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**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 second round of sampling and testing**

Deliverable D.I.12

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UNIVPM – Università Politecnica delle Marche  
SLU – Swedish University of Agricultural Science

Revision 1

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Dissemination Level

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	15/12/2009	SLU, CTI, UNIVPM	-

## **1. Introduction**

The aim of Task I.2 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. Experimental design for round 2 of Task I.2 Sample planning**

At a meeting in Ancona, Italy the 5<sup>th</sup> of August 2009 the results from the first round of Task I.2 were discussed in the WP I-group. From these results the second round for the sampling and testing of the various materials in Task I.2 were decided as described below.

### **2.1 Sampling and testing plan for bark**

The results from the first round of task I.2 for bark showed good agreement with the results from Task I.1. The WP I-group therefore made the judgement that further analyses would not gain any more knowledge and that a second round for bark was not needed.

### **2.2 Sampling and testing plan for wood chips**

Since the time period for the sampling of wood chips in round 1 of Task I.2 was only 2 weeks due to the delay in the plant (see D.I. 10), a second round was performed where the sampling of 11 samples were carried out during a period of 12 weeks. An equal experimental design as in the first round was used in the second round.

### **2.3 Sampling and testing plan for pellets (8mm diameter)**

As was reported in the delivery D.I.10 Report on the first round on sampling and testing, the sampling of 8mm pellets in the first round had to be carried out from an earlier produced heap that had been stored during a couple of weeks, since the plant had got a large order of 6mm pellets. The results were therefore not reliable especially for the moisture content. A second round was therefore performed during a 10 week period. An equal experimental design as in the first round was used in the second round except that the pellets were sampled from the heap directly after the production.

### **2.4 Sampling and testing plan for pellets (6mm diameter)**

Since there was no possibility of performing the sampling for further 10 weeks in the same pellet production plant, it was therefore decided - during the first round of Task I.2 - that for the 6mm pellets, 4 samples a week during 10 weeks should be sampled and analysed during the first round, but where only 2 samples a week were used for the statistical calculation of the first round. In the second round instead, all samples were used in the evaluation.

### **2.5 Sampling and testing plan for olive residue**

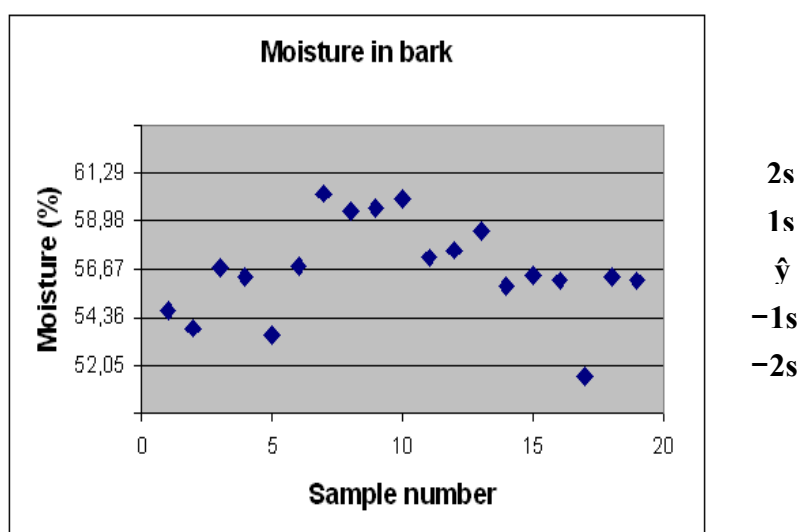
Since the processing period of olives is very short during October and November, and the shipments of olive residues from other countries are generally not planned, it was realised that it should not be possible to perform a second round of Task I.2 in 2009 without breaking the time schedule for WP I. Moreover, during the first round of Task I.2 due to the fact that a limited number of lorries of olive residues were received at the power plant, it was not possible to perform a second round sampling as for grape residues in section 2.1.

## 2.6 Sampling and testing plan for grape residue

Since the production period for grape residue is very short during September and October, it was realised during the planning of the first round of Task I.2 Sample planning that it should not be possible perform a second round of Task I.2 in 2009 without breaking the time schedule for WP I. It was therefore decided that for grape residue, 4 samples a week during 5 weeks should be sampled and analysed during the first round, but where only 2 samples a week were used in the statistical calculation of the first round. In the second round instead, all samples were used in the evaluation. An equal experimental design as in the first round was used in the second round.

## 2.7 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 (see figure 1 below). The feature of 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.

