

Study on the Product Lifecycles, Waste Recycling and the Circular Economy for Nanomaterials

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Study on the Product Lifecycles, Waste Recycling and the Circular Economy for Nanomaterials

November 2021

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Glossary of Terms

Best Available Techniques (BATs) "means the most effective and advanced stage in the development of activities and their methods of operation which indicates the practical suitability of particular techniques for providing the basis for emission limit values and other permit conditions designed to prevent and, where it is not practicable, to reduce emissions and the impact on the environment as a whole:

- 'techniques' includes both the technology used and the way in which the installation is designed, built, maintained, operated and decommissioned;
- `available techniques' means those developed on a scale which allows implementation in the relevant industrial sector, under economically and technically viable conditions, taking into consideration the costs and advantages, whether or not the techniques are used or produced inside the Member State in question, as long as they are reasonably accessible to the operator;
- 'best' means most effective in achieving a high general level of protection of the environment as a whole" (European Parliament, 2010).

Biological degradation (biodegradation) is "the microbially mediated process of chemical breakdown of a substance to smaller products caused by micro-organisms or their enzymes" (European Environment Agency, n.d.).

Circular economy "means rejecting the linear take-make-waste economy and adopting a regenerative model: using processes that restore, renew or revitalise their own sources of energy and materials and wasting as little as possible" (European Commission, n.d.).

Closed-loop recycling product system is a system in which "material from a product is recycled in the same product system" (International Organization for Standardization, 2006).

Emissions "means the direct or indirect release of substances, vibrations, heat or noise from individual or diffuse sources in the installation into the air, water or land" (European Parliament, 2010).

Incidental nanomaterial is "nanomaterial generated as an unintentional by-product of a process" (European Committee for Standardization, 2017).

Incineration means "the thermal treatment of wastes with or without recovery of the combustion heat generated. This includes the incineration by oxidation of waste as well as other thermal treatment processes such as pyrolysis, gasification or plasma processes in so far as the substances resulting from the treatment are subsequently incinerated" (European Parliament, 2000).

Incineration plant "means any stationary or mobile technical unit and equipment dedicated to incineration. This definition covers the site and the entire incineration plant including all incineration lines, waste reception, storage, on-site pre-treatment facilities, waste-fuel and air supply systems, boiler, facilities for the treatment of exhaust gases, on-site facilities for treatment or storage of residues and wastewater, stack, devices and systems for controlling incineration operations, recording and monitoring incineration conditions" (European Parliament, 2000).

Landfill "means a waste disposal site for the deposit of the waste onto or into land (i.e., underground), including:

- Internal waste disposal sites (i.e., landfill where a producer of waste is carrying out its own waste disposal at the place of production), and
- A permanent site (i.e., more than one year) which is used for the temporary storage of waste,

but excluding:

- Facilities where waste is unloaded in order to permit its preparation for further transport for recovery, treatment or disposal elsewhere, and
- Storage of waste prior to recovery or treatment for a period less than three years as a general rule, or
- Storage of waste prior to disposal for a period less than one year" (Council Directive, 1999).

Leachate "means any liquid percolating through the deposited waste and emitted from or contained within a landfill" (Council Directive, 1999).

Manufactured nanomaterial is "intentionally produced to have selected properties or composition" (European Committee for Standardization, 2017).

Municipal solid waste "means:

- a) mixed waste and separately collected waste from households, including paper and cardboard, glass, metals, plastics, bio-waste, wood, textiles, packaging, waste electrical and electronic equipment, waste batteries and accumulators, and bulky waste, including mattresses and furniture;
- b) mixed waste and separately collected waste from other sources, where such waste is similar in nature and composition to waste from households" (European Parliament, 2008).

Nanoparticle is a "nano-object with all three external dimensions in the nanoscale" (European Committee for Standardization, 2015).

Nanowaste is "wastes containing high concentrations of nanomaterials and generated by nanomaterial production" (OECD, 2016).

OECD Guidelines for the Testing of Chemicals "are a unique tool for assessing the potential effects of chemicals on human health and the environment. They are split into five sections: Section 1: Physical-Chemical properties; Section 2: Effects on Biotic Systems; Section 3: Environmental fate and behaviour; Section 4: Health Effects and Section 5: Other Test Guidelines. Accepted internationally as standard methods for safety testing, the Guidelines are used by professionals in industry, academia and government involved in the testing and assessment of chemicals (industrial chemicals, pesticides, personal care products, etc.). These Guidelines are continuously expanded and updated to ensure they reflect the state-of-the-art science and techniques to meet member countries regulatory needs" (OECD, n.d.).

Open-loop recycling product system is a system in which "material from one product system is recycled in a different product system" (International Organization for Standardization, 2006).

Occupational exposure limit "means, unless otherwise specified, the limit of the timeweighted average of the concentration of a chemical agent in the air within the breathing zone of a worker in relation to a specified reference period" (Council Directive, 1998).

Quantum dot is a "nanoparticle or region which exhibits quantum confinement in all three spatial directions" (European Committee for Standardization, 2021).

Recycling "means any recovery operation by which waste materials are reprocessed into products, materials or substances whether for the original or other purposes. It includes the reprocessing of organic material but does not include energy recovery and the reprocessing into materials that are to be used as fuels or for backfilling operations" (European Parliament, 2008).

Sludge "means residual sludge, whether treated or untreated, from urban wastewater treatment plants" (Council Directive, 1991).

Substances of Very High Concern (SVHC) include substances that are carcinogenic, mutagenic, and toxic for reproduction (CMR); persistent, bioaccumulative and toxic (PBT); very persistent and very bioaccumulative (vPvB), have endocrine-disrupting properties (ED) or those for which there is scientific evidence for serious effects to human health or the environment that give rise to an equivalent level of concern to those substances that listed in the Article 57 ((a) to (e) list). The latter are identified on a case-by-case basis as outlined in Article 59 (European Parliament, 2006).

Waste is "any substance or object which the holder discards or intends or is required to discard" (European Parliament, 2008).

Waste management "means the collection, transport, recovery and disposal of waste, including the supervision of such operations and the after-care of disposal sites, and including actions taken as a dealer or broker" (European Parliament, 2008).

Waste treatment "chemical or physical processing, or both, of waste for interim or ultimate disposal" (European Committee for Standardization, 2019).

Executive Summary

This study updates and expands on the document "Nanomaterials in Waste Streams – Current Knowledge on Risks and Impacts" published by OECD in 2016. It covers ten topics:

- Waste streams containing nanomaterials.
- Behaviour and fate of nanomaterials in waste processes.
- Exposure of waste management workers to nanomaterials.
- Benefits and challenges of nanomaterials posed to the circular economy.
- Impact of nanomaterials on recycling.
- Main streams of nanomaterial recyclates.
- Recycling abatement systems residues.
- Potential for substitution of hazardous substances by nanomaterials in the recyclate streams.
- Emission of nanomaterials.
- Emission control and best available techniques.

The review covered 276 publications, including books, research reports, research and review papers, databases, and other web resources. These publications were reviewed irrespective of the nanomaterial terminology used. However, the study specifically focuses on manufactured nanomaterials and incidental nanomaterials. This report refers to the definitions provided in CEN ISO/TS 80004-2:2017, where manufactured nanomaterial is "intentionally produced to have selected properties or composition", and incidental nanomaterial is "generated as an unintentional by-product of a process". The study focuses on the European Union situation and developments in nanomaterials, although relevant studies from other countries were reviewed where appropriate.

To complement and validate the findings, twenty interviews were conducted with experts from academia, industry, international associations, national authorities, and non-profit organisations. The research topics have been addressed in three thematic sections of the study – "Nanomaterials in Waste", "Nanomaterials in Waste Management Processes", and "Nanomaterials in the circular economy".

Based on the findings, nine conclusions and four recommendations have been formulated:

CONCLUSION 1. Currently, it is not possible to give a sound evidence-based conclusion about the quantities of nanomaterials on the European market and in waste streams. To date, comprehensive quantitative information on the manufacturing volumes of nanomaterials in Europe is absent. Since 1 January 2020, manufacturers and importers of nanomaterials have to report specific information in accordance with the revised annexes to the REACH Regulation. However, the information on the quantity manufactured or imported per year may not be specific to the nanoforms of a chemical substance. Under REACH, the obligation to register nanoforms is triggered by the total manufactured or imported volume of both nonnanoforms and nanoforms of the same substance. Data on the presence of nanomaterials in consumer products can be obtained from public databases on nanomaterials, such as PEN CPI, NanoData, NanoDB, NPD. However, the existing databases do not provide quantitative data on nanomaterials in EU consumer products.

The absence of quantitative data about nanomaterials on the EU market and in consumer products complicates the identification of the predominant waste streams containing nanomaterials. The current research suggests that nanomaterials could be present in all major sources of waste generated in the EU, such as construction and demolition waste, manufacturing waste, municipal solid waste, wastewater, and its by-products. However, the available research

provides only qualitative data about presence of nanomaterials and there are no means to give a quantitative evaluation of their presence and concentration.

CONCLUSION 2. Public information about nanomaterials is important to waste managers, scientists, regulatory bodies and consumers. Despite deficiencies in the quantification of nanomaterials in waste, public information sources provide valuable information to waste managers for determining the composition of waste and its classification to fulfil obligations under the Waste Framework Directive and related waste legislation. These sources of information are widely used by scientists who make estimations of mass flows of nanomaterials to waste management facilities and their fate in the environment. Some of these mass flow models can support regulatory decision-making in the safety assessment of nanomaterials. Finally, public data sources about nanomaterials in products allow consumers to make informed decisions about specific goods.

RECOMMENDATION 1. The development of public datasets containing information about nanomaterials and their presence in products should be promoted for practical and regulatory decision-making and the advancement of scientific research.

CONCLUSION 3. Research on behaviour and fate of nanomaterials focuses on relevant nanomaterials in certain waste management facilities and is mostly conducted in a laboratory setting. The reviewed publications focus on specific nanomaterials, mainly titanium dioxide, nanosilver, zinc oxide and some carbon-based nanomaterials. Most studies were conducted in a laboratory setting and addressed fundamental processes of nanomaterial-matrix interactions. However, only a few field or pilot scale studies can be used to assess the mass fluxes of nanomaterials. The lack of field research was highlighted in the expert consultation.

