Deliverable report for

SUN

Sustainable Nanotechnologies

Grant Agreement Number 604305

Deliverable D 3.5
Report on methods for characterizing of the composition and physical properties of NOAA-containing waste

Due date of deliverable: 30/09/2015
Actual submission date: dd/mm/yyyy

Lead beneficiary for this deliverable: *Technical University of Denmark - DTU*

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CO	Confidential, only for members of the consortium (including the Commission Services)	X

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1. Description of task

The deliverable 3.5 "Report on methods for characterizing of the composition and physical properties of NOAA-containing waste" is part of Task 3.4 "Measurements of release of NOAA during treatment and disposal of end-of-life nanoproducts", where the term NOAA includes "manufactured nanomaterials, their aggregates and agglomerates".

The objectives of Task 3.4 were:
- testing available methods and procedures currently employed for characterizing waste properties;
- attempting quantification of the release of NOAA in selected waste treatment plants.

The present deliverable 3.5 focuses on methodological aspects and issues related to nanowaste characterization. D3.5 reports on the experimental work performed at DTU Environment on nanowaste.

It should be noted that the present activities within Task 3.4 are significantly delayed and D3.5 is partly incomplete (especially with respect to quantification of the release). The reason is that a key member of the working team at DTU Environment is currently on sick leave with unscheduled return date. In addition, while many of the planned experiments were completed, results are currently not accessible. In the present we thus briefly described what was achieved so far, what is planned next and what will be included in the final version of this delivery.

2. Description of work & main achievements

2.1. Introduction on characterization of waste and nanowaste

With the term characterization, we mean to cover a number of different aspects and properties of end-of-life (EOL) products containing NOAA. Thus, besides the chemical composition of nanowaste, other physical and chemical properties that may influence the unwanted release of NOAA to the environment are addressed. Within the resent, we chose to focus on direct approaches, as indirect approaches are either already partially covered in WP7 (specifically in Task 7.4 and 7.5) or may not be applicable. A brief explanation of what is meant with direct and indirect characterization methods is hereby provided.

2.1.1. Direct vs. indirect methods for chemical composition

Approaches for waste characterization can be classified in four groups (partly after Brunner & Ernst, 1986; Riber et al., 2009), as shown in Figure 1.
- Direct waste analysis (a direct method) involves physical sorting, sampling, weighing and analysis of the waste. It can be implemented at the source point (e.g. households) to estimate waste generation potentials, or at the treatment site. Drawbacks of this method are, for instance, a large residual fraction (where all unidentified materials are classified) and uncertainty regarding determination of trace elements (Brunner & Ernst, 1986), as could be the case for NOAA.
- Market product analysis is based on MFA approach and can be applied to a predefined region. The amount of waste generated and its composition is estimated based on information regarding goods entering the region and taking into account the expected lifetime of products. Drawbacks of this method could be the availability of

data and their large-scale aggregation, which may represent a barrier for local studies (Brunner and Ernst, 1986). This could clearly be an issue with respect to EOL nanoproducts, as also mentioned in Milestone 7.2, where this approach is adopted to identify the types of nanoproducts entering the waste system.

- In proximity studies, proximity data are combined with social, economic and commercial data to extrapolate the waste composition of a region with respect to a region with similar characteristics where data on waste composition are available. Because it is largely based on estimations and assumptions, a drawback of this approach is that results cannot be verified and uncertainty cannot be estimated. As for the previous method, the general lack of information on nanoproducts entering the market may severely hinder using this approach.

