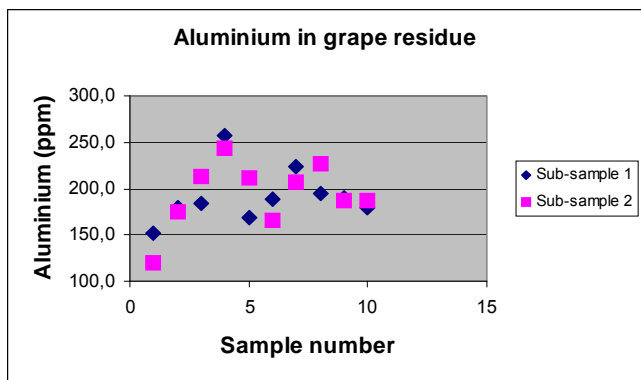
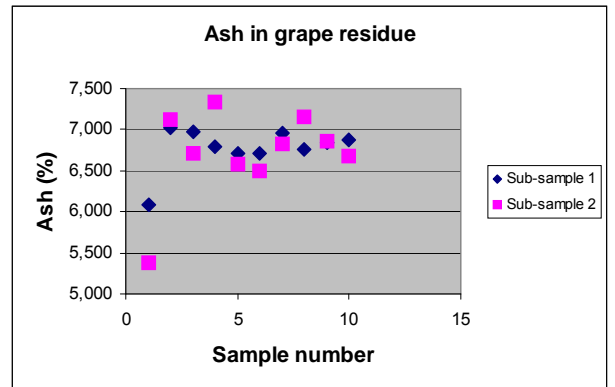
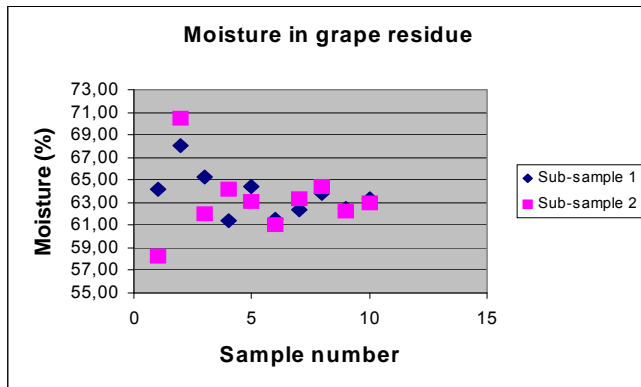


Figure 12 Variation of moisture, ash and 8 major elements in grape residue during ??? weeks of sampling. The points represent the average of the two sub-samples.