CONCLUSION 4. Generic mass flow models or fate models have been widely used to provide a general overview of the distribution of specific nanomaterials in the environment. The literature review has shown an increasing number of research publications that use mass flow models to transform smaller and larger volumes of data into meaningful distribution patterns and provide generalised data (e.g., for entire regions and periods). The prediction accuracy of models is substantially limited by the lack of quality input data on the production volumes of nanomaterials per year and the presence of nanomaterials in consumer products. Furthermore, multimedia nanomaterial fate models have been developed but not yet widely used. Both model concepts contribute with valuable but different estimates that are useful for researchers, professionals and regulators.

CONCLUSION 5. Substantial progress has been made in developing analytical tools for the characterisation and measurement of nanomaterials. Available tools can provide qualitative and quantitative information about nanomaterials. Achievements have been observed in detection, characterisation and quantification of inorganic nanomaterials. However, challenges remain in distinguishing between natural, incidental and manufactured nanomaterials, characterisation of nanomaterials in complex media and specific quantification issues. These challenges were also highlighted in the expert consultation.

RECOMMENDATION 2. Predictions from statistical model calculations should be compared to field-scale experiments to assess the quality of the predictions. Measurement and characterisation of nanomaterials in a real-life setting allow checking the accuracy of predictions provided by current tools for modelling the behaviour and fate of nanomaterials. Further field studies of the behaviour and fate of manufactured and incidental nanomaterials in waste treatment and recycling plants would be beneficial, as it would be further work on improving detection, characterisation and quantification of nanomaterials.

CONCLUSION 6. No studies about workers' exposure to nanomaterials in waste management facilities were identified; however, existing studies focusing on manufacturing and research sites indicate exposure to nanomaterials through

inhalation during manual activities. Few mentions of case studies of workers' exposure to nanomaterials in recycling were identified, but they were considered to provide low-quality evidence. Many studies about occupational exposure to nanomaterials in manufacturing and research sites are available, with some covering activities that are also relevant to waste facilities, e.g., handling, cleaning, grinding, etc. According to the available studies, manual activities such as handling, cleaning, finishing, transferring, etc., are likely to lead to exposure to airborne nanomaterials. Exposure by inhalation was predominant in the literature and emphasised by the expert interviews as an important exposure route of nanomaterials to the human body. Most studies addressed the exposure to carbon-based, metal and metal oxide nanoparticles.

RECOMMENDATION 3. Field research on the exposure to manufactured and incidental nanomaterials in waste management and recycling facilities should be performed. Analysis of the occupational exposure at waste management facilities would be helpful to understand what activities pose the highest risk of exposure to manufactured nanomaterials contained in waste and to incidental nanomaterials formed during waste treatment operations. Information from field research would allow comparisons with other industrial facilities and enable the determination of the most effective risk mitigation measures.

CONCLUSION 7. The available research shows the high efficiency of incineration and wastewater treatment (for TiO₂, ZnO, CeO₂, Ag, Au, Al, Ce, Co, Cu, Fe, Ti, Zn, Mn) in limiting emissions of nanomaterials to the environment. Several case studies in real waste incineration plants and experiments that simulated incineration showed high efficiency (close to 100% as reported by some studies) of bag filters in preventing nanomaterials emission into the air. Similarly, high efficiency of removing nanoparticles was shown in the studies of wastewater treatment that claimed 76% to almost 100% removal rates for TiO₂, ZnO, CeO₂, Ag, Au, Al, Ce, Co, Cu, Fe, Ti, Zn and Mn at diverse stages of treatment. The efficiency of landfilling systems has not been addressed systematically.

CONCLUSION 8. Management of nanomaterials in waste is prescribed by general regulatory provisions, and nano-specific guidance is emerging. The analysis of grey literature and legislation have shown that the definition of nanowaste and specific provisions to nanomaterials are absent in the Waste Framework Directive. Outcomes of the current discussion about the applicability of the Globally Harmonised System (GHS) to nanomaterials can potentially trigger changes in the EU waste management legislation, as classification of waste is based on the CLP Regulation that adopts the GHS principles. However, the need for such changes remains to be clarified. Internationally accepted guidance documents on analytical tools for the detection, characterisation, and quantification of nanomaterials have been developed. Advice on managing waste containing nanomaterials is largely absent. In this context, guidance on managing waste from manufacturing and processing of nanomaterials is an important step to facilitate practical actions in managing nanowaste.

CONCLUSION 9. Several potential contributions of nanomaterials to the circular economy were outlined in research publications; however, there is no evidence of circularity, economic feasibility and environmental safety of the proposed applications. The analysis of literature identified several areas of research, where it was envisioned that nanomaterials could contribute to the circular economy. These areas covered green synthesis of nanomaterials – including synthesis of nanomaterials from biowaste, use of nano-additives in the recycling of plastics and construction and demolition waste, facilitation of recovery of rare-earth elements from waste using nanomaterials and application, were identified in the stakeholder consultation. In accordance with the European Commission's circular economy action plan, circular solutions/applications should be capable to restore, revitalise or renew sources of energy or materials and produce as little waste as possible. However, the circularity of the solutions based on the application of nanomaterials proposed in the literature is questionable, and the research is, at the moment, purely theoretical. Most publications are case studies that exclusively focus on proposing and characterising specific methods of

nanomaterial applications. The status of the commercial application of proposed solutions is unknown. The systematic analysis of the economic viability of the proposed methods, along with evaluation of safety concerns, is absent.

RECOMMENDATION 4. The systematisation of current research and evaluation of the economic, environmental and social impact of the proposed applications of nanomaterials in the circular economy should be supported. It implies interdisciplinary collaboration between different researchers, including representatives of social sciences. Closer collaboration and exchange of ideas between researchers and industry is necessary to conclude on the needs for nanotechnology solutions and launch appropriate research initiatives.

1. Introduction

This study aims to update and expand on the 2016 literature review "Nanomaterials in Waste Streams – Current Knowledge on Risks and Impacts" by the OECD by including the circular economy dimension.

For the purpose of this study, a wide-ranging interpretation of what constitutes a **nanomaterial** is applied to ensure that we assess a broad range of research publications and reports. All publications that consider nanomaterials are covered irrespective of the nanomaterial terminology used. However, the study specifically focuses on **manufactured nanomaterials and incidental nanomaterials**. We use the definitions provided in CEN ISO/TS 80004-2:2017 where:

- **manufactured nanomaterial** is 'intentionally produced to have selected properties or composition'.
- incidental nanomaterial is 'generated as an unintentional by-product of a process'.

The key **research questions** addressed in this report can be grouped into ten subtopics:

- **Topic 1: sources** What is currently known regarding the main sources contributing to nanomaterials in waste in terms of substances or uses/processes?
- **Topic 2: behaviour and fate in waste processes** Are there studies assessing the effectiveness of field scale operations such as existing plants or pilot plants incorporating all stages of waste treatment processes and using actual waste products? What is the status of the knowledge of nanomaterials' fate in activated sludge processes of wastewater treatment, in flue gas treatment of incinerators, in recycling facilities and landfills?
- **Topic 3: waste management workers' exposure** What information is available on the exposure of workers operating in recycling/waste management facilities to (specific) nanomaterials?
- **Topic 4: benefits and challenges for the circular economy** Does the use of nanomaterials create any particular benefits or challenges for the circular economy?
- **Topic 5: impacts on recycling** Does the presence of nanomaterials in waste streams hinder or bring detrimental impacts on recycling from technical and regulatory perspectives? (e.g., due to specific hazards, or leading to classifying certain waste streams as more hazardous)?
- **Topic 6: recyclate streams** What are the main nanomaterial-containing recyclate streams, and how do nanomaterials behave in the circular economy?
- **Topic 7: abatement system residues** What issues arise from incorporating abatement system residues containing nanomaterials in residue-based secondary products? What is the impact of the agricultural application of sludge containing NMs?
- **Topic 8: waste management and recycling applications** What positive applications/impacts do nanomaterials have on waste management and recycling? (e.g., different nanomaterial-based technologies for water remediation and other waste treatments, and the challenges faced by these technologies).
- **Topic 9: substitution** Is there evidence that the use of nanomaterials could lead to a reduction in other waste streams (e.g., the substitution of harmful materials problematic in waste treatment by nanomaterial-containing materials)?
- Topic 10: emissions, emission control and BATs What is the effectiveness of BAT waste treatment technologies in retaining or eliminating NMs and protecting workers from exposure to NMs? What is the effectiveness of sub-standard waste treatment technologies (e.g., incinerators with inadequate flue gas treatment, clay liners in older landfills or

uncontrolled landfills)? Are there other measures to effectively capture, divert or eliminate NMs from waste streams and residual waste? What is the effectiveness of landfills in serving as a final sink for NMs? Are there potential risks of secondary materials that contain NMs?

To address the ten topics, a **literature review** and an **expert consultation** were conducted. The literature review focused on research publications and grey literature, mainly targeting research reports by various reputable organisations, strategic and legal documents, websites, popular magazines, or internet media (only for finding relevant examples of applications of nanomaterials in the industry). The expert consultation was aimed at complementing and cross-checking the information found in the literature with expert judgement. The experts were selected through an internet poll and consulted by using a semi-structured interviewing method. Thematic analysis was applied for the interpretation of the interview results.

It should be noted that the study focuses on the **European Union situation and developments in nanomaterials**, although the relevant studies from other countries are covered where appropriate.

In the study, we reviewed **276 publications**, including books, research reports, research and review papers, databases and other web resources.

The study consists of the following sections:

- Section 2 details the methodology followed for the literature search and the expert consultation.
- Section 3 *Nanomaterials in Waste* presents the review of the main sources of nanomaterials in various waste streams, focusing on the products containing nanomaterials.
- Section 4 Nanomaterials in Waste Management Systems discusses the routes of nanowastes to waste treatment facilities, their behaviour and fate in incineration, recycling, landfilling and wastewater treatment, the exposure of workers to nanomaterials during waste treatment operations, nanoemissions to the environment and the best available technologies to handle them. The case study of recycling nanomaterials is provided in Annex 5.
- Section 5 Nanomaterials in the Circular Economy reviews the ways of using nanomaterials to reach the goals of the circular economy. It covers different areas of application of nanomaterials, including green synthesis of nanomaterials, recovery of rare-earth elements, waste recycling. The case study on nanomaterials in wastewater treatment is provided in Annex 5.
- Section 6 presents the analysis of the findings of the expert consultation.
- Section 7 presents the conclusions and recommendations of the study.