- Waste product analysis is based on sampling the outputs/products/by-products of a waste treatment. For example, data on air emissions, bottom ash, fly ash and waste water composition could be used for back-estimating some characteristics of waste delivered at an incineration plant (Riber et al., 2007). The advantages of such method are more homogeneous flows of material (which is a good condition for implementing representative sampling techniques), and the possibility of better intercepting trace contaminants if the primary sampling is performed on large amounts of materials. The drawbacks of this approach are that only conservative substances can be estimated (Riber et al., 2009), meaning that complete physicochemical characterization of waste is not possible when using only this method. Sampling of waste products was for instance performed by Walser et al. (2012) when investigating the distribution of CeO within a waste incineration process. However, generally, it is not clear whether such method can be applied to back calculate the initial content of NOAA in the waste, as much is still to be clarified about potential transformations of NOAAs during waste treatment processes (Lowry et al., 2012; Mitrano et al., 2015).
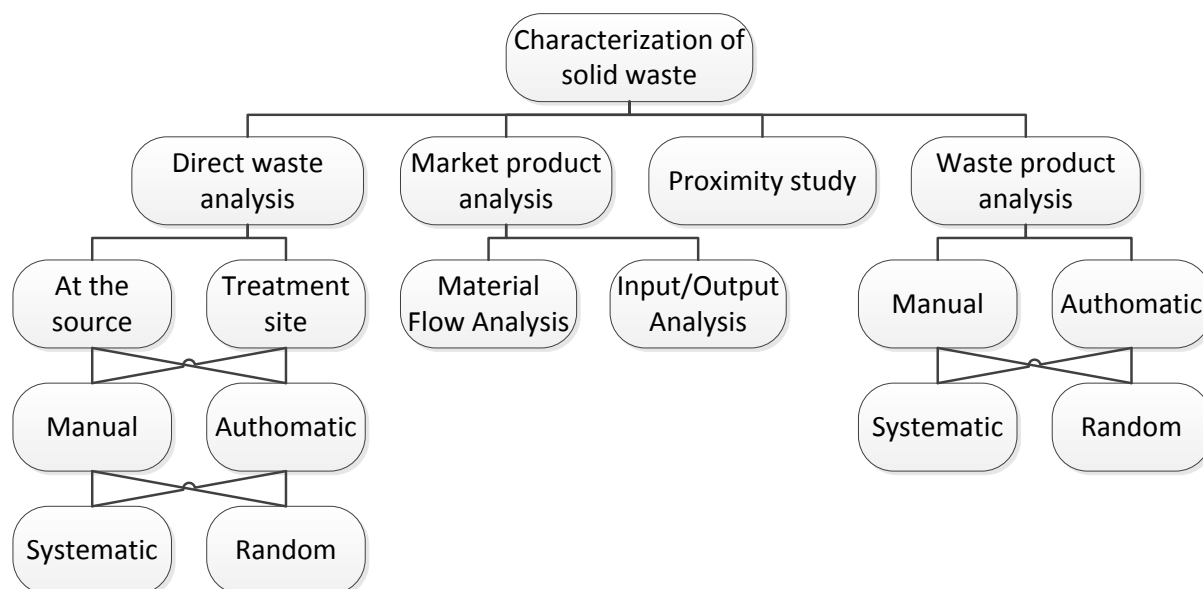
Figure 1 – Approaches for characterization of solid waste materials.

2.2. Chemical charaterization

2.2.1. Analytical methods

With respect to analytical methods, we mostly focused on developing methods for particle size characterization on SP-ICP-MS. Initial work involved development of capabilities the available Agilent 7700x, where a method for TiO_2 was established. Measurements were however very time consuming and potentially affected by uncertainty, because of

different aspects such as dwell time and manual integration of the results. After purchase of a new instrument, analytical development mostly occurred on the Perkin Elmer NexION 350D, which now allows for almost routine measurements of Ti and Cu particles, as well as potentially Ag and Au.

We are currently attempting to develop methods for the analytical quantification of

- Irgazin in GC-MS instrument (after depolymerization of PET)
- CNT on ICP-MS via Y-Co determination (after depolymerization of PET), based on Reed et al. (2013) procedure.

In addition, we have been developing expertize and competence on TEM and SEM.

2.2.2. Sample preparation

Prior to chemical analysis, waste sample are typically prepared to reduce both the mass and particle size of the initial sample. This is often a challenging operation, as to ensure that few grams of a laboratory sample are representative of large amounts (in some cases several hundred tons) of waste. This is especially the case for trace compounds.

To assess the suitability of standard sample preparation procedures when it comes to nanomaterials, we studied the recovery of NOAA during sample preparation in two different ways:

- We looked at the recovery of the different metal compounds, which are found in trace concentration; these compounds can be in different forms, not only in nanosize. This activity is completed, and results are presented in the following section.
- We attempted assessing the recovery of NOAA during sample preparation. As reference material with known NOAA concentration is not available, the assessment is thus of comparative nature. This activity is not completed, while the experimental plan is described in the following section.

Recovery of trace elements during sample preparation

We assessed the recovery rates of individual trace elements in machineries and tools that we normally utilize for sample preparation of solid materials, prior to analytical work in the lab. We focused on materials undergoing particle size reduction and acid digestion, prior to elemental characterization in ICP-MS. The recovery rates were estimated using manually crushed samples as a baseline for comparison, thereby assuming that the manual crashing does not affect the content of individual elements. We focus on nine elements (Ag, Au, Ca, Cu, Fe, P, Si, Ti, Zn), four of which (Cu, Fe, Si, Ti) could be linked to NOAA relevant to the SUN project, whereas the remaining five (Ag, Au, Ca, P, Zn) were included because they could be linked to NOAA which are produced in significant amounts and contained in many applications.

As we normally employ different machineries depending on the type of material being processed, we selected two different materials and tested them as follows:

- Hard material, gravel, typically pulverized using *crushing* devices. The tested solutions included:
  - o Reference: hammer (with sample placed inside a plastic bag), followed by agate disc mill.
  - o Jaw crusher (RETSCH, Figure 2) (used when materials to be reduced are still in large chunks and cannot enter e.g. a disc mill), followed by agate disc mill (Figure 3) for fine pulverization.
  - o Tungsten-carbide disc mill (Figure 3), employed for fine pulverization. This option is tested in order to compare the performance of tungsten-carbide in comparison to agate.
- Soft material, paper, typically size reduced using *cutting* devices. The tested solutions included:
  - o Reference: hand cutting by means of scissors. Because of the small contact

surface between paper and scissors, it is expected that this solution should not significantly affect the content of analyzed elements.