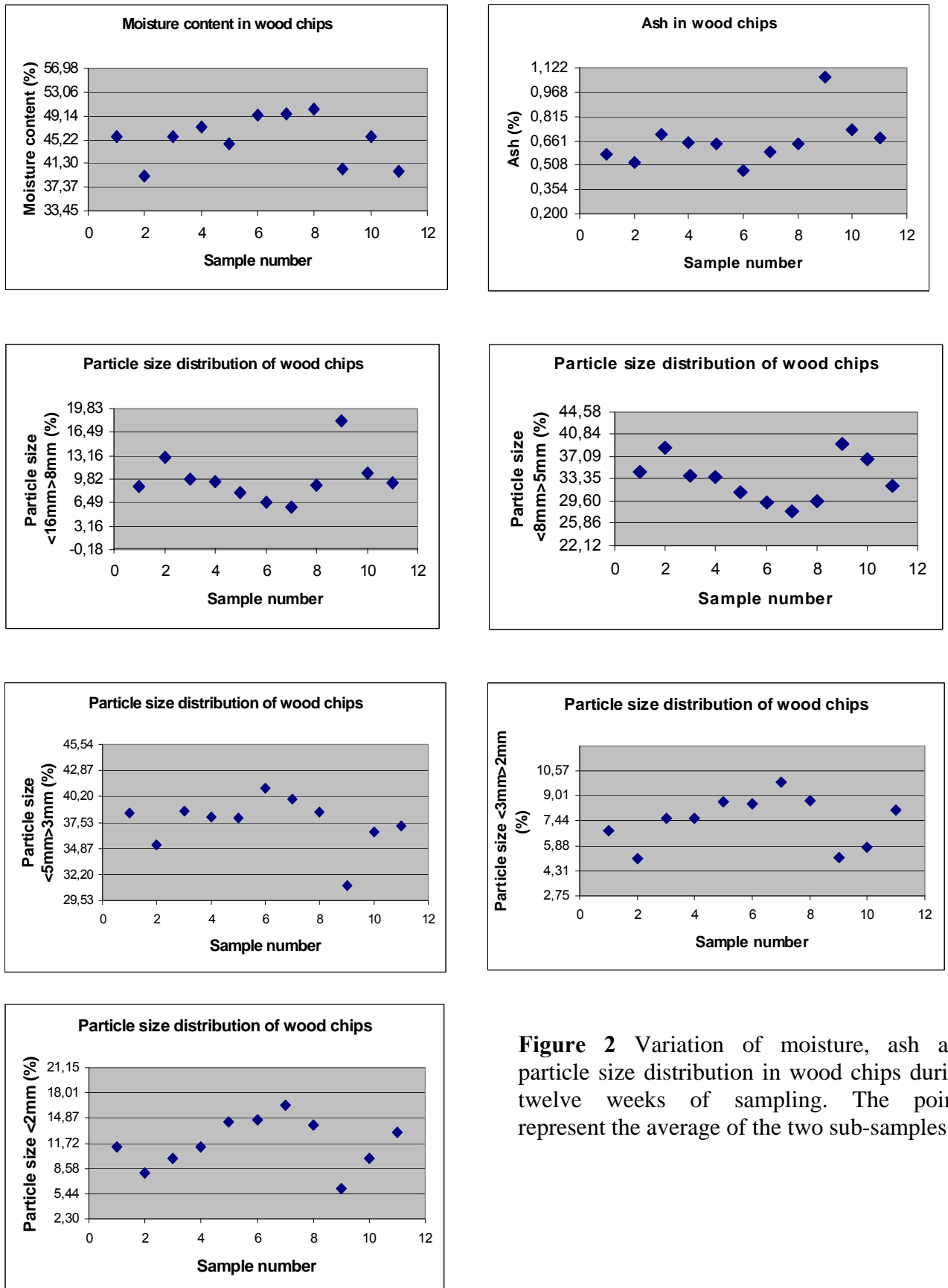


**Figure 1** Example of a Shewhart control chart

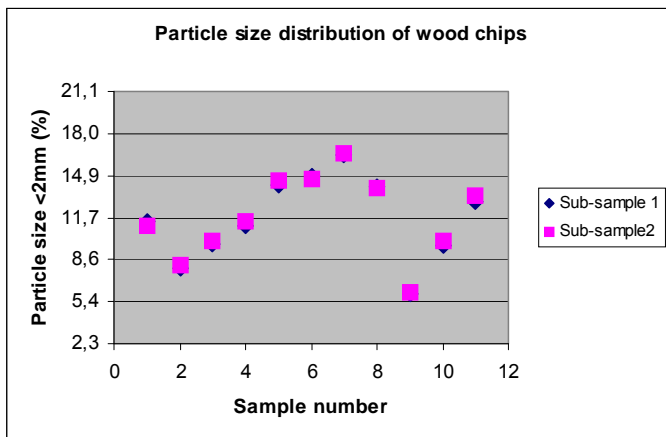
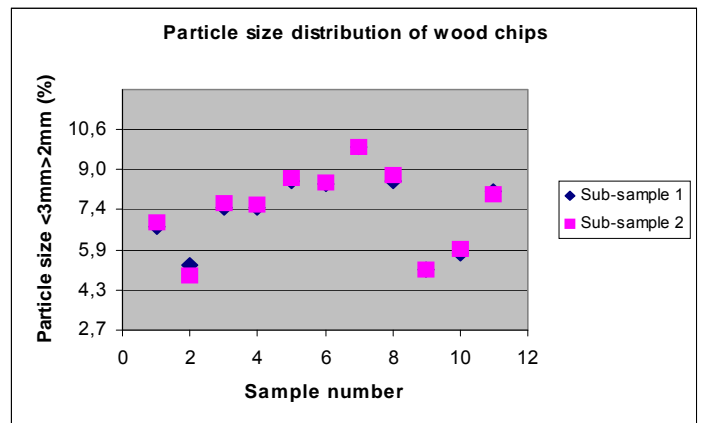
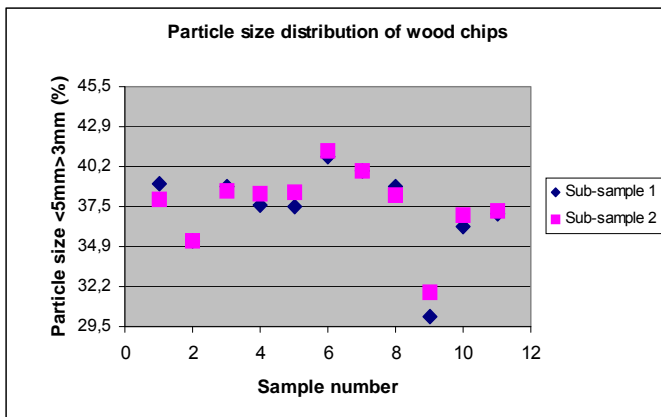
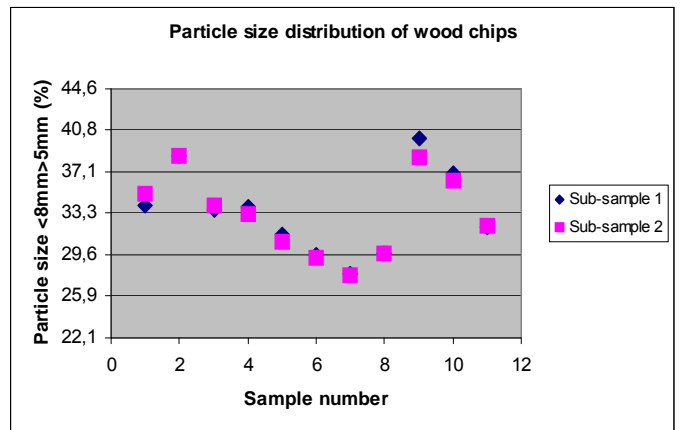
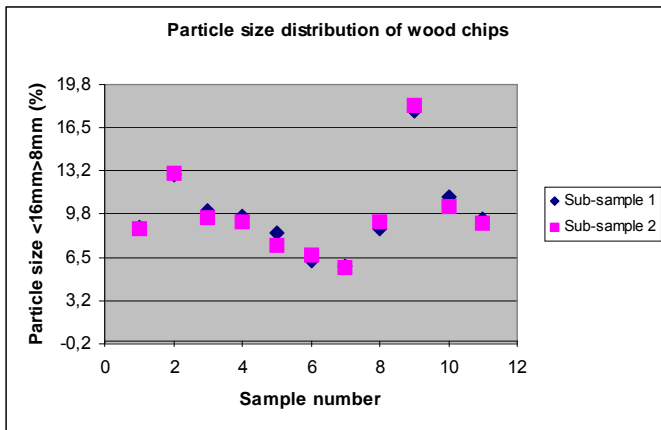
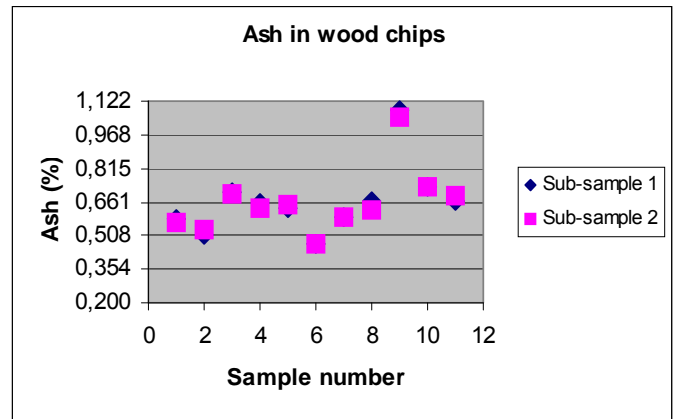
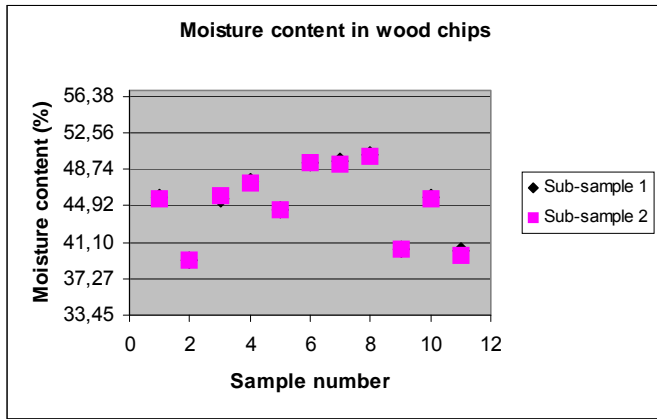
In addition, a comparison of the corresponding total standard deviations in Task I.1 and Task I.2 was performed by using a significance test of variances (F-distribution). If no significant differences between the variances are found, the results may be considered as representative for the material under 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 Wood chips