2. Methodology

2.1 Literature search strategy

The project team used the 2016 OECD report "Nanomaterials in Waste Streams: Current Knowledge on Risks and Impacts" as a starting point for the subsequent in-depth analysis of peer-reviewed scientific publications and reports from public authorities and industry available in the public domain. Papers and reports published in 2015-2021 were considered.

The collection of the relevant literature was carried out by:

- Automated keyword extraction by using Python scripts; the keywords are used for searching relevant literature.
- Refining and complementing of search results by reviewing the titles and abstracts of the papers collected and by following a snowballing approach.
- Gathering links to relevant publications through expert consultation (see section 2.2).
- Conducting additional searches in nanotechnology databases (NanoDatabase, <u>https://www.nanodb.dk/;</u> Statnano, Nanotechnology Products Database, <u>https://product.statnano.com/</u>).

These two methods are applied to both **scientific publications** and the **deliverables of projects** funded through the EU Seventh Framework Programme, LIFE and Horizon 2020. Additional searches were conducted to find relevant **examples of industrial nanotechnology applications**.

The procedure of data collection is summarised in Figure 1.

Figure 1: Data collection procedure



As shown in Figure 1, the first task was the **identification of a start set of papers**. The identification of the start set was based on keywords selected by the project team based on the research questions specified in the Terms of Reference. Further selection was informed by the review of the OECD (2016) paper and consultation with the Expert Advisory Group and the client (ECHA).

Two information discovery platforms of scholarly, policy and patent literature, Lens and Dimensions, were used for identification of a start set papers. These platforms provide access to the world's largest publicly available databases with internal transparency metrics. **Dimensions** an inter-linked research information svstem provided bv Digital is Science (<u>https://www.dimensions.ai</u>) with over 120 million records. We have chosen this system because of the huge amount of data it provides, including the number of citations and social networks presence per publication and other relevant metrics, but also because it offers an API to perform queries using a specific DSL (Domain Specific Language). Lens (lens.org) has over 197 million Scholar records sourced from Microsoft Academic (the major source), Pubmed, and Crossref, and it is used as a consistency gateway.

As a result of searches, the start set of 25 papers was identified. The number of papers found for various research topics is summarised in Table 1.

Research topics	Number of papers
Sources of nanomaterials in waste (topic 1)	6
Behaviour and fate of nanomaterials in waste treatment processes (topic 2), including emissions (topic 10)	5
Nanomaterials in recycling and waste management (topics 5, 6, 7, 8, 9)	7

Table 1: Start set of papers according to research topics

Research topics	Number of papers
Waste management workers' exposure to nanomaterials (topic 3)	3
Benefits and challenges of nanomaterials in the circular economy (topic 4)	4

As shown in Table 1, in research publications, several research topics were often covered. The identified papers were processed to **extract keywords**.

For keywords' extraction, the textual content of these papers was pre-processed with tokenisation, lower casing and minimal cleaning using python built-in functions and common tools and packages (e.g., Pandas, NLTK corpus). Three methodologies to extract keywords were applied:

- **TF-IDF:** Text Frequency Inverse Document Frequency analysis, at a high level, finds the words that have the highest ratio of occurrences in the document analysed and give them scores.
- **TextRank algorithm (with Gensim):** Gensim is a Python NLP library created to automatically extract semantic topics from documents. It is an open-source vector space modelling and topic modelling toolkit using NumPy, SciPy. The Gensim coding implementation is based on the popular TextRank algorithm. It also allows lemmatisation of the words.
- **RAKE Algorithm:** RAKE Algorithm refactors Python's search algorithm to capture the cooccurrences (two words appearing in proximity). The project team built a co-occurrence matrix that showed the number of times a 'term X appeared near a 'term Y'. This matrix provides combinations of key terms that could be useful for searches.

The project team "fed" the selected papers to the algorithms that produced lists with words and occurrence values. The first 30-40 rows were considered. In addition, "comparison CSV lists" were produced, analysing the intersection of words for each of the methods used and identifying the keywords that were present in all the papers on each subtopic. Keywords occurring the most in each paper and across papers are presented in Annex 1. The resulting keywords have been further enhanced by the project team and used to carry out iterative searches using Dimensions.ai.

Following keywords extraction, **the snowballing of the start paper set** was performed. "Snowballing" is the use of the reference list of the reviewed papers, citations and authors to identify additional papers. The approach also benefits from looking at where the papers were actually referenced and cited. The use of references and citations is referred to as backward and forward snowballing. Both techniques were applied on the start set of seminal and highly cited papers in the areas investigated. Through backward snowballing, the project team looked at the reference list of the start set of papers for each subtopic and excluded those papers that did not fulfil the basic criteria, such as language, publication year and type of publication. For snowballing, a text scraping programme in python was created. It used open-source libraries such as NumPy, PANDAS, or PyPDF2, which can extract all the citations within the papers included in the start set and count the number of citations. This data mining strategy allowed to assign relevance scores to citations based on the number of organic appearances throughout the different sections of the documents.

Using the extracted keywords, **iterative searches** were performed. The **search results were screened for inclusion** in the data sources of this research. The publications were included with an outlook to the scientific metrics of the publication (e.g., impact factor for scientific journals) and a number of citations and altmetrics. The fact that the newest literature sources may get fewer citations because of a short period after publication than older ones was considered in the analysis of the results. Because of the substantial volume of research in many topics of this study, priority was given to literature reviews and bibliometric/scientometric studies where appropriate. Recommendations by ECHA and Scientific Advisory Board were considered. Papers suggested by the participants of the expert consultation were screened and included. Papers outside of the temporal scope of this research were included if no newer publications on the topic were identified. Several search iterations were performed for this study, based on the discussions with ECHA and the assessment of the literature review quality in the Interim report.

As a result of searches and screening, we reviewed **276 publications**: 180 papers in scientific journals, 6 books, 23 websites and 67 other sources (e.g., policy documents).

Importantly, due to the broadness of the ten research topics addressed in this study, all literature searches were exclusively focused on nanomaterials. This focus brought limitations and excluded research publications that have not explicitly mentioned nanomaterials. For instance, the issues of nanomaterial release from landfills could be addressed from the perspective of colloid science and could apply to nanomaterials. However, these studies were not included as they do not mention nanomaterials.

2.2 Expert consultation

The project team carried out **semi-structured interviews** with experts to collect new information and triangulate the information gained through the literature review. Semi-structured interviews are an effective technique of data collection considering:

- The broad spectrum of research questions we need to address (grouped in ten subtopics);
- Varying levels of depth of each subtopic;
- A diverse level of expertise of the interviewees across the subtopics.

The major advantages of semi-structured interviews are the ability to achieve the maximum level of detail on each topic and the opportunity to get comparable results from different interviews by using the same interview template.

To reach the pool of relevant experts, we combined **convenience and purposive sampling**. First, we used the networks of RPA and RPA Europe and ECHA EUON to identify experts in nanotechnology. Second, we sought researchers and practitioners who possess expertise in any of the ten subtopics (or a combination of those). Third, we focused on experts who represent different organisations active in the study field (e.g., academic researchers, representatives of small and medium-sized enterprises, industry associations, governmental agencies, etc.).

To develop an adequate **sample of experts**, on 9 February 2021 the team launched a poll to survey the interests and availability of a selected number of nanotechnology experts taking part in the consultation for this study. The invitation was sent to around 50 experts from academia, industry, authorities and NGOs and was later circulated through the OECD Working Group on Nanomaterials and the European Union Observatory for Nanomaterials (EUON) LinkedIn webpage.

The experts were asked to indicate the areas (the ten subtopics listed in the Introduction) for which they have information to share with the team. Based on the poll results, the team prepared the "state of knowledge" material on each topic area to be shared ahead of the interviews. We received 32 complete replies. Annex 2 provides an overview of the poll findings.

Eight research topics required a short discussion that fits in 1 to 3 questions, while two topics (topic 2 – behaviour and fate in waste processes and topic 10 – emissions, emission control and BATs) needed an extensive discussion (6 and 5 questions respectively). Therefore, the study team carried out separate interviews for topics 2 and 5 while combining two topics in one

interview for the other eight research themes. The **template** with general introductory/closing questions for all interviews and topic-specific questions is provided in Annex 3.

To make an adequate **sample size** for addressing all ten subtopics, the team used the concept of data saturation, which was employed as guidance for non-probabilistic sampling. Data saturation refers to the data collection stage when no new themes emerge in the interviews. The widely cited experiment with data saturation by Guest et al. (2006) suggested that six interviews are enough to reveal the main sub-themes within one research topic, while 12 interviews allow reaching the full data saturation. Depending on the availability of experts, we used data saturation as guidance for data collection.

For **data interpretation**, we used **thematic analysis**, a widespread qualitative method applied for interpreting textual research data. It allows mapping of the key topics in the text without quantifying them.

3. Nanomaterials in Waste

This chapter **aims** to identify the main sources of nanomaterials in various waste streams. For this purpose, the main waste streams generated in the EU were analysed along with available evidence about the presence of nanomaterials in them. Furthermore, products that contain nanomaterials and enter waste streams were reviewed. Different sources and methods for evaluating products containing nanomaterials were discussed in the chapter. Practical and regulatory concerns related to the state-of-the-art knowledge about waste streams were reviewed as well.

3.1 Main sources of nanomaterials in waste

Various definitions are employed to conceptualise the presence of nanomaterials in waste. The OECD report (2016) used the term "waste containing nanomaterials" to cover any type of waste where manufactured nanomaterials could be present, irrespective of their concentrations. The report also mentioned the concept of "nanowaste" – wastes containing high concentrations of nanomaterials and generated by nanomaterial production (OECD, 2016: p. 16-17). Differently, Part et al. (2018) provided a more detailed definition (where nanowaste and waste containing nanomaterials are synonyms) that specifies different sources of nanomaterials in waste – nanomaterials as a single fraction, end-of-life products containing nanomaterials and waste materials that were contaminated with nanomaterials. In the study, the terms "nanowaste" and "waste containing nanomaterials" are used synonymously.