- o Cutting mill (Retsch 2000SM, Figure 4), fast rotating, used for fine reduction (1-10 mm, depending on the mesh).
- o Shear shredder (Figure 5, often used for initial reduction of bulky items) followed by cutting mill (Figure 4). This option is tested in order to isolate the effect of the shear shredder.

Figure 2 – Retsch (Haan, Germany) jaw crusher.

Figure 3 - Siebtechnik IS100A (Mülheim an der Ruhr, Germany) vibratory disc mill (left). Tungsten-carbide and agate discs (right).

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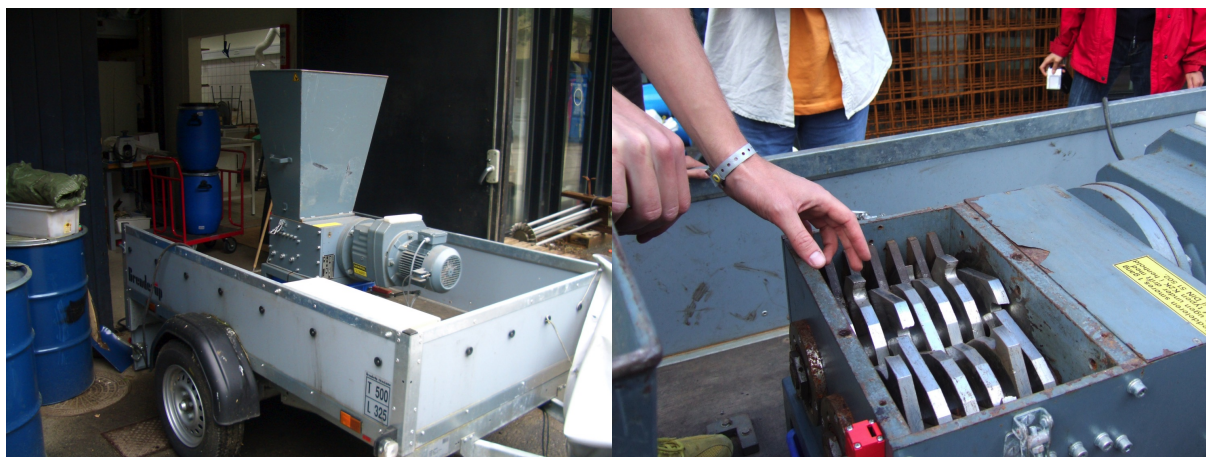*Figure 4 – Retsch 2000SM (Haan, Germany) cutting mill.*

Figure 5 - ARP SC 2000 (Brovst, Denmark) shear shredder.

The resulting material with reduced particle size was mass reduced by-means of riffle-splitter and three replicates of 0.2 g were digested by microwave-assisted digestion (Multiware Anton Paar 3000) with HNO_3, HCl, HF and H_3BO_3, following the standard EN 13656:2003, and then analysed by ICP-MS (7700x, Agilent Technologies). The content of Cu, Fe, Si, Ti, Ag, Au, P, Zn on ICP-MS was determined on ICP-MS (Agilent 7700x series), while content of Ca was determined on ICP-OES [Varian MXP], whose accuracy was controlled with standard solutions. Reference materials were used to validate the result of the digestion procedure.

The recovery efficiencies (Δ_i, %) for the different treatments were calculated as:

$$\Delta_i[\%] = \frac{C_{i,treatment} - C_{i,reference}}{C_{i,reference}} \cdot 100$$

where $C_{i,treatment}$ is the concentration of compound -i in samples produced from the tested

device, $C_{i,reference}$ is the concentration of compound -*i* in samples produced with the reference procedure.

$Δ_i$ was calculated using mean values from the three replicates. To determine whether the concentrations in samples produced with the tested device were significantly different from the concentrations in samples generated from the reference method, results were compared with ANOVA tests.

Results are shown in Table 1, while an overview of the statistical comparison is shown in Figure 6, Figure 7, Figure 8, Figure 9, Figure 10, Figure 11, Figure 12, Figure 13, and Figure 14. The results clearly show that, for some specific machinery, the recovery rates for individual compounds are rather unsatisfactory. In most cases, the concentrations measured were below the reference crushing procedure, indicating a loss of analytes during the comminution procedure. Differences were particularly significant for hard materials, and it is speculated that the loss may be connected with the generation and dispersion of fine dust during the crushing operations. In some few cases, the measured concentrations were above the reference crushing method, suggesting that, despite thorough cleaning of the equipment between tests, cross contamination may have occurred. While the origin of this is much unknown and unexplainable, it may suggest that different cleaning procedures may have to be implemented in the future.

While this test was not focusing on NOAA and does hence not allow for concluding on suitability of current available sample preparation techniques with respect to NOAA, it still indicates that analysis of trace compounds may be rather difficult, especially in case of hard materials where significant production of dust occurs.