**Figure 2** Variation of moisture, ash and particle size distribution in wood chips during twelve weeks of sampling. The points represent the average of the two sub-samples.



**Figure 3** Individual sub-sample analyses results of moisture, ash and particle size distribution in wood chips during twelve weeks of sampling.

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

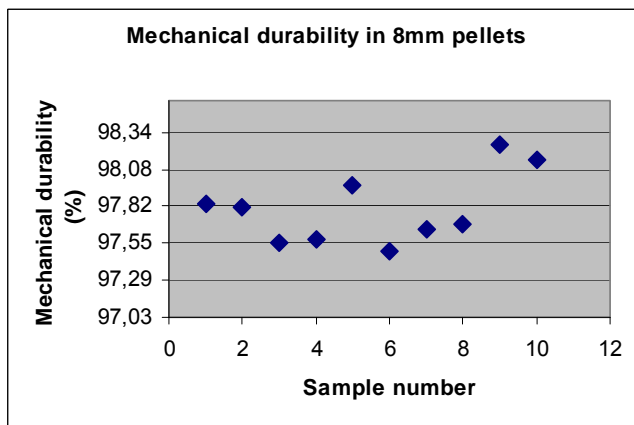
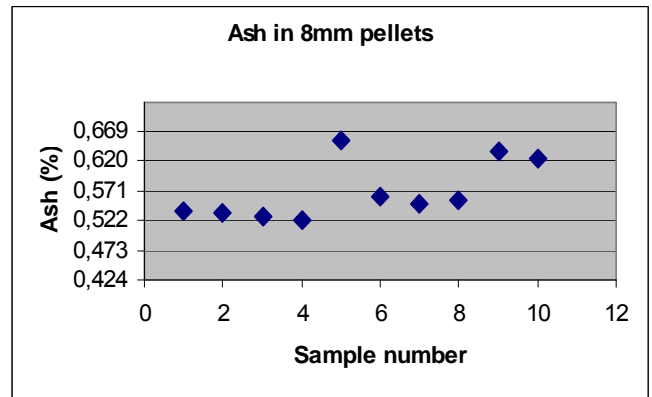
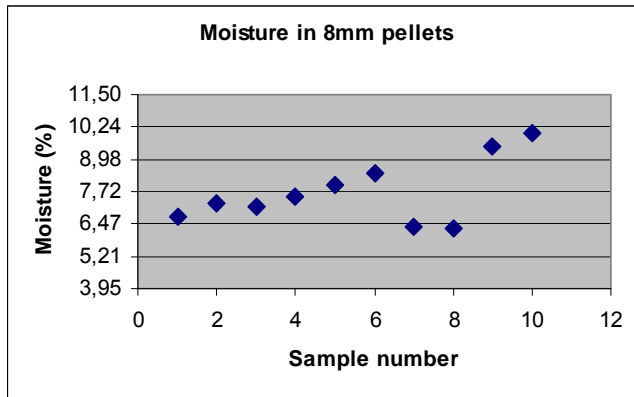
<b>Parameter</b>	<b>Overall std.dev. in Round 1 of Task I.2</b>	<b>Overall std.dev. in Round 2 of Task I.2</b>	<b>F-value overall variation</b>	<b>F<sub>crit</sub></b>	<b>Sub-sample std.dev. in Round 1 of Task I.2</b>	<b>Sub-sample std.dev. in Round 2 of Task I.2</b>
<b>Moisture</b>	4,17	3,33	1,57	2,84	0,18	0,093
<b>Ash</b>	0,13	0,15	1,33	2,54	0,022	0,012
<b>Particle size &lt;16mm&gt;8mm</b>	3,67	4,21	1,32	2,54	0,89	0,68
<b>Particle size &lt;8mm&gt;5mm</b>	3,13	3,43	1,20	2,54	0,63	0,60
<b>Particle size &lt;5mm&gt;3mm</b>	3,43	3,77	1,21	2,54	0,66	0,52
<b>Particle size &lt;3mm&gt;2mm</b>	1,20	1,32	1,21	2,54	0,21	0,15
<b>Particle size &lt;2mm</b>	2,16	2,49	1,33	2,54	0,20	0,13