The research publications on nanomaterials in waste management do not provide sound quantitative data to ground the statements about the predominant types of waste containing nanomaterials and their quantities. Mostly, the available research focuses on specific types of waste (e.g., Part et al., 2018) and/or consumer products (e.g., Heggelund, 2017) and/or specific nanomaterials (Rajkovic et al., 2020; Adam et al., 2021; Zheng & Nowack, 2021), often in combination with a focus on the specific waste type.

To distinguish predominant types of waste containing nanomaterials, it is useful to evaluate the overall waste streams. It should be noted that the current absence of quantitative data on the manufacturing of nanomaterials, their use in products and routes to different streams of waste, does not guarantee that predominant waste streams contain more nanomaterials than other types of waste. However, due to the absence of any other method for identifying the predominant waste streams containing nanomaterials, the estimation of overall waste streams could be a useful starting point. According to Eurostat (2020), construction waste made up the leading share of waste generated in the European Union in 2018 (see Figure 2).

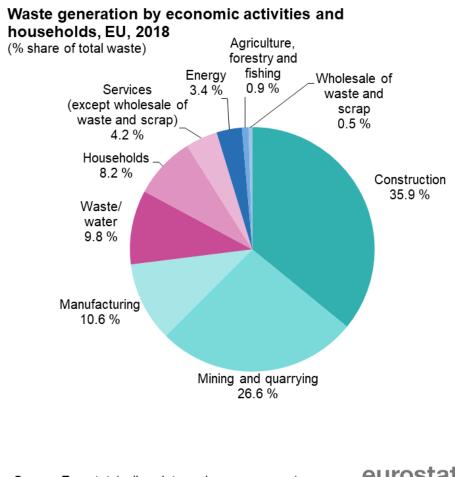


Figure 2: Waste generation statistics reproduced from Eurostat (2020)

Source: Eurostat (online data code: env_wasgen)

eurostat 🖸

Other significant waste streams come from mining and guarrying, manufacturing, wastewater and water services and households. When excluding mineral waste, waste and water services and households become significant sources of waste. The generation of waste in water services and households has increased over time. Between 2004-2008 the levels of waste generation in wastewater and water services increased by 176% and by 6% in households, while in manufacturing, the numbers of waste decreased by 25%. However, the situation globally is different due to varying waste generation patterns in high/middle/low-income countries. According to the World Bank report (Kaza et al., 2018), the generation of industrial wastes is 18 times higher than of municipal solid waste. The generation of industrial waste increases with the income level of the countries.

Comparing the general waste statistics in the EU with the main waste sources of nanomaterials identified in the OECD report (2016), a general agreement on the predominant types of waste emerges: municipal solid waste and sewage sludge originating from wastewater treatment. However, construction and demolition and manufacturing waste should also be considered. Although mining and quarrying waste makes up a large fraction of waste in Europe, there is no sound evidence about the presence of manufactured nanomaterials.

The largest fraction - construction and demolition waste - results from construction and demolition of buildings and public infrastructure, road planning and maintenance. It includes various materials, such as bricks, concrete, gypsum, wood, glass, metals, plastics, solvents, asbestos, excavated soil, etc. (European Commission, n.d.a). Nanomaterials in municipal waste flows were analysed by various researchers in Switzerland (Hincapie et al., 2015; Caballero-Guzman et al., 2015) and Japan (Suzuki et al., 2018). Hincapie et al. (2015) reported that in

Europe nanomaterials are mainly applied in cement, insulation materials and paints. Construction materials might contain titanium dioxide, zinc oxide, silicon dioxide and aluminium oxide nanoparticles. Jones et al. (2016) built a database of 156 construction products containing nanomaterials that were available on the UK market. The most common of them included coatings, glass, concrete, steel, insulation, and composites. The review mentioned diverse nanomaterials, including silica, titanium, metal oxides, carbon nanotubes, nanoclays, aluminium, etc. The growing application of nanomaterials in the construction industry implies their presence in construction and demolition waste streams.

The second-largest fraction of waste originates from mining and quarrying; however, no publications on the presence of nanomaterials were found.

The third-largest fraction of waste is generated by **manufacturing activities** that produce industrial wastewater and different residues containing nanomaterials. Most manufacturing processes generate high volumes of polluted water (Jassby et al., 2018) and nanomaterials used in the manufacturing may be discharged with wastewater (Kunhikrishnan et al., 2015). Various manufacturing activities also produce high volumes of sludge that could contain nanomaterials. Liu et al. (2019) and Bhattacharya et al. (2020) reported on sludges from chlorate industries, electroplating sludge, slags, and sludges from metal industries (e.g., red mud, boron mud) that contain nanomaterials. Importantly, manufacturing activities cover various industries, which differ in their contribution to waste streams. The most significant fraction of industrial waste originates from the metal industry (29% of manufacturing waste) (Eurostat, 2020); however, there is no data about its contribution to waste streams containing nanomaterials.

Another significant fraction of waste by mass is **municipal solid waste** that "covers household waste and waste similar in nature and composition to household waste" (cited from Eurostat, 2017). This type of waste originates from households, commerce and trade, small businesses, office buildings and institutions, and waste from selected municipal services (Eurostat, 2017). Municipal solid waste contains nanomaterials from a broad spectrum of discarded products that enter waste treatment facilities. In OECD (2016), municipal solid waste was considered one of the main sources of nanomaterials. With the increasing application of nanomaterials in products, the presence of nanomaterials in waste streams also grows. Among the most mentioned nanomaterials are silver, titanium, zinc and carbon-based nanomaterials (Part et al., 2018).

Wastewater is a significant source of waste in Europe. OECD (2016) mentioned wastewater and sewage sludge as important sources of nanomaterials. Wastewater originates from industrial and household activities. The latest studies on the routes of nanomaterial-containing wastes through treatment facilities indicate that wastewater is a significant source of nanomaterials (Zheng & Nowack, 2021; Rajkovic et al., 2020). Phalyvong et al. (2020) detected nano cerium oxide and titanium oxide originating from anthropogenic activities, among them a wastewater treatment plant in the Loire River (France). Mehrabi et al. (2021) detected nanoparticles rich in Ce-La, Fe-Al, Ti-Zr, Zn-Cu from anthropogenic activities in the water samples from the influent and effluent of five wastewater treatment plants in Switzerland. Furthermore, nanomaterials have been increasingly found in outdoor urban environments. Urban runoffs have been extensively studied as sources of manufactured and incidental nanomaterials in waste (Baalousha et al., 2016; Wang et al., 2020; Zheng et al., 2020). However, since 2015, the team identified only one field research study: Wang et al. (2020). The authors identified and characterised nano titanium dioxide in the samples of urban runoff collected in California, USA. Earlier research on the presence of nanomaterials in urban runoffs that is out of the scope of this study has been cited in the research literature (Peters et al., 2020).

Sewage sludge covers solids that are separated from water during wastewater treatment. It is used in agriculture as a fertiliser or treated in incineration plants and landfilled (Eurostat, 2020). Sewage sludge is produced in municipal and industrial wastewater treatment. Municipal sewage sludge contains nanomaterials from commonly used products. In the literature review on sludge containing nanomaterials, Liu et al. (2019) quote the presence of titanium dioxide, silicon dioxide, zinc oxide, iron and iron oxides, aluminium oxide, and other nanomaterials in sewage

sludge. Few studies examine samples of municipal sewage sludge or water to determine the presence of nanomaterials. For instance, Hennebert et al. (2017) examined thirteen sewage sludge samples in France and discovered nano-silver, titanium, zinc, and cerium. Gogos et al. (2020) analysed five samples of sewage sludge collected at a Swiss wastewater treatment plant and detected nano-cerium of industrial origin (Gogos et al., 2020). Liu et al. (2019) reported the presence of nano-sized metals and metal oxides in sludges from chemical and electroplating industries.

OECD report (2016) distinguished seven main sources of waste potentially containing nanomaterials:

- Municipal solid waste.
- End-of-life products.
- Sludge and biosolids from wastewater treatment plants.
- Fly ash and bottom ash from incinerators.
- Landfill leachate.
- Household drainage.
- Commercial and industrial sewage.

The report further categorised them according to the specific waste management process they usually enter. Based on the above discussion of significant streams of waste containing nanomaterials and extensive literature review on nanomaterials in municipal solid waste by Part et al. (2018), we updated the OECD (2016) list (see Table 2). An additional waste management phase – biological treatment – was included. Part et al. (2018) reported the use of biological treatment for food, food packaging, textile and other products contained in municipal solid waste, sewage sludge, and biosolids. Biological treatment of waste is an essential process in wastewater treatment and modern landfilling systems (Part et al., 2018).

Waste management phase	Waste sources of nanomaterials	
Biological treatment	Municipal solid waste Sludge and biosolids from wastewater treatment plants	
Recycling	Municipal solid waste End-of-life-products Construction and demolition waste	
Incineration	Municipal and industrial (manufacturing) solid waste Sludge and biosolids from wastewater treatment plants	
Landfilling	Municipal solid waste Fly ash and bottom ash from incinerators (municipal solid waste and sewage sludge) Sludge and biosolids from wastewater treatment plants Construction and demolition waste	
Wastewater treatment	Household sewage Commercial and industrial sewage Landfill leachate Process water from wet scrubber (municipal solid waste) Urban runoff	
Source: adopted from OECD (2016) and updated		

Table 2: Potential sources of nanomaterials in waste streams

Industrial and consumer products are important sources of nanomaterials in waste. In the subsequent section, we discuss the availability of products containing nanomaterials on the market.

3.2 Products containing nanomaterials on the market

In research literature, consumer products that reach the end-of-life are considered one of the primary sources of nanomaterials in waste (Part et al., 2018; Heggelund et al., 2017; Younis et al., 2018; Kunhikrishnan et al., 2015). Therefore, researchers refer to various sources that provide data on nanomaterial-containing products to understand the potential volume of nanomaterials in waste. For instance, Hansen et al. (2016) reported about eight databases of national and international scope. The latter include Nanotechnology Products Database, NPD (Younis et al., 2018), the Nanodatabase, NanoDB (Hansen et al., 2016), Consumer Product Inventory of the Project on Emerging Nanotechnologies, PEN CPI (Vance et al., 2015; Hansen et al., 2016; Heggelund, 2017) and NanoData (EUON, n.d.a). While NPD, NanoData and PEN CPI have a global focus, the NanoDB provides a European perspective.