Table 1 – Recovery of elements in equipment for size reduction. Sign.= statistically significant difference (based on Tukey-Kramer HSD test). Values underlined/bold present Δ>20% and a difference which is statistically significant.

|	Gravel (hard)				Paper (soft)			
	WC disc mill		Jaw crusher		Cutting mill		Shredder	
Element	Δ [%]	Sign.	Δ [%]	Sign.	Δ [%]	Sign.	Δ [%]	Sign.
SUN materials								
Cu	**150%**	yes	31%	no	-95%	no	-96%	no
Fe	**40%**	Yes	**40%**	Yes	-2%	no	**41%**	Yes
Si	3%	no	-7%	Yes	-3%	no	6%	no
Ti	**33%**	Yes	**36%**	Yes	-16%	no	-8%	no
Other of interest								
Ag	17%	no	42%	no	-7%	no	30%	no
Au	-5%	no	4%	no	-2%	no	1%	no
Ca	-18%	Yes	**36%**	Yes	-6%	Yes	-7%	Yes
P	**37%**	Yes	**185%**	Yes	-3%*	No	0%*	No
Zn	**44%**	Yes	**26%**	Yes	-22%	No	5%	no
* Some of the measured values were below detection limit.								
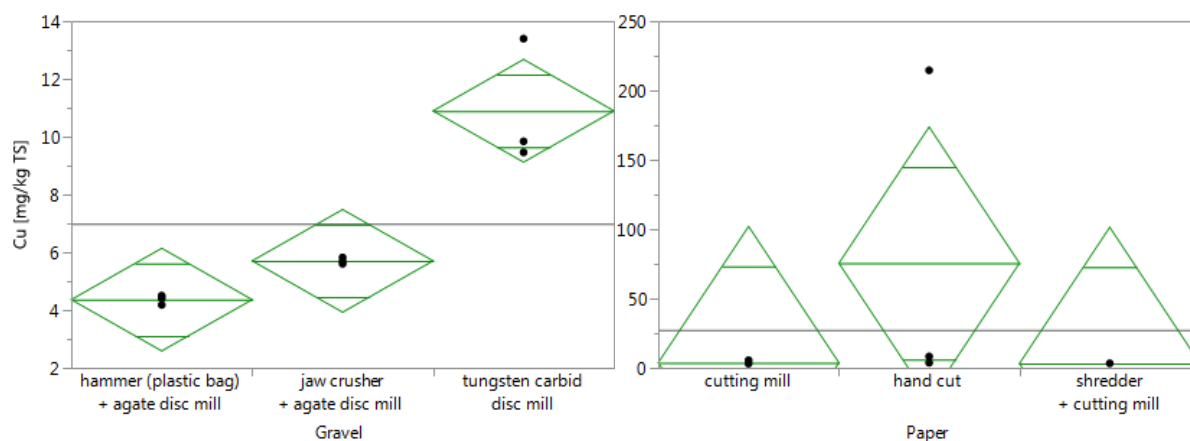
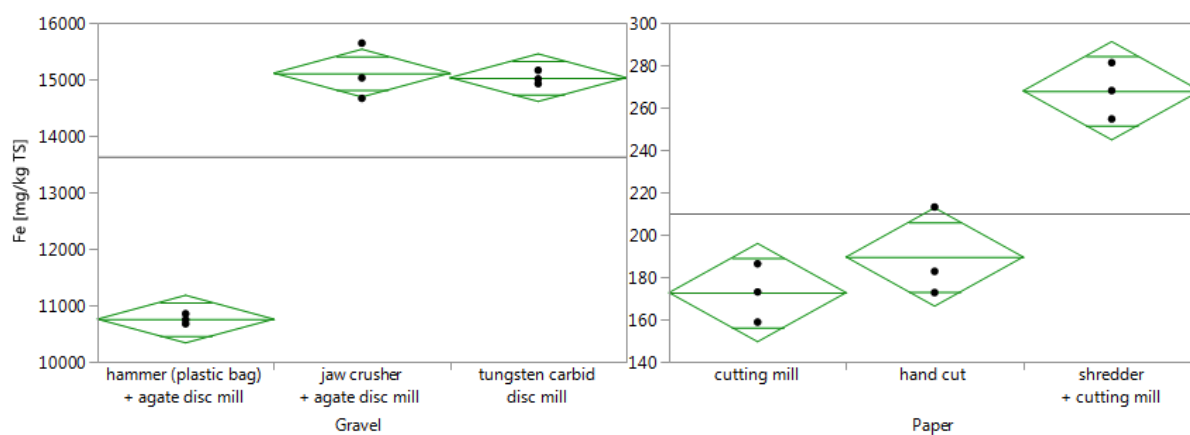Figure 6 – Content of cupper in analyzed samples.