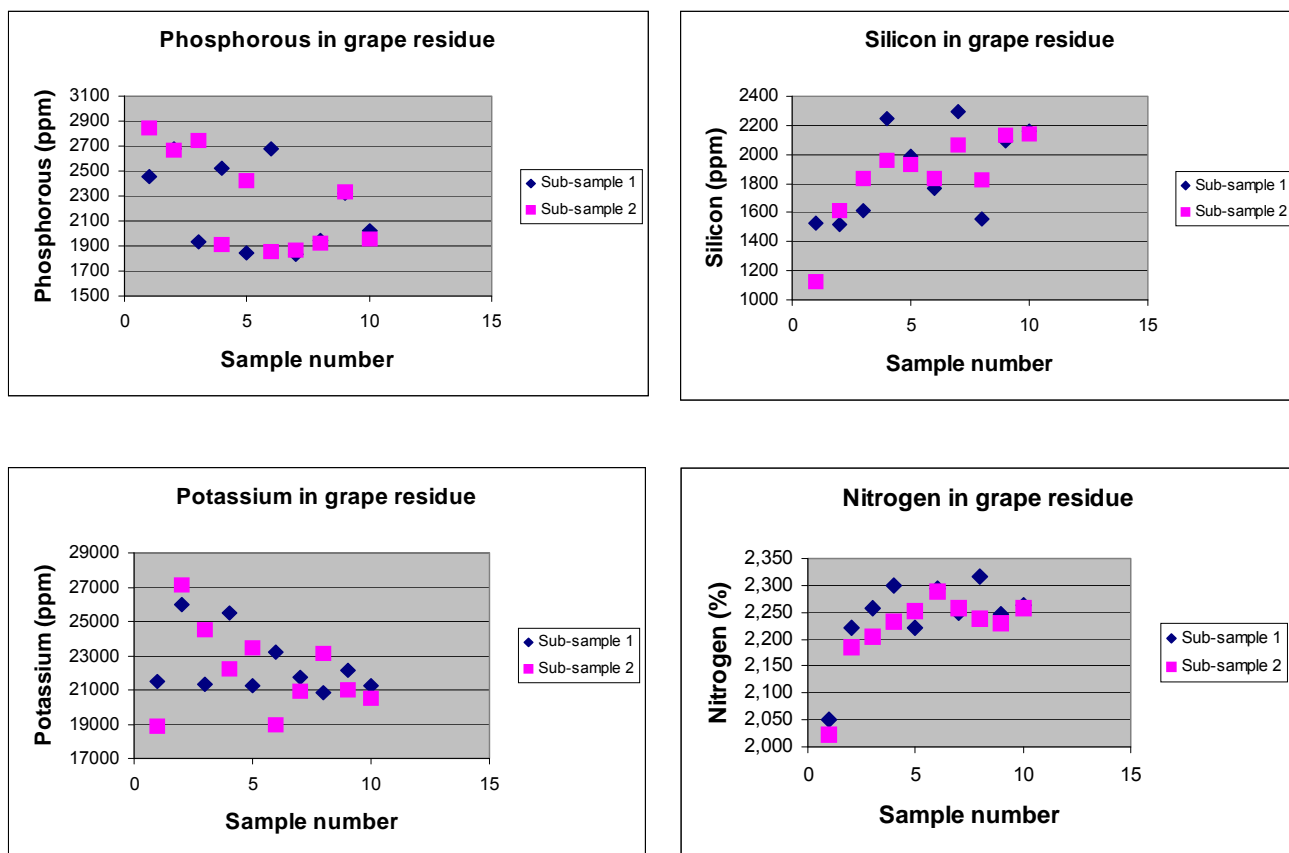


Figure 13 Individual sub-sample analyses results of moisture, ash and 8 major elements in grape residue.

Table 6 Comparison of total standard deviation in Task I.1 and Task I.2 of the analyses of moisture, ash and 8 major elements in grape residue.

Parameter	Overall std.dev. Task I.1	Overall std.dev. Task I.2	F-value overall variation	F _{crit}	Sub-sample std.dev. Task I.1	Sub-sample std.dev. Task I.2
Moisture	2,64	2,26	1,36	3,63	1,48	1,79
Ash	0,30	0,39	1,69	6,00	0,41	0,24
Aluminium	54	30	3,24	3,63	54,6	16,9
Calcium	1542	669	5,31	3,63	1291	1112
Magnesium	100	149	2,22	6,00	86,8	141
Sodium	95	110	1,34	6,00	19,1	49,8
Phosphorous	203	277	1,86	6,00	195	333
Silicon	146	288	3,89	6,00	294	147
Potassium	1643	1837	1,25	6,00	1152	1717
Nitrogen	0,056	0,072	1,65	6,00	0,062	0,029

In figure 12 the variations of moisture, ash and 8 major elements in grape residue are shown. A suspicious outliers was detected for nitrogen according to Dixon´s outlier test. No trend in the data was found.

In figure 13 the individual subsample standard deviations for moisture, ash and 8 major elements in olive residue are shown..

In table 6 a comparison of the overall standard deviation between Task I.1 and Task I.2 are shown. The results from the F-test indicate that there is no significant difference in variation between the two investigations except for calcium. In addition, the sub-sample standard deviation is presented for comparison with the overall variation. Significant differences between the sub-sample standard deviations of the two tasks were found for aluminium, sodium, silicon and nitrogen.

4. Discussion

Very good agreement between overall and sub-sample standard deviations for all parameters in bark from Scots pine was obtained. This would indicate that the obtained values of variation may be considered as reliable and representative for the studied material.

Also for wood chips a good agreement between the two tasks was obtained even if a significant difference in overall and sub-sample standard deviation was found for particle sizes <3mm>2mm and <2mm, respectively. A reason to the good results might be explained by the short period of sampling as was described in section 2.5. In the second round a longer period of sampling will be applied.

Considerable differences in overall standard deviation between the two tasks for moisture content and mechanical durability in 8mm pellets were obtained. The reason is since the pellet heap was stored for a couple of weeks before sampling the moisture content had time to level out with a smaller variation as a result. For the same reason the pellets may be stabilized during the storage with a smaller variation in durability as a result. For the ash content no difference was found since this parameter is not affected by storage time.

Very large differences in variation between the two tasks were found for all parameters in 6mm pellets. The main reasons for this are that the sampling experiments were performed at two different pellet plants that use quite different raw materials in the production.

Even for olive residue a significant difference in variation between the two tasks was found. The suspicious trend for the first samples may be explained by the strange behaviour of samples 3 and 4. However, even if these samples are excluded the difference in variation remains. The reason to this difference is probably due to the fact that the sampling was performed from two different shipments with a different origin.

For grape residue relatively good agreement between the two tasks was obtained and no trends in the overall and the sub-sample standard deviations were found. This can be explained by the fact that the sampling was performed from materials of the same producer of grape residue.