When using the databases, it is essential to understand their limitations (see Table 3). The comparative analysis of several databases of nanomaterial-containing products by Heggelund (2017) revealed the different pace of update, gaps in data that occur due to the lack of up-to-date information about the presence of nanomaterials in the products, the absence of consistent monitoring of the products entering/exiting the market or losing their status of nanoproducts. Additionally, the databases include new products based on the manufacturer's claims and the user suggestions (due to crowdsourcing features, e.g., in PEN CPI and NanoDB) (Hansen et al., 2016; Vance et al., 2015). Although the database curators approve all new records, misreporting may occur.

Database and focus	Data update dynamics	Ownership
PEN CPI, http://www.nanotechproject .tech/cpi/ Consumer products	2013: 1628 products, 1543 companies, 30 countries (PEN Consumer Product Inventory, 2021) 2017: 1827 products (Heggelund, 2017) 2021: 1833 products, 706* companies, 33 countries (PEN CPI accessed on 04/02/2021)	Project on Emerging Nanotechnologies: Wilson Center and Virginia Tech
NanoData, https://euon.echa.europa.e u/lt/nanodata	The database claims that data were uploaded from 2013 to 2017: 1087 products, organisation and country information cover not only manufacturers but research and non-profit organisations	European Union Observatory for Nanomaterials
NanoDB, https://nanodb.dk/en/ Consumer products	2017: 3000 products (Heggelund, 2017) 2021: 5000 products, 1115* companies, 59 countries	DTU Environment
NPD https://product.statnano.co m/ Products, including those for industrial use	2017: 6970 products, 1378 companies, 52 countries (cited from Younis et al. (2017)) 2021: 8948 products, 2499 companies, 63 countries (NPD accessed on 03/02/2021)	StatNano
Note: *the number of companies was counted manually from the lists provided in databases		

Table 3: Nanomaterial-containing product information in databases

*Note: *the number of companies was counted manually from the lists provided in databases (04/02/2021)*

Table 3 shows that only two databases demonstrate consistent data updating – the NanoDB and NPD. Due to a broader scope of the registered products, NPD contains 44 per cent more products than the NanoDB. The NPD collects information about products for industrial use as well (e.g., products for the petrol, chemical and aerospace industries, industrial machinery etc.), while NanoDB focuses on consumer products, biocidal products and treated articles. NanoDB curators have recently added information on human and environmental hazards (NanoRiskCat).

Researchers follow different approaches to identify the most common nanomaterials on the market:

- Looking at available statistics on the production and consumption volume of nanomaterials, in tonnage per year (e.g., Younis et al., 2018; Part et al., 2018);
- Considering the most common nanomaterials contained in products, based on the claims of the product manufacturers (Younis et al., 2018; Heggelund, 2017; Hansen et al., 2016);
- Referring to the estimates of the market value of nanomaterials, based on expert surveys (Younis et al., 2018; Part et al., 2018).

Due to substantial gaps in data, the risk for a bias in judgment about the prevalent nanomaterials on the market is high. The market value does not reflect how widespread nanomaterials are on the market. The presence of nanomaterials in a product does not inform about their concentration or mass, and the data on production volume is incomplete and not reliable (Part et al., 2018).

Important to note, most research papers are focused on specific nanomaterials, so there is no reliable data on other nanomaterials present on the European market. For instance, to determine production volumes of specific nanomaterials, Giese et al. (2018) carried out a literature review and a survey of organisations engaged in manufacturing, trade, and research of nanomaterials. The results revealed discrepancies between volumes provided in the literature and those reported by the surveyed experts. For example, the literature review showed that production volume of silicon dioxide is reported in quantities ranging from 100,000 to 1.5 million tonnes per year. The expert survey resulted instead in wider range, from 100,000 to 3 million tonnes per year. Significant discrepancies between literature review and survey data were also observed for nano-silver and cerium dioxide (Giese et al., 2018). Table 4 summarises nanomaterials common on the global and/or European market, according to recent studies and information presented in the databases listed in Table 3.

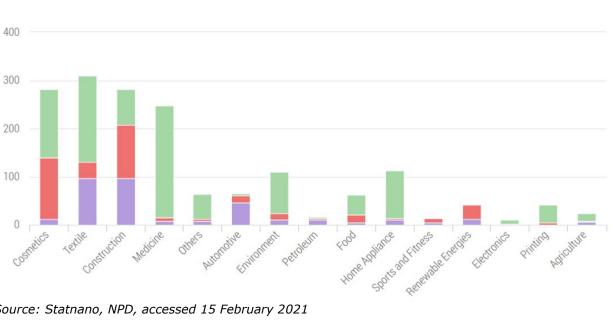
Source, method, scope	Nanomaterials	
Part et al., 2018 Consumption (tonnage/year) Market value Global scope	Silicon dioxide, titanium dioxide, zinc oxide, aluminium oxide, aluminium hydroxides and aluminium oxo- hydroxides, iron oxides, cerium dioxide, zirconium dioxide, other oxide nanomaterials, calcium carbonate, metal (aluminium, silicon, tungsten) nitrides, carbides, sulphates, gold, silver	
Heggelund, 2017 Presence in consumer products (Denmark, UK, EU)	Silicon dioxide, bamboo charcoal, carbon nanotubes, carbor products titanium dioxide, titanium, silver, gold, zinc oxide, graphite	
NanoDB (as of 4 February 2021) Presence in consumer products (>50) European Union scope	Silver, titanium, titanium dioxide, carbon, carbon nanotubes, gold, silicon dioxide, phosphate	

Table 4: Nanomaterial presence on the global and/or European market

Source, method, scope	Nanomaterials
NPD (accessed 4 February 2021) Presence in consumer products Global scope	Silver, titanium dioxide, silicon dioxide, tungsten disulphide, clay
Younis et al., 2018 Presence in consumer products Consumption (tonnage/year) Market value Global scope	Silicon dioxide, titanium dioxide, zinc oxide, carbon nanotubes, iron oxide, cerium oxide, aluminium oxide, silver, quantum dots, fullerenes

Table 4 shows that all sources mention silicon dioxide, titanium dioxide, and silver, while at least three sources also mention gold, zinc oxide, and carbon nanotubes. Analysis of publications revealed the papers re-use and re-cite data and projections from older studies and sources. Instances of cited data include the Second Regulatory Review on Nanomaterials by the European Commission in 2012 and the survey study conducted by Piccinno et al. in the same year (see Part et al., 2018). This increases the gap in new data and further complicates the analysis. Figure 3 shows the number of different products containing three of the most often mentioned nanomaterials - silver, titanium dioxide, and silicon dioxide - per product category.

Figure 3: Silver, titanium dioxide and silicon dioxide in products (no. of products)



O Silver O Titanium dioxide O Silicon dioxide O Tungsten disulfide O Clay O others

Source: Statnano, NPD, accessed 15 February 2021

NanoDB covers products from various countries of the world that could be purchased both in shops and online. In NanoDB, silver is present in brush or comb, nutritional supplements, straighteners, food consumption products, textile; titanium dioxide is contained in cosmetics (sunscreen, foundation/concealer, face creams); silicon dioxide can be found in cosmetics, paints, etc.

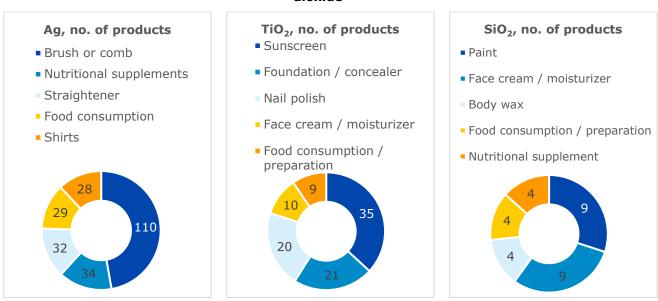


Figure 4: A snapshot of consumer products containing silver, titanium dioxide and silicon dioxide

Source: NanoDB, accessed 12 March 2021

3.3 Regulatory and technical concerns related to nanomaterials in waste

As the review of nanomaterials in waste has shown, the main challenge for evaluating the predominant sources of nanomaterials in waste is the absence of authoritative information about their production volumes and presence in products that later determine waste streams. The lack of quantitative information on the manufacturing and use of nanomaterials in products (e.g., characteristics and quantities of nanomaterials in a product) was mentioned both in research publications and international reports (e.g., Pavlicek et al., 2021; United Nations, 2018; Joint Research Centre, 2020b; Part et al., 2015). As a result, it is not possible to track the movement of nanomaterials from manufacturing to use and end-of-life stages (Pavlicek et al., 2021; Hansen et al., 2016; Part et al., 2015). However, similar arguments can be made for conventional chemical substances. Production volumes, distributions of nanomaterials in products and characterisation of their properties are useful as primary data inputs necessary to predict the flows of nanomaterials through waste management facilities, their emissions, and the ultimate fate in the environment. Currently, the tools for predicting the behaviour and fate of nanomaterials in waste treatment processes and the environment compile these data from a variety of resources such as research literature, expert estimations and market reports. The varying quality of available data increases the uncertainty of the projections (Nowack et al., 2017; Furberg et al., 2016).

Information on nanomaterial flows is useful for **making sound waste management and recycling decisions**. Currently, waste management operators do not possess reliable information on the presence of nanomaterials in waste entering their facilities (United Nations, 2018; Pavlicek et al., 2021). An important obligation of waste managers under the Waste Framework Directive (WFD) 2008/98/EC is the classification of waste as hazardous or nonhazardous. Outcomes of waste classification determine further obligations of waste managers in terms of waste treatment, handling, etc. For classification purposes, information about hazardous substances in waste can be collected from various available sources (European Parliament, 2008). For waste classification, waste managers should collect information about waste composition. One source of information covers data from the manufacturer of substances or products before they become waste (e.g., safety data sheets, product labels) (European Commission, 2018).