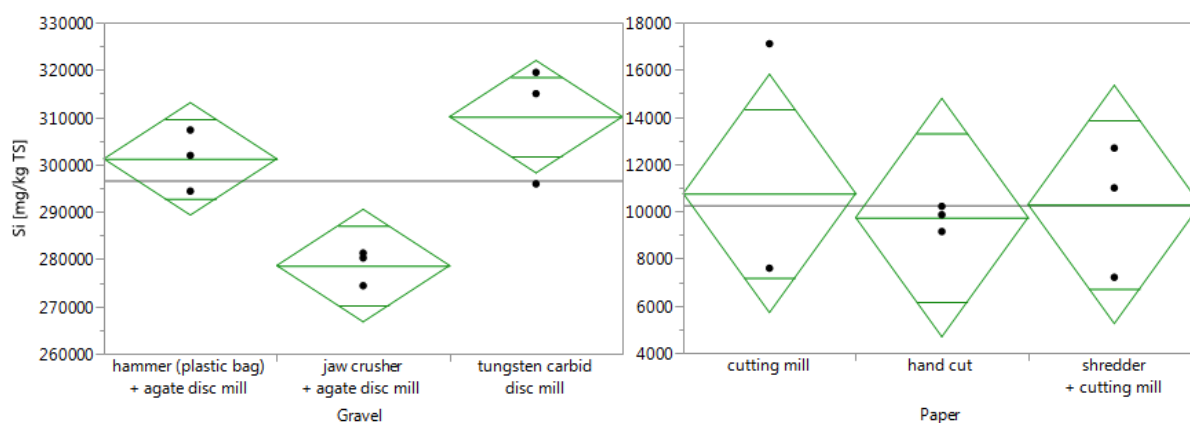
Figure 7 – Content of iron in analyzed samples.

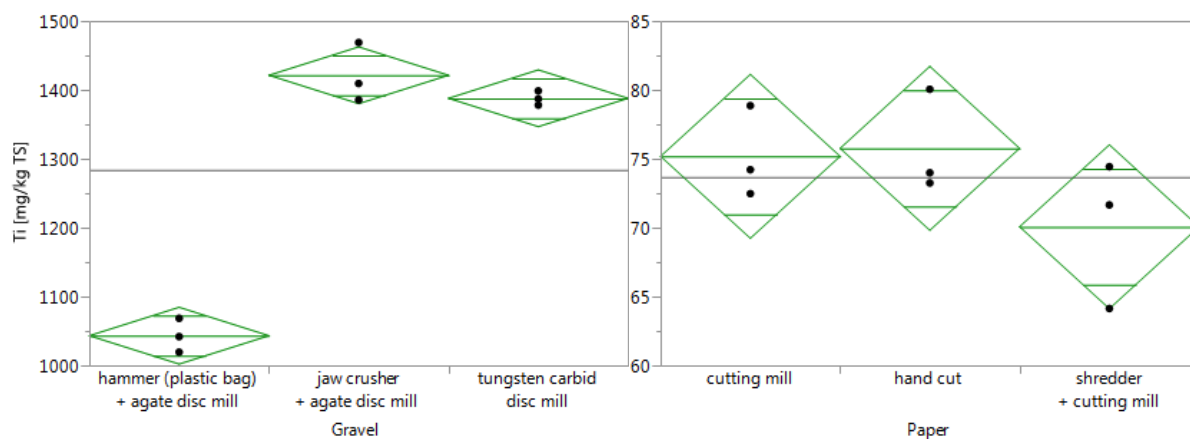Figure 8 – Content of silicium in analyzed samples.

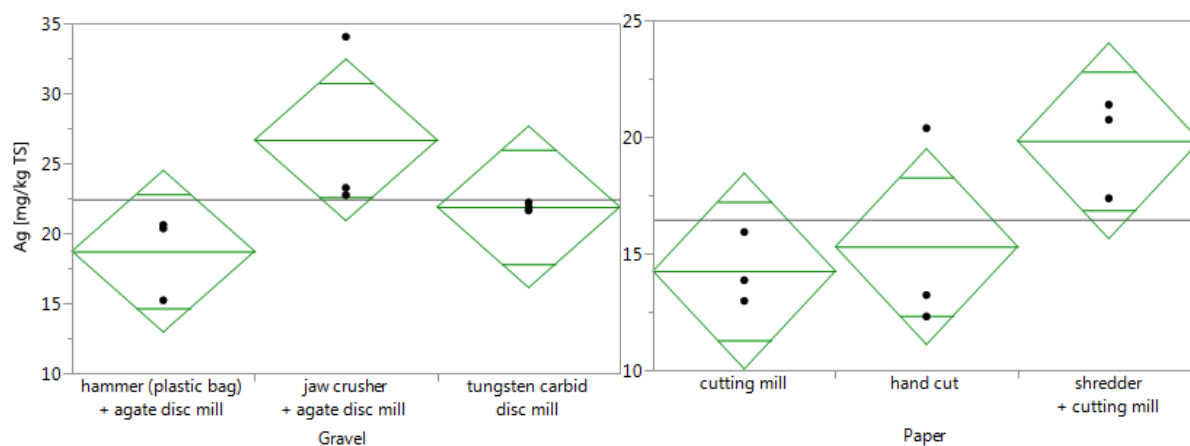*Figure 9 – Content of titanium in analyzed samples.*