In figure 3 the variations of moisture, ash and particle size distribution in wood chips over a time period of twelve weeks are shown. No outliers or trends were detected for all three materials.

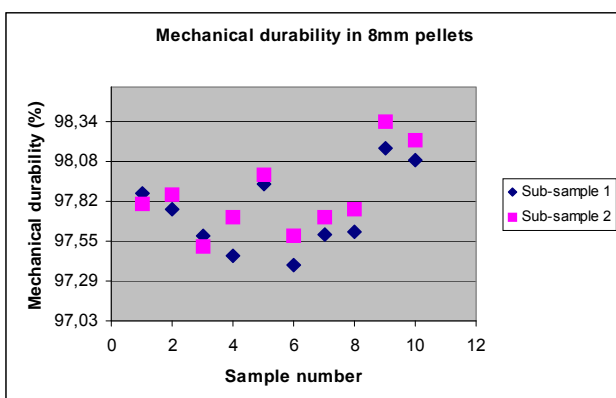
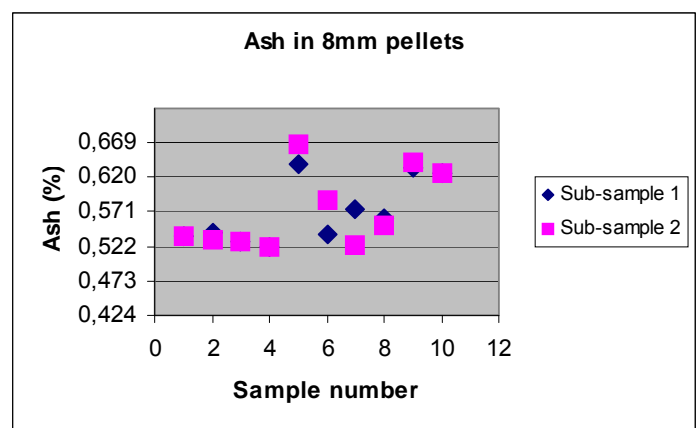
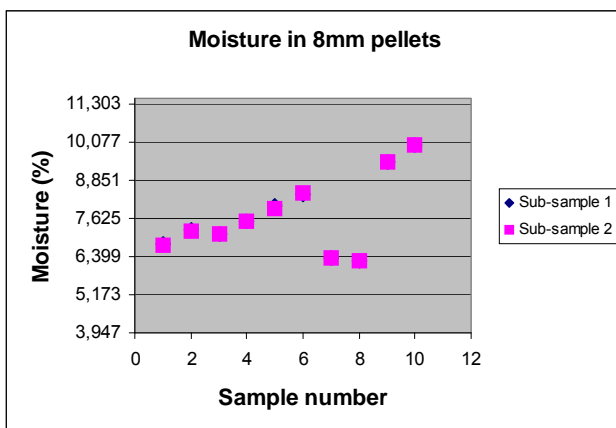
In figure 4 the individual subsample standard deviations for moisture, ash and particle size distribution in wood chips are shown. The sub-sample variation is very small and contributes almost nothing to the overall standard deviation of all parameters.

In table 1 a comparison of the overall standard deviation between round 1 and round 2 of 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. Only small deviations between the two rounds are shown except for moisture and ash content where the variation in round 1 is significant higher than in round 2. However, the sub-sample standard deviation is negligible compared to the overall standard deviation and will not effect the final result.

### 3.2 Pellets (8mm)



**Figure 4** Variation of moisture, ash and mechanical durability in 8mm pellets during ten weeks of sampling. The points represent the average of the two sub-samples.



**Figure 5** Individual sub-sample analyses results of moisture, ash and mechanical durability in 8mm pellets during ten weeks of sampling.

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

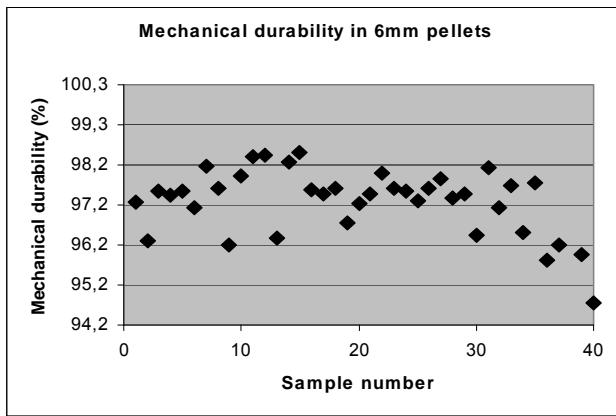
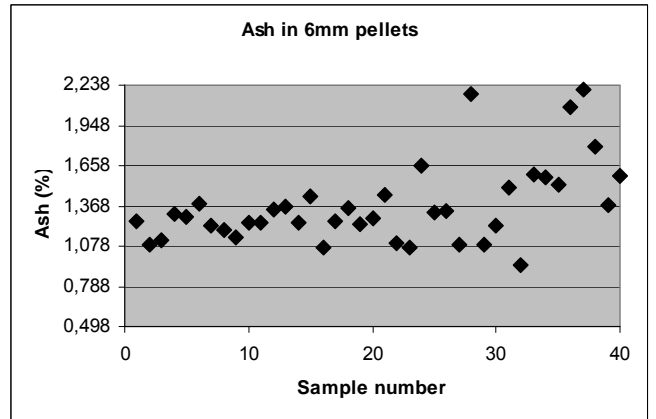
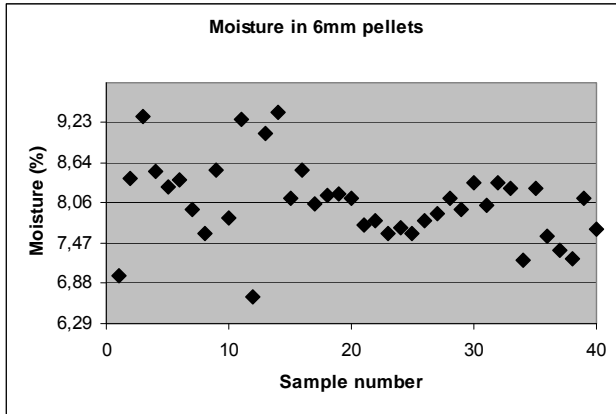
<b>Parameter</b>	<b>Overall std.dev. in Round 1 of Task I.2</b>	<b>Overall std.dev. in Round 2 of Task I.2</b>	<b>F-value overall variation</b>	<b>F<sub>crit</sub></b>	<b>Sub-sample std.dev. in Round 1 of TaskI.2</b>	<b>Sub-sample std.dev. in Round 2 of TaskI.2</b>
<b>Moisture</b>	0,27	1,26	21,8	2,42	0,063	0,019
<b>Ash</b>	0,040	0,049	1,5	2,42	0,016	0,012
<b>Mechanical durability</b>	0,13	0,26	4,0	2,42	0,081	0,071