Managers of nanowaste who collect information about nanomaterials may benefit from the general developments under the REACH Regulation that were aimed at all substances (i.e., not specifically at nanomaterials). According to REACH Article 33, producers of articles containing substances of very high concern (SVHC) in a concentration above 0.1 w/w shall provide the recipient of the article with sufficient information available to the supplier, to allow safe use of the article (European Parliament, 2006). Substances of very high concern are defined in the REACH Regulation (Article 57) and include substances that are carcinogenic, mutagenic, and toxic for reproduction (CMR); persistent, bioaccumulative and toxic (PBT); very persistent and very bioaccumulative (vPvB), have endocrine-disrupting properties (ED) or those for which there is scientific evidence for serious effects to human health or the environment that give rise to an equivalent level of concern to those substances that listed in the Article 57 (a) to (e) list). The latter are identified on a case-by-case basis as outlined in Article 59 (European Parliament, 2006a). The list of SVHCs is provided in the **Candidate List of Substances of Very High Concern for Authorisation**, which is maintained by the European Chemicals Agency (ECHA). It is managed by ECHA based on the proposals to include a particular substance on the list, which is submitted by the EU Member States or by ECHA. As long as the Candidate List does not specifically exclude nanomaterials, the calculation of the concentration of a Candidate List substance covers the total quantity of the substance (both nanoform and bulk, if relevant) in the article.

Under WFD, producers of articles must notify ECHA about SVHCs in their articles (see Article 9(1)(i)). This **obligation is fulfilled by submitting information about SVHCs to the SCIP** (**S**ubstances of **C**oncern **I**n articles as such or in complex objects (**P**roducts)) database, maintained by the ECHA (see Article 9(2))). These WFD provisions cover all substances (not specifically nanomaterials). From 5 January 2021, all suppliers of articles containing SVHCs from the Candidate List in a concentration above 0.1% weight by weight should submit information about SVHCs to the SCIP database. The SCIP database contains information on the SVHCs in articles supplied on the EU market and it is therefore a valuable source of information about hazardous substances, including nanomaterials. However, according to the REACH Regulation, it should be noted that nanomaterials "may have specific toxicological profiles and exposure patterns and may therefore require specific risk assessment and adequate sets of risk management measures" (European Parliament, 2018c).

Mandatory reporting of nanomaterials is required in several EU Members States (EUON, n.d.). Demands for formalised reporting schemes originate from several reasons, ranging from governments' wishes to know what is on their national market to calls for the consumer's right to know made by NGOs and consumer organisations, to market analysts' and policymakers' interest in the extent of innovation through and commercialisation of nanomaterials.

Diverse concepts for information gathering schemes have emerged. Some regulatory authorities sought simple notification of materials on the nanoscale as part of an existing substance or chemical authorisation process (e.g., Norway and Sweden), while others have set up traceability schemes that apply throughout a supply chain and enable the registration of nanomaterials in both raw material form and final consumer products and waste disposal contexts (e.g., France, Belgium and Denmark) (Pavlicek et al., 2020).

In 2013, France launched a mandatory declaration for nanomaterials (R-Nano, n.d.). Before April 30 each year, importers or manufacturers of nanomaterials in France must make a declaration for each nanomaterial produced, imported or distributed for the previous calendar year in quantities larger than 0.1 kg (Pavlicek et al., 2020).

Denmark set up its registration of nanomaterials (VIRK, n.d.) in 2015, Belgium in 2016 (The Federal Public Service Health, Food Chain Safety and Environment, 2021) and Sweden in 2018 (KEMI, 2020). The four schemes are similar in the sense that they all base their definitions of nanomaterial on the 2011 EC recommendation. However, there are also considerable differences between the schemes as they cover different aspects and require different information. Notably, the Danish scheme focuses on substances that are marketed to the consumer and excludes

professional use, whereas the French, Belgian and Swedish schemes cover professional uses, and consumer uses are excluded. In Europe, also Norway has a register that includes information on nanomaterials (Norwegian Environment Agency, n.d.).

According to EU legislation, nanomaterials are labelled in cosmetic, biocidal and novel food products, and food additives. **Labelling nanomaterials in consumer products** is a positive step in building knowledge about the presence of nanomaterials in products and, subsequently, waste streams. Currently, the following legal acts regulate the labelling of nanomaterials in consumer products:

- Biocidal Products Regulation (BPR) 528/2012 (European Parliament, 2012) specifies that nanomaterials used in biocidal products must be clearly indicated on their labels (Article 58(3)(d)) with the word 'nano' in brackets following the name of an ingredient. Biocidal products are defined as "any substance or mixture, in the form in which it is supplied to the user, consisting of, containing or generating one or more active substances, with the intention of destroying, deterring, rendering harmless, preventing the action of, or otherwise exerting a controlling effect on, any harmful organism by any means other than mere physical or mechanical action" or "any substance or mixture, generated from substances or mixtures which do not themselves fall under the first indent, to be used with the intention of destroying, deterring, rendering harmless, preventing the action of, or otherwise exerting a controlling effect on, any harmful organism by any means other than mere physical or mechanical action." The types of biocidal products are provided in Annex V of the BPR and are divided into four main groups: disinfectants, preservatives, pest control products, and other products (European Parliament, 2012).
- Cosmetic Products Regulation 1223/2009 (European Parliament, 2009) specifies that all ingredients containing nanomaterials must be clearly indicated (Article 19(1)(g)) in the list of ingredients with the word 'nano' in brackets following the name of an ingredient. The Regulation 1223/2009 defines the cosmetic product in Article 2 as "any substance or mixture intended to be placed in contact with the external parts of the human body (epidermis, hair system, nails, lips and external genital organs) or with the teeth and the mucous membranes of the oral cavity with a view exclusively or mainly to cleaning them, perfuming them, changing their appearance, protecting them, keeping them in good condition or correcting body odours" (European Parliament, 2009).
- Food Information to Consumers (FIC) Regulation 1169/2011 (European Parliament, 2011) specifies that all engineered nanomaterials present in food products must be clearly indicated in the list of ingredients. The word 'nano' in brackets must follow the name of an ingredient. The FIC Regulation uses the definition of 'food' laid down in General Food Law Regulation 178/2002 (Article 3), where 'food' "means any substance or product, whether processed, partially processed or unprocessed, intended to be, or reasonably expected to be ingested by humans" (European Parliament, 2002). The labelling provisions of the FIC Regulation apply to novel food and food additives as well. According to the Novel Food Regulation 2283/2015, "novel food' means any food that was not used for human consumption to a significant degree within the Union before 15 May 1997, irrespective of the dates of accession of Member States to the Union" (see European Parliament, 2015, Article 3(2)(a)). Food additives are defined in Regulation on Food Additives 1333/2008 and cover "any substance not normally consumed as a food in itself and not normally used as a characteristic ingredient of food, whether or not it has nutritive value, the intentional addition of which to food for a technological purpose in the manufacture, processing, preparation, treatment, packaging, transport or storage of such food results, or may be reasonably expected to result, in it or its by-products becoming directly or indirectly a component of such foods" (European Parliament, 2008a).

However, for other products that are not required to have a list of ingredients or composition (except those mentioned above), information on the presence of nanomaterials is not available. Several legislations specifically mention nanomaterials, in addition to the ones already stated.

For instance, in 2011, the Commission published a Regulation (EU) No 10/2011 on plastic materials and articles intended to come into contact with food (European Commission, 2011) that specifically includes provisions for nanomaterials. The EU Regulation on Medical Devices, (EU) 2017/745 (European Parliament, 2017) provides a definition of nanomaterials (in Article 2(18-21) that is based on the 2011 recommendation. Interestingly, this definition includes 'natural', which potentially could give rise to measurement issues of abrasion from medical devices not intentionally made of nanomaterials, thus giving rise to incidental nanomaterials.

The challenge for the implementation of labelling of nanomaterials in all products is related to gaps in robust and standardised methods for detecting, identifying and quantifying nanomaterials in complex matrixes of the products (Rauscher et al., 2017). So far, guidance for voluntary labelling of nanomaterials in products is provided in *CEN ISO/TS 13830 Nanotechnologies - Guidance on voluntary labelling for consumer products containing manufactured nano-objects* (European Committee for Standardisation, 2013). Furthermore, life cycle assessment methodology was adapted to address manufactured nanomaterials by the European Committee for Standardisation in *CEN/TS 17276: 2018 Nanotechnologies - Guidelines for Life Cycle Assessment - Application of EN ISO 14044:2006 to Manufactured Nanomaterials.* It allows the evaluation of the environmental performance of products containing nanomaterials throughout their life cycle (European Committee for Standardisation, 2018). These developments provide useful advice to producers of goods about sharing information on nanomaterials in their products.

Amendments to several annexes in the REACH (Registration, Evaluation, Authorisation and Restriction of Chemicals) Regulation in 2018 by the Commission Regulation (EU) 2019/1881 require more information on nanomaterials placed on the EU market (Schwirn et al., 2020; Pavlicek et al., 2020). The most profound change is that REACH Annex VI now includes a legally binding definition of nanomaterial, referred to as nanoform in the Annex, which is based on the 2011 European Commission recommendation. It should be noted that REACH does not regulate waste. However, knowledge about the production volumes of nanomaterials is useful for understanding what nanomaterials are present in waste streams. Under the REACH Regulation, from 1 January 2020, manufacturers and importers of manufactured nanomaterials are obliged to indicate if their registered substance has nanoform(s). This obligation applies if the total amount of a manufactured or imported substance (irrespectively of its form) exceeds one tonne per year. It means that for the registrants of non-nanoforms and nanoforms of the same substance, its total manufactured or imported volume determines the need for registration and information requirements (ECHA, 2019). Nanomaterial-related provisions in the REACH regulation enable ECHA to collect specific information related to nanoforms of a substance. By the end of 2020, ECHA received 190 registrations of 90 substances covering nanoforms. According to EUON estimations, 334 unique substances may occur in nanoforms (ECHA, 2021).

Annex VI of REACH defines **'nanoform**' as "a form of a natural or manufactured substance containing particles, in an unbound state or as an aggregate or as an agglomerate and where, for 50% or more of the particles in the number size distribution, one or more external dimensions is in size range 1 nm-100 nm, including also by derogation fullerenes, graphene flakes and single-wall carbon nanotubes with one or more external dimensions below 1 nm" (European Parliament, 2006; ECHA, 2019). Registrants should provide **information describing nanoform(s)**, which includes shape, particle distribution and range, crystallinity, specific surface area, surface functionalisation/treatment (ECHA, 2019). Additionally, depending on the tonnage, various **toxicological and ecotoxicological information**, as laid out in REACH Annexes VII to XI, should be provided (ECHA, 2016). Importantly, for nanoforms, REACH Annexes VII-XI include specific information requirements (e.g., dustiness) or modifications to the existing ones (i.e., adaptations or limitations of waiving possibilities) (ECHA, 2019).