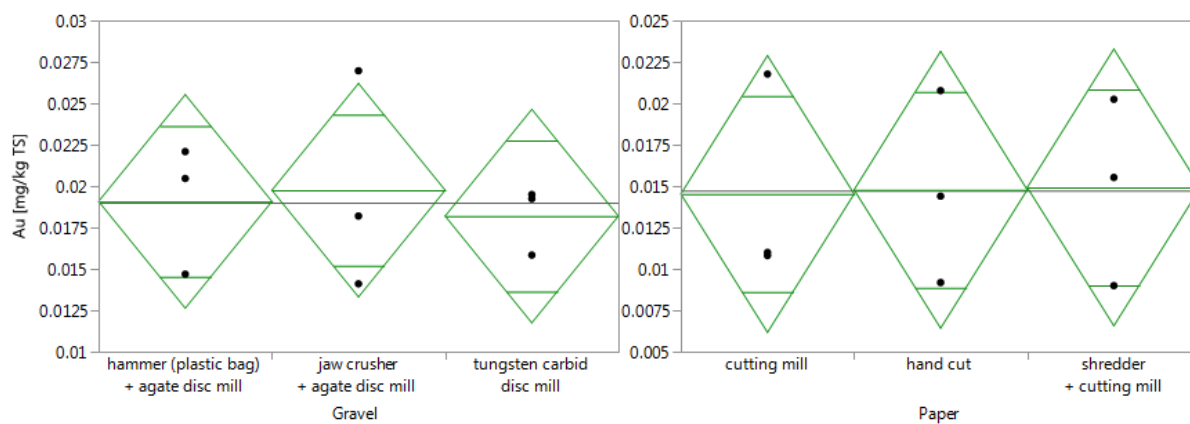*Figure 10 – Content of silver in analyzed samples.*

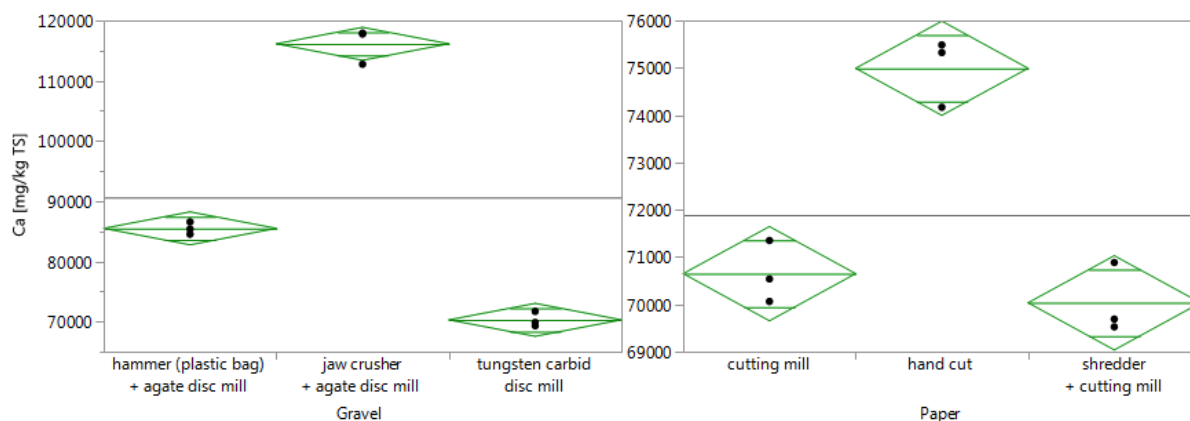*Figure 11 – Content of gold in analyzed samples.*
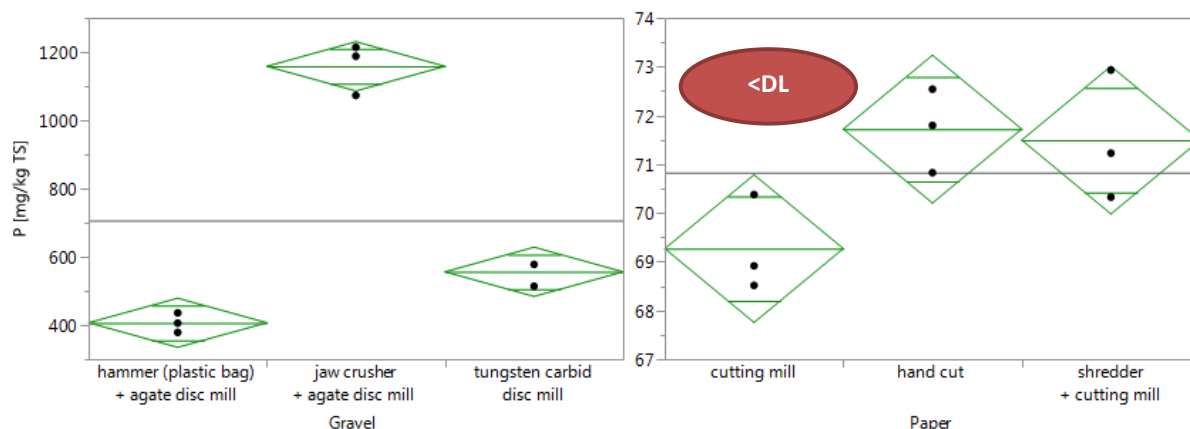
Figure 12 – Content of calcium in analyzed samples.