In figure 4 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 increase in moisture content with sample number was found except for sample 7 and 8. This can be explained from the weather situation with increasing humidity except during the sampling of sample 7 and 8.

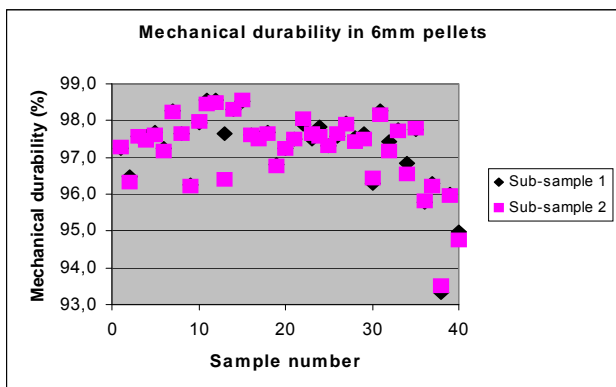
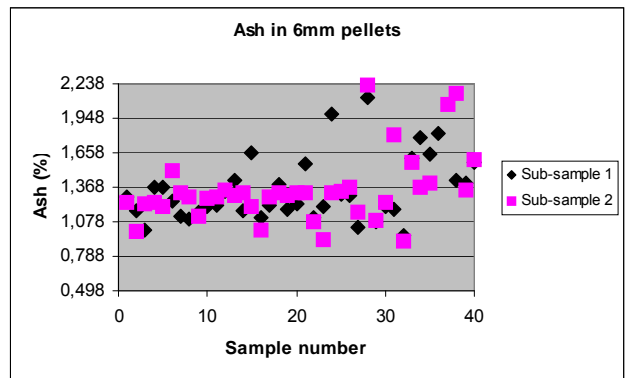
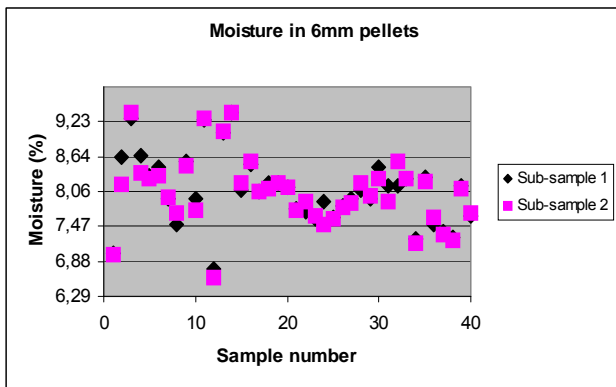
In figure 5 the individual subsample standard deviations for moisture, ash and mechanical durability in 8mm pellets are shown.

In table 2 a comparison of the overall standard deviation between round 1 and round 2 of 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 with a higher variation in the round 2 experiment. However, the results from round 2 are in accordance with the results from Task I.1 where the same type of pellets was sampled. In addition, the sub-sample standard deviation is presented for comparison with the overall variation. A significant difference between the sub-sample standard deviations for moisture content was found. The sub-sample standard deviation is, however, negligible compared to the overall variation.

### 3.3 Pellets (6mm)



**Figure 6** Variation of moisture, ash and mechanical durability in 6mm pellets during ten 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 6mm 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 6mm pellets.