Under REACH, nanomaterials can be grouped into '**sets of similar nanoforms'**, which are defined as "a group of nanoforms characterised in accordance with section 2.4 where the clearly defined boundaries in the parameters in the points 2.4.2 to 2.4.5 of the individual nanoforms within the set still allow to conclude that the hazard assessment, exposure assessment and risk

assessment of these nanoforms can be performed jointly" (European Parliament, 2006; ECHA, 2019). This option enables registrants to group nanoforms for predicting their properties, in other words, to exercise a **read-across approach** for the characterisation of nanomaterials (ECHA, 2019a).

Comprehensive information about the properties of nanomaterials, their environmental fate and toxicity should be provided by the registrants to comply with the amended REACH Regulation. To test the safety of nanomaterials, standardised **test guidelines** should be used. Importantly, the OECD test guidelines enable mutual acceptance of data, i.e., sharing test data between OECD countries and, consequently, reducing testing on animals. The OECD Working Party on Manufactured Nanomaterials (WPMN) is continuously working on the adaptation of existing standardised test guidelines and the development of new ones to address the issues of nanomaterials (Rasmussen et al., 2019). EUON tracks the development of test guidelines for regulatory purposes and provides an up-to-date list to facilitate the registration of nanomaterials (EUON, 2020). Currently, together with partners (including several Directorates-General of the European Commission, eighteen European countries, non-governmental organisations, universities, and industry), ECHA takes part in the **Malta Initiative**. It aims to **update existing and develop new OECD Test Guidelines to adapt them for nanomaterials** and lay the ground for the practical implementation of the REACH Regulation (Federal Ministry for the Environment, Nature Conservation and Environmental Safety, 2020).

The importance of international initiatives in adaptation and development of new standardised test guidelines for nanomaterials was confirmed by recent research that analysed the availability and suitability of the methods that are necessary to carry out tests for complying with the information requirements for registration of nanoforms set in the REACH Annexes VII-XI (Nielsen et al., 2021). The study found that to fulfil 20 information requirements that are specific to nanoforms:

- International test guidelines or standards were available for three information requirements ('Further information on physicochemical properties', 'Simulation testing on ultimate degradation in surface water' and 'Hydrolysis as a function of pH').
- Test guidelines under development were available for five information requirements (e.g., methods related to solubility and dissolution rate, dustiness; characterisation of particle size distribution, shape and specific surface area).
- Modified standard methods, advice, best practices in the scientific literature or OECD, ECHA guidance or technical reports/specifications by ISO were available for eight information requirements. These methods are related to growth inhibition studies on aquatic plants, short-term toxicity testing on fish and invertebrates, and activated sludge respiration inhibition testing, methods to assess bioaccumulation in aquatic species and effects on terrestrial organisms, methods for description of surface functionalisation or treatment, characterisation of particle aggregation and agglomeration.
- It requires more research to adopt adequate regulatory methods for four requirements, including assessing adsorption/desorption and the partition coefficient n-octanol/water and abiotic transformations of NMs in environmental media (Nielsen et al., 2021).

Work in developing standardised testing guidelines that can address specific features of nanomaterials continues. Some of these are required to fulfil the REACH standard information requirements.-Researchers argued that fate models or probabilistic material flow analysis models that are currently used for developing exposure scenarios could not be used alone to justify that there is a low or no exposure to nanomaterials (Nielsen et al., 2021).

There are a lot of regulatory and standardisation initiatives in the EU to make information about manufactured nanomaterials accessible, and the amendments to the REACH Regulation are expected to increase the availability of information on nanomaterials in the EU. It should help to increase knowledge about nanomaterials on the market and in waste streams. For identifying waste streams composed of end-of-life products containing nanomaterials, additional information about the presence of nanomaterials in products is required. Currently, product labelling for food, biocidal and cosmetic goods is mandatory. For other goods, however, producers provide information about nanomaterials only on a voluntary basis.

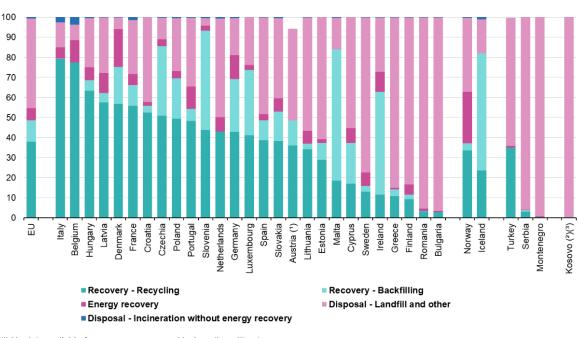
4. Nanomaterials in Waste Management Systems

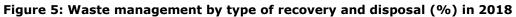
OECD (2016) discussed three ways of managing waste – recycling, incineration, and landfilling, and analysed the behaviour and fate of nanomaterials in these processes. Additionally, waste treatment in sewage treatment plants and agricultural applications was covered. In a recent review of the fate and behaviour of nanomaterials in municipal solid waste, Part et al. (2018) discussed the biological treatment of food packaging, food and beverages and other waste that could potentially contain nanomaterials. Biological waste treatment involves the decomposition of biodegradable wastes by living microbes and is applied in wastewater treatment and landfills.

This chapter aims to discuss the routes of nanowastes to waste treatment facilities and their behaviour during incineration, recycling, landfilling and wastewater treatment, and the exposure of workers to nanomaterials during waste treatment operations, emissions of nanomaterials to the environment and the best available technologies to handle them. A case study on recycling nanomaterials is provided in Annex 5.

4.1 Routes of nanomaterials to waste management facilities

According to Eurostat, in 2018, 2,149 million tonnes of waste were treated in the EU-27. In 2004-2018 the volume of waste recovered, recycled, and used for backfilling or incinerated grew by 34%. In the same period, the total share of disposed waste decreased by 4%. However, there are significant differences in waste management across the EU, with disposal still playing an important role (see Figure 5) (Eurostat, 2020).





(1) No data available for energy recovery and incineration without energy recovery.

⁽²⁾ No data available for incineration without energy recovery.

(³) This designation is without prejudice to positions on status, and is in line with UNSCR 1244/1999 and the ICJ Opinion on the Kosovo Declaration of Independence.

eurostat O

Source: Eurostat, 2020

Figure 5 shows that despite the increasing role of recovery and recycling, disposal and, especially, landfilling is still a significant waste management route in many European countries.

The data on biological treatment activities are available from the European Compost Network. In 2019, 47.5 million tonnes of biowaste (40% of all collected biowaste) were biologically treated predominantly by composting, but also by anaerobic digestion and by a combination of composting and anaerobic digestion (Siegert et al., 2019).

Nanomaterial flow models have been developed to understand the routes of nanomaterials through various waste management processes and facilities and evaluate their fate. **Material flow analysis models** (MFA) cover all stages, from production to disposal and/or release to the environment. These follow a generic modelling approach that allows for describing and calculating any stocks and flows of materials. First, the problem and the system's boundaries (e.g., geographical, temporal, or functional etc.) are defined, then the stocks and flows of materials are quantified, and finally, the results are presented and assessed. Importantly, the model relies on the conservation of mass, i.e., a complete mass balance through the system processes, although transformations of materials will occur. Mass balance of inputs, outputs and stocks in the system processes is used to verify the model results (Furberg et al., 2016). MFA models are often used for decision-making by regulators and other stakeholders (Sorensen et al., 2019). For the purposes of this study, material flow analysis provides useful information about the routes of nanomaterials to different waste facilities and the environmental compartments (e.g., water, soil, and air). However, the limitations of MFA in the context of nanomaterials should be understood to interpret the MFA findings correctly.

For MFA of nanomaterials, the lack of primary quantitative information about nanomaterials and varying complexity of models (e.g., in terms of considering various physical and chemical properties of nanomaterials and their transformations) poses inherent limitations to the validity of the estimations (Furberg, 2016; Wigger et al., 2020; Nowack, 2017). Nowack (2017) reported that the following three parameters contributed the most to the uncertainties in MFA estimations: production volume of nanomaterials, distribution of the mass of nanomaterials to product categories and releases of nanomaterials from products and application. However, there are also medium level uncertainties in other parameters, such as transfer factors during recycling and environmental compartments. Importantly, the quantitative data about the production volumes of nanomaterials and their presence in the products are mostly absent. To collect this information, the researchers rely on available estimations, fragmented data in scientific publications, expert opinions and market reports that lead to high uncertainty (see the more detailed discussion in section 3.3 of this report). Nowack (2017) reported that MFA rarely includes important parameters of nanomaterials (e.g., form, size distribution, etc.) and does not consider nanomaterial transformations (e.g., some models consider dissolution, while others do not). Most researchers emphasise that the models were never validated using analytical measurements to show whether the model accurately represents the real world (Sorensen et al., 2019; Nowack, 2017). Importantly, over time MFA models for nanomaterials have been significantly improved and made more complex by considering various parameters. For instance, dynamic probabilistic MFA considers that some products containing nanomaterials enter waste streams after a certain period (e.g., construction and demolition waste) and make appropriate corrections in releases over time (Wigger et al., 2020). In a recent paper, Zheng and Nowack (2021) included particles size distributions in the MFA of nano titanium dioxide.

Because of the absence of quality input data, the results of MFA modelling exercises should be taken with caution. For instance, Rajkovic et al. (2020) reported relative uncertainties above 0.5, which showed that the standard deviations of probability distributions generated in a modelling exercise were at least half of their means. Therefore, the results of MFA provide a qualitative overview of mass flows, but the uncertainties in production volumes limit the quantifications.

The most recent studies covering European countries are Adam et al. (2021), Zheng and Nowack (2021) and Rajkovic et al. (2020). These and similar earlier studies employ different variations of material flow analysis (MFA). According to Wigger et al. (2020), between 2008-2019, 31% of studies calculated the mass flows of selected elements along different pathways in the European Union, while 3% had a global focus. Basic information and findings of the newest MFA studies with a European focus are summarised in Table 5.