Figure 13 – Content of phosphorous in analyzed samples.
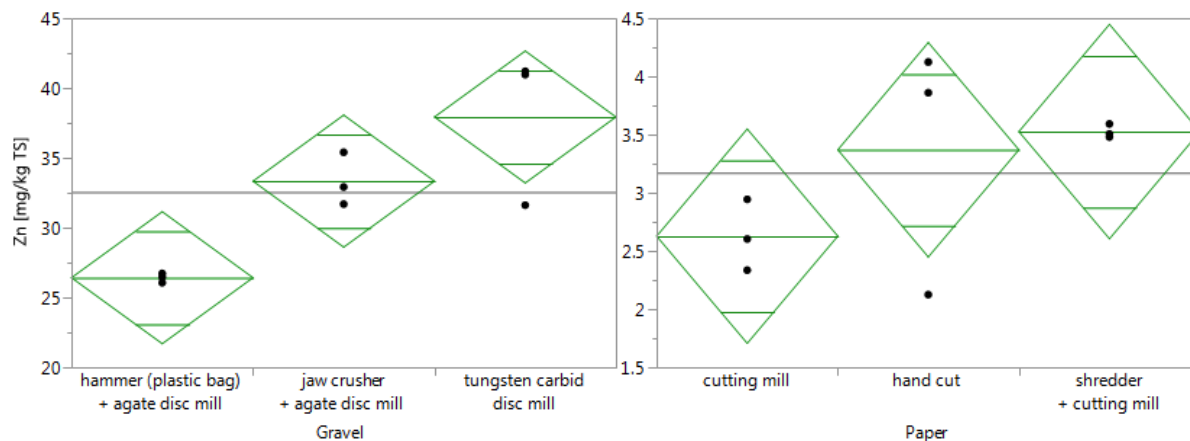
Figure 14 – Content of zinc in analyzed samples.

Recovery of NOAA during sample preparation

This test is not yet completed, but it is planned as follows. The test will focus on four products, which were selected among the SUN materials in order to have both hard and soft materials and thereby test both crushing and cutting devices. The NOAA types were selected according to the availability (or upcoming availability) of analytical methods for NOAA (see section 2.2.1). The materials to be tested include:

- TiO_2-coated tiles (hard)
- TiO_2-containg concrete (hard)
- CNT-containing car bumpers (soft)
- Irgazin-containing car bumpers (soft)

The following two materials could also be potentially tested, they are however available in too little amount. The tests will be carried out if additional amounts of materials will be retrieved from suppliers.
- Fe_2O_3–containing PET plastic (soft)
- CuO-coated wood blocks (soft)

This experiment will be performed similarly to the one described above, this time focusing on the recovery of NOAA in the samples. The analytical procedure will include spICP-MS to assess the recovery rate for TiO_2 and (potentially) Cu, while also evaluating whether the particle size distribution is affected by the sample preparation procedure.
Experimental results will be statistically treated similarly to the previous experiment, and will be presented in a similar fashion to the ones above.

2.3. Release during recycling processes

The potential release of NOAA during pre-treatment processes is currently being investigated in collaboration with the National Research Centre for the Working Environment (NSCWE) and within Task 5.2. Samples of different SUN products are being processed in a shear shredder (see Figure 5) and emission of NOAA is measured. This is considered a relevant scenario, as a broad range of materials are size reduced prior to being fed to mechanical and thermal recycling processes. While the focus of Task 5.2 is on the working environment and the potential exposure for workers, the experiment will generate some relevant information also from an end-of-life (EOL) perspective. In particular, the release of NOAA quantified by NSCWE will be compared and assessed with the recovery rates determined in our experiments (see section 2.2.2) for different grinding processes. The materials, which are being tested are:

- TiO_2-coated tiles
- TiO_2-containg concrete
- CNT-containing car bumpers
- Irgazin-containing car bumpers

Samples of materials from the shredding tests are being collected and will undergo leaching tests to assess the release of NOAA (see next section 2.4).