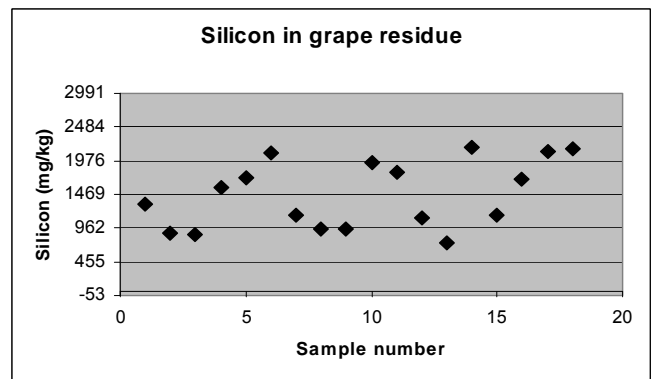
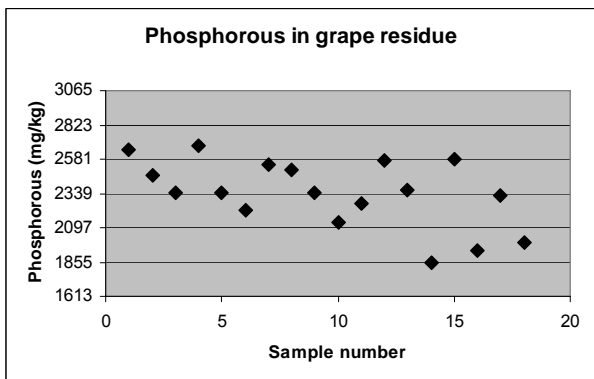
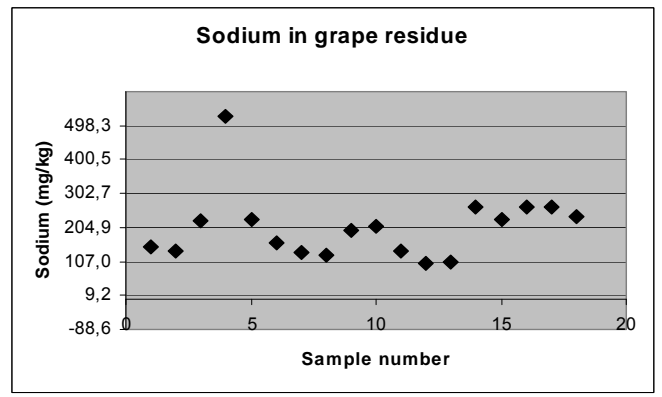
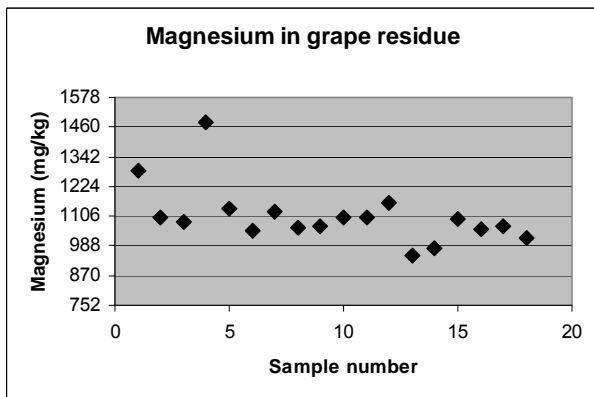
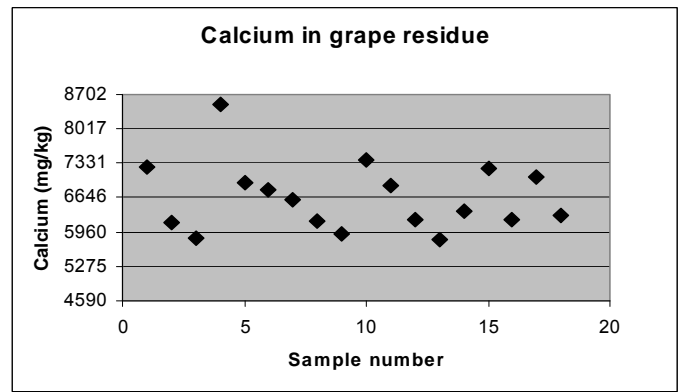
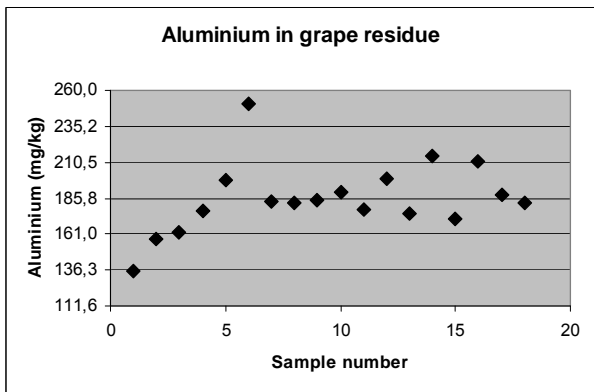
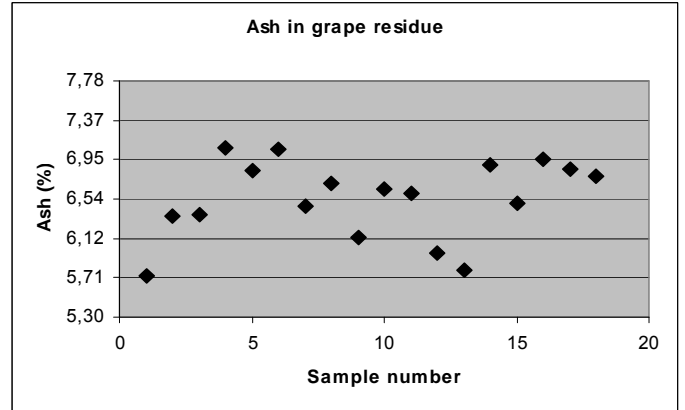
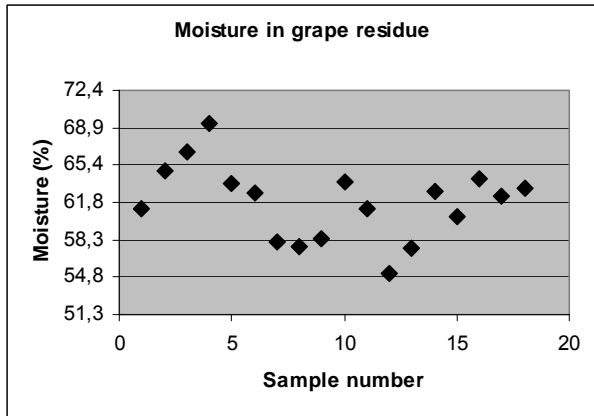
<b>Parameter</b>	<b>Overall std.dev. in Round 1 of Task I.2</b>	<b>Overall std.dev. in Round 2 of Task I.2</b>	<b>F-value overall variation</b>	<b>F<sub>crit</sub></b>	<b>Sub-sample std.dev. in Round 1 of Task I.2</b>	<b>Sub-sample std.dev. in Round 2 of Task I.2</b>
<b>Moisture</b>	0,69	0,59	1,37	1,85	0,12	0,11
<b>Ash</b>	0,24	0,29	1,46	2,03	0,11	0,18
<b>Mechanical durability</b>	0,81	1,01	1,55	2,03	0,42	0,32

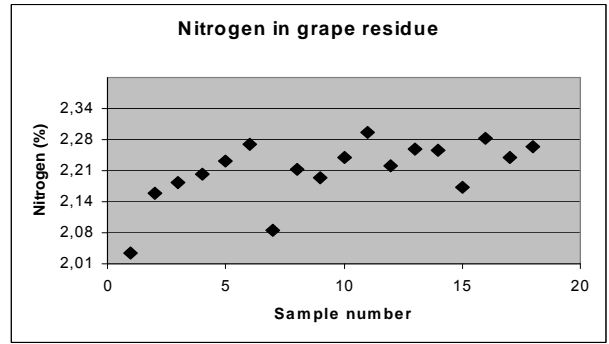
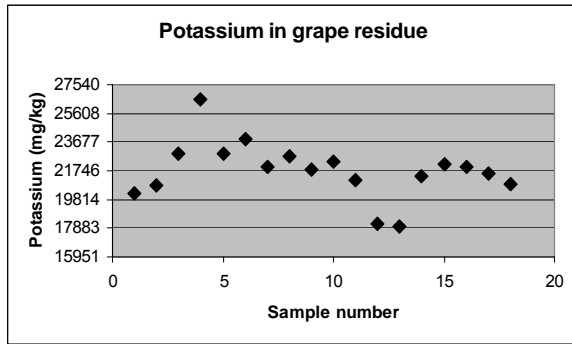
In figure 6 the variations of moisture, ash and mechanical durability in 6mm pellets are shown. No outliers or trends were detected for moisture content. For ash content an increase of ash content was found for the last ten samples, while a corresponding decrease in mechanical durability was found for the same samples. An explanation might be that a change in raw material supply occurred during the end of the investigation that affected the ash content and the mechanical durability.

In figure 7 the individual subsample standard deviations for moisture, ash and mechanical durability in 6mm pellets are shown.

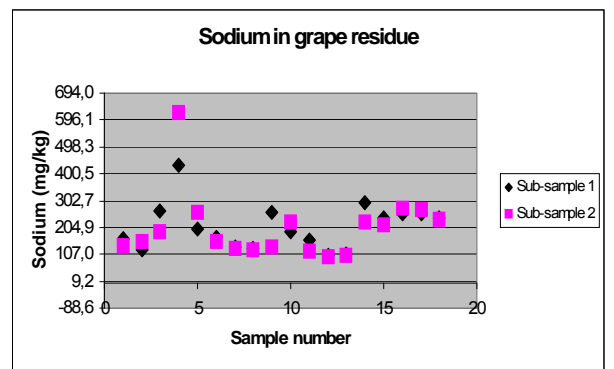
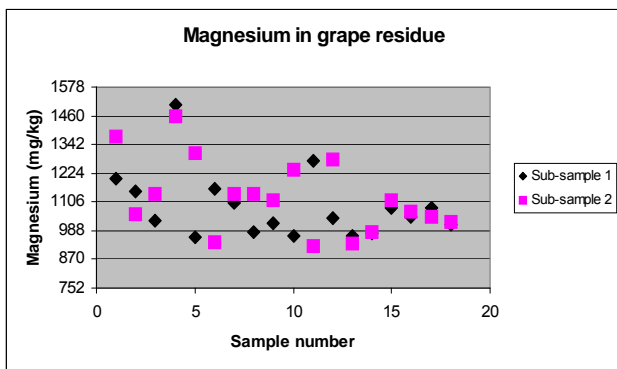
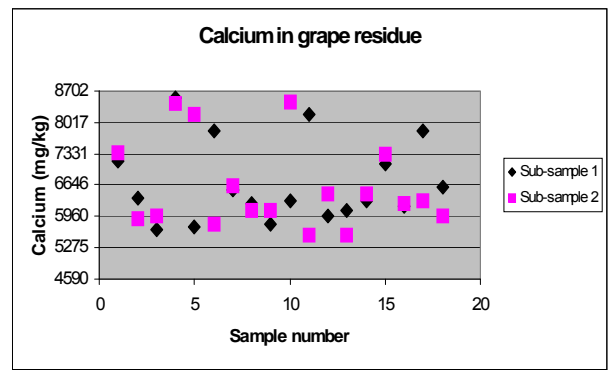
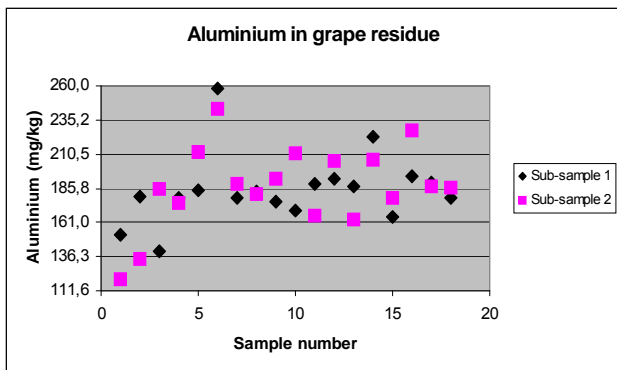
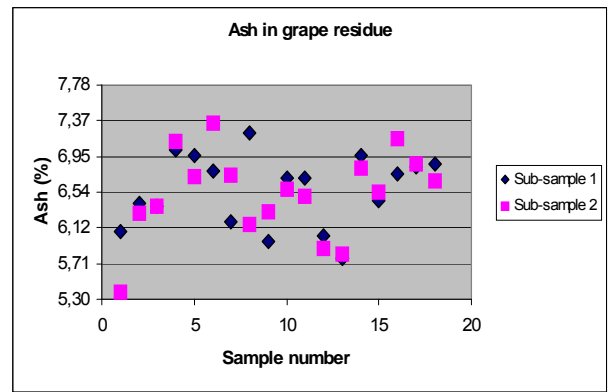
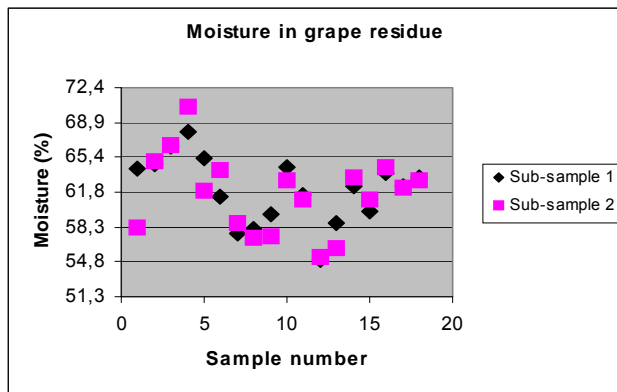
In table 3 a comparison of the overall standard deviation between round 1 and round 2 of Task I.2 are shown. The results from the F-test indicate that there is no significant difference in variation between the two investigations for all three parameters. In addition, the sub-sample standard deviation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