2.4. Leaching properties

EOL nanoproduct may be disposed in landfills or recycled/reuse for other purposes than the original one. In several situations, the release of NOAA may potentially occur when these materials are in contact with water. The potential release can be evaluated by means of leaching tests, which are experimental procedures in which a liquid (i.e. leachant) is put into contact with the material being tested in different modalities. The resulting leachate (also called eluate) is collected and analysed. Different types of leaching tests exist, the simplest being batch tests, where distilled water is used as leachant and where the material is stirred for a pre-defined time (e.g. 24 hours) at a fixed ratio between the leachant and the material (the so-called liquid-to-solid ratio, or L/S). This a widespread type of leaching test, used in many countries to define the acceptance of waste materials into landfill. By varying the experimental conditions, batch tests can be also used to assess the influence of pH or L/S ratios on the release of different substance. Other types of leaching tests also exist, where the release can be assessed as a function of L/S (i.e. in percolation tests also known as column leaching tests).
We have tested the suitability of compliance tests for assessing the release of NOAA from products. The initial tests made use of TiO_2–coated ceramic tiles while focusing on

establishing the experimental setup and testing the usability of existing protocols. Release of nano titanium from TiO_2–coated ceramic tiles was thus assessed using compliance one-stage batch test (DS/EN: 12457-1), 24 hours, L/S=2. Uncoated tiles were used as reference material for comparison. As the presence of cations and organic matter in the liquid phase may affect aggregation of NOAA, release tests were conducted at various concentrations of calcium chloride and humic acid in leachant media. An overview of the performed tests is provided in Table 2. The leachate samples were analysed immediately after the end of the test using a SP-ICP-MS.

Table 2 – Overview of tests performed on TiO_2-coated tiles to assess the release of nano titanium.

Media		Ceramic tiles	
		TiO_2-coated	Reference (uncoated)
Distilled water		x	x
CaCl$_2$	100 mg/l	x	x
	200 mg/l	x	x
	500 mg/l	x	x
Humic acid	25 mg/l	x	x
	50 mg/l	x	x
	100 mg/l	x	x

The tests on TiO_2-coated tiles showed that:
- No significant differences in the amount of TiO_2 released were seen when comparing coated and uncoated tiles. Release tests on uncoated glass tiles are currently being performed in order to understand the origin of NOAA in the uncoated tiles
- The presence of $CaCl_2$ and organic matter may not significantly affect particles aggregation.

With respect to the testing procedure, it was seen that the filtration step normally used in compliance tests using 0.45µm filter may be problematic, as particles seem to be removed, possibly because they tend to associate with large suspended particles. TEM analysis is planned to clarify on this aspect and conclude on whether nano titanium is associated with larger suspended solids.

Within the next months, the developed protocols will be used to assess release of NOAA from the following SUN materials:

- TiO_2-coated tiles
- TiO_2-coated tiles (from NSCWE tests)
- TiO_2-containg concrete (from NSCWE tests)
- CNT-containing car bumpers (from NSCWE tests)
- Irgazin-containing car bumpers (from NSCWE tests)
- Weathered/aged CuO-coated wood blocks (obtained from CEREGE as a result of activities in Task 3.5).

3. Deviations from the Workplan

The activities associated with D3.5 are significantly delayed, because a key member of the working team is currently on sick leave with unscheduled return date. So far, most of the experimental procedures have been established, but systematic testing of different materials has not been completed. The present D3.5 is also incomplete in the sense that results of the experiments so far conducted are not accessible.
The planned experiments include:

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- Assessing the recovery/losses of NOAA during sample preparation prior to lab analysis, for the following tools and materials:
  o Tools: jaw crusher, disc mill, cutting mill, shear shredder
  o Materials: TiO_2-coated tiles, TiO_2-containg concrete, CNT-containing car bumpers, Irgazin-containing car bumpers
- Release batch tests on the following materials: TiO_2-coated tiles, TiO_2-containg concrete, CNT-containing car bumpers, Irgazin-containing car bumpers, Weathered/aged CuO-coated wood blocks

The above-mentioned activities should provide the following findings:

- An assessment of potential artefacts and losses/modification of NOAA, occurring during sample preparation prior to laboratory analysis to determine content and size of NOAA.
- A protocol for batch tests aimed at quantifying the release of NOAA to aqueous media (landfill-like conditions)
- Quantification of potential release of NOAA to aqueous media (landfill-like conditions) for a selected range of SUN materials

4. Performance of the partners

D3.5 was not much depending on other partners of the project. According to agreements, materials were timely delivered. This included weathered/aged CuO-coated wood blocks from CEREGE, TiO_2-coated tiles from Colorobbia, and car bumpers (with CNT and Irgazin) from Magneti Marelli.

5. Conclusions

D3.5 so far reports on development of procedure and protocols for characterizing a number of properties of EOL nanoproducts. Within Task 3.4 and D3.5, we:

- Developed analytical capabilities for measuring the content of NOAA in different EOL products as well as in by-products from waste processes (e.g. leachate).
- Initiated tests to assess the recovery of NOAA during samples preparation prior to lab analysis.
- Established procedures for leaching tests aiming at assessing the release of NOAA when nanoproducts come in contact with water in EOL relevant scenarios.
- Collaborated with partners in WP5 in setting up measurements campaigns targeting the release of NOAA during pre-treatment of waste prior to recycling processes.

In the coming months, the developed methods and procedures will be employed to systematically test several of the SUN materials. The results obtained so far indicate that:

- It may be difficult to obtain correct info on the content of NOAA, as sampling artifacts may easily occur.
- Leaching tests aiming at assessing release of NOAA do need some adjustments compared with the standard protocols, whereas additional tests may be needed on the side (e.g. TEM).

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