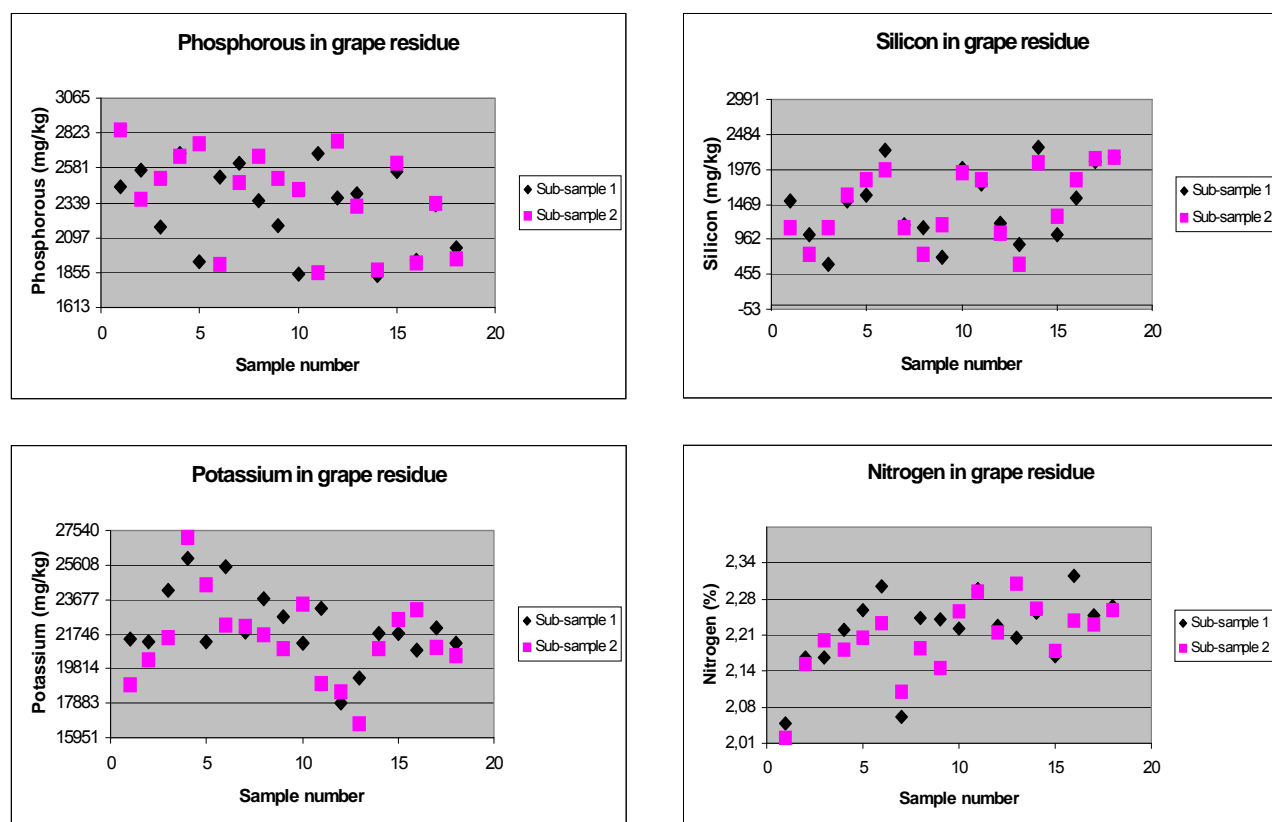
### 3.4 Grape residue





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





**Figure 9** Individual sub-sample analyses results of moisture, ash and 8 major elements in grape residue.

**Table 4** 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. in Round 1 of Task I.2	Overall std.dev. in Round 2 of Task I.2	F-value overall variation	F <sub>crit</sub>	Sub-sample std.dev. in Round 1 of Task I.2	Sub-sample std.dev. in Round 2 of Task I.2
Moisture	2,26	3,53	2,44	2,32	1,79	1,48
Ash	0,39	0,41	1,11	2,32	0,24	0,28
Aluminium	30	24,7	1,48	2,03	16,9	17,6
Calcium	669	685	1,05	2,32	1112	845
Magnesium	149	118	1,59	2,03	141	120
Sodium	110	97,8	1,27	2,03	49,8	44,9
Phosphorous	277	242	1,31	2,03	333	276
Silicon	288	507	3,10	2,32	147	193
Potassium	1837	1931	1,10	2,32	1717	1509
Nitrogen	0,072	0,066	1,19	2,03	0,029	0,034

In figure 8 the variations of moisture, ash and 8 major elements in grape residue are shown. No trend in the data was found.

In figure 9 the individual subsample standard deviations for moisture, ash and 8 major elements in olive residue are shown..

In table 4 a comparison of the overall standard deviation between round 1 and round 2 of 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 moisture and silicon. The discrepancy of moisture content might be explained by different weather situation during the sampling periods. In addition, the sub-sample standard deviation is presented for comparison with the overall variation. No significant differences between the sub-sample standard deviations of the two investigations were found.

## 4. Discussion

For wood chips, 6mm pellets and grape residue good agreement between round 1 and round 2 of Task I.2 was obtained for the overall and the sub-sample standard deviations. This would indicate that the obtained values of variation may be considered as reliable and representative for the studied material. However, it may be noted that this is probably true only for material of similar origin, i.e. pellets from the same plant, grape residue from the same region or wood chips from the same type of wood material. The results for 6mm pellets and grape residue also indicate that differences in sampling frequency do not affect the standard deviation.

Considerable differences in overall standard deviation between the two rounds for moisture content and mechanical durability in 8mm pellets were obtained. The reason is since the pellet heap in round 1 was stored for a couple of weeks before sampling (see section 2.3 and DI 10 Report on the first round of sampling and testing) 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. Compared to the sampling experiments in Task I.1 where the same type of material was studied, no differences in variations were found. For the ash content in 8mm pellets no difference was found since this parameter is not affected by storage time.