European Union (EU-28), Norway and Switzerland 2000-2020 Ag, TiO ₂ , ZnO Integrated dynamic probabilistic material flow analysis (IDPMFA)	Only the case of the UK was considered as an example. The main routes were: ZnO: WWTP*** (1689 t), WIP**** (366 t), landfills (248 t) Ag: reprocessing (270 kg), reuse (160 kg), landfills (80 kg) TiO ₂ : reprocessing (1.46 t of sorted metal; 1.13 t of sorted glass and 0.96 t of sorted plastic), reuse (2.59 t) and landfill (0.58 t).
Europe TiO ₂ pigments 2016 Size-specific, dynamic, probabilistic MFA (ss-DPMFA)	WWTP (4640 t), sorting (2160 t) and reprocessing (1060 t), WIP (1400 t) were the most significant technical compartments for titanium dioxide pigments, with landfills (80000 t) and sludge-treated soil (40760 t) – as the largest environmental compartments.
Europe 2000-2020 Ag, TiO ₂ , ZnO, CNT** Municipal solid waste, construction and demolition waste, waste electrical and electronic equipment, other waste (e.g., metals, vehicles) Dynamic probabilistic MFA (DPMFA)	Ag: WWTP (40 t); reprocessing (45 t); landfills (105 t), TiO ₂ : WWTP (45000 t); reprocessing (24000 t); WIP (16000 t); landfills (69000 t), ZnO: WWTP (9000 t); reprocessing (2050 t); landfills (2077 t); sorting (1030 t), CNT: sorting (132 t); WIP (300 t); landfills (1042 t).
Europe 2013 Nano silica Probabilistic MFA (PMFA)	Recycling (135300 t); cement kiln (78900 t); WIP (101830 t); landfills (121700 t)
Europe Not specified Wood coatings containing CuO; car bumpers with diketopyrrolopyrrole (DPP) or Fe ₂ O ₃ ; polymeric car parts with CNT; pancake mixtures with SiO ₂ Probabilistic MFA (PMFA)	CuO: WIP (48 t); recycling and reuse (17 t); landfills (33 t), DPP: recovery (10 t); WIP (11 t); elimination (10 t), landfill (6.8 t), Fe_2O_3 : recovery (10 t); WIP (11 t); landfills (13 t), CNT: recovery (1.5 t); WIP (1.7 t); elimination (1.5 t), landfill (1 t), SiO_2 : WWTP (16 t); WIP (7 t); landfills (7.4 t).
ETAST EXPraa(C EXFF EF/E())F	2000-2020 Ag, TiO ₂ , ZnO Integrated dynamic probabilistic material flow analysis (IDPMFA) Europe FiO ₂ pigments 2016 Size-specific, dynamic, probabilistic MFA (ss-DPMFA) Europe 2000-2020 Ag, TiO ₂ , ZnO, CNT** Municipal solid waste, construction and demolition waste, waste electrical and electronic equipment, other waste (e.g., metals, vehicles) Dynamic probabilistic MFA (DPMFA) Europe 2013 Nano silica Probabilistic MFA (PMFA) Europe Not specified Nood coatings containing CuO; car pumpers with diketopyrrolopyrrole (DPP) or Fe ₂ O ₃ ; polymeric car parts with CNT; pancake mixtures with SiO ₂

Table 5: Nanomaterial flow modelling studies

CNT – carbon nanotubes; *WWTP – wastewater treatment plant; ****WIP – waste incineration plant

Table 5 shows that a limited number of nanomaterials was considered in the latest studies. Having analysed 35 modelling studies, Wigger et al. (2020) reported the focus on other nanomaterials, such as quantum dots, fullerenes, nano gold, and cerium oxide.

Depending on the type of nanomaterials, products and waste streams in focus, nanomaterials can follow different routes to waste management facilities. However, it can be seen that **recycling (i.e., sorting and reprocessing), wastewater treatment, incineration and landfilling are predominant technical compartments** for various types of nanomaterial-containing waste in different studies. Interestingly, each study provided innovative solutions. For instance, Caballero-Guzman and Nowack (2018) introduced the element 'elimination' that considered transformations of nanomaterials into bulk forms (e.g., because of combustion). Adam et al. (2021) and Zheng and Nowack (2021) improved the modelling exercise itself.

Another tool that provides estimations of the flows of wastes containing nanomaterials to waste management facilities is NanoDB. It gives an overview of waste flows to four waste management options (incineration, recycling, landfilling, anaerobic digestion/composting). Figure 6 provides a snapshot of such routes for a range of nanomaterials frequently used in consumer products.

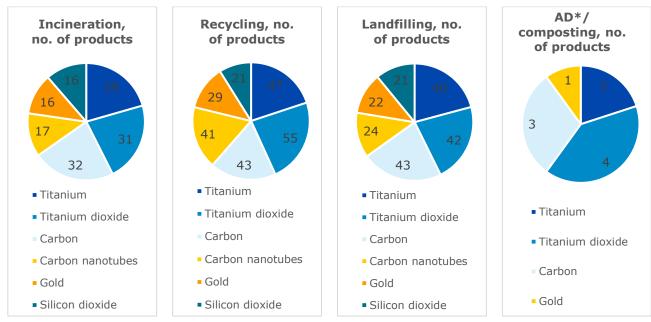


Figure 6: Waste treatment management options for nanomaterials in the European Union

Source: the NanoDB, accessed 12 March 2021

Note: *AD – anaerobic digestion

It should be noted that for the majority of nanomaterial-containing products listed in NanoDB, the route to waste treatment facilities is still unknown. However, it makes a useful summary for well-known and frequently mentioned nanomaterials and products that contain them.

4.2 Behaviour and fate of incinerated nanomaterials

At waste incineration plants, waste is combusted at high temperatures, typically 850-1,100°C, with higher temperatures for certain hazardous wastes (Joint Research Centre, 2019). As an outcome of combustion, polluted flue gas is produced. This undergoes a cleaning process, and cleaned gas is released into the atmosphere. Two types of residues emerge after the incineration: bottom ash (the combustion residues) and fly ash (flue gas cleaning residues). Both types of residues can be landfilled or reused (OECD, 2016).

Different conditions of the incineration, physical and chemical processes and properties of nanomaterials can lead to various outcomes such as the concentration of nanomaterials in certain types of incineration residues and/or their emissions to the environment. During the incineration, the **physical changes of particles depend on nucleation, aggregation, and**

agglomeration processes as well as on high-temperature transformation and heterogeneous reactions with gaseous species (Part et al., 2018). Ounoughene et al. (2017) reviewed the literature on the incineration of waste containing nanomaterials to investigate the potential methodology for assessing and managing risk to human health and the environment. The study has indicated that **nanostructures can be transformed or destroyed during the combustion process or remain unchanged** (Ounoughene et al., 2017). For instance, nanoparticles such as TiO₂, CeO₂ and sometimes nanosilica remained the same, nanoclays aggregated but retained their nanostructure, and organic nanomaterials such as carbon nanotubes, fullerene, and black carbon were usually destroyed (Ounoughene et al., 2017). However, the knowledge and understanding of the behaviour of **nanocomposites** during the incineration process is lacking. Hence, chemical, physical, and morphological changes of nanocomposites such as nanofillers, their release with by-products in soot or residue ash, and the hazards arising from these by-products need to be investigated, all the more so nanocomposites are becoming widely used in polymer matrices to enhance mechanical properties or improve fire behaviour (Chivas-Joly et al., 2019).

Temperature is an important factor determining the fate of nanomaterial in the incineration process, as nanoparticles have different melting and boiling points (Ounoughene et al., 2017). Thus, nanoparticles with lower boiling points than the temperature inside the furnace will most likely be destroyed or evaporated and potentially condensate in the flue gas stream when it cools and would not return to its nanoscale form. Similarly, molten nanomaterials would not return to their original form, species, or shape (Part et al., 2018). Redox reactions and solid-phase transformations also influence the fate of nanomaterials during incineration (Part et al., 2018).

Another important behaviour of nanoparticles in the incineration process is their **association with and incorporation into materials**, which determines whether they will be easily released from their product matrix or a substrate, increasing the probability of being emitted with the flue gas, or they will accumulate in the bottom ash as a fused-in component. Furthermore, some nanomaterials can influence the combustion process by either increasing or decreasing emissions. For instance, metal oxide nanoparticles decreased the emissions of polycyclic aromatic hydrocarbons, whereas nano-silver enhanced overall emissions (Part et al., 2018). Overall, the incineration processes lead to changes in the physical and chemical properties of nanomaterials that can influence their fate and, subsequently, emissions. Individual nanomaterials may be destroyed during the thermal treatment, whereas others may largely survive. The fate depends on the properties of the nanomaterials themselves, but also on the complex waste matrices surrounding them.

In this report, several case studies were identified that focused on the combustion of zinc, copper, and its compounds (Tarik & Ludwig, 2020; Foppiano et al., 2018; Wielenski et al., 2019), nanocoatings (Singh et al., 2019), cerium oxide (Gogos et al., 2018), nanosilver (Meier et al., 2016), titanium dioxide (Wielinski et al., 2021; Tarik & Ludwig, 2020; Oischinger et al., 2019), and nanocomposites (Chivas-Joly et al., 2019; Ounoughene et al., 2019). The studies are summarised in Table 6.

Source	Scope	Summary of findings
Wielinski et al., 2021	Transformation of titanium dioxide in the incineration of sewage sludge	The study found significant changes in titanium speciation and reactions of titanium dioxide particles to phases on the hematite-ilmenite solid solutions series or substitution of titanium with iron in hematite. Faster reaction kinetics was observed for anatase in comparison to larger rutile particles. These transformations could lead to releases of titanium to the environment from the ultimate disposal sites.

Table 6: Studies on behaviour and fate of nanomaterials under thermal treatment

Source	Scope	Summary of findings
Tarik & Ludwig, 2020	Release of zinc oxide , copper oxide and titanium dioxide in cellulose-based matrices containing KCl and/or SiO2 during thermal treatment	No Ti evaporation was observed at high temperatures (>700 0C). In the case of copper and zinc, matrix compositions (chlorine and silicon) played a key role in their evaporation at high temperatures.
Singh et al., 2019	Decomposition of nano- enabled coatings in combustion	There is release potential for metal oxide (Fe2O3 and CuO) and organic (DPP) nanofillers. The study showed that inorganic nanofillers remained in residual ash as loosely held nanoparticles, while organic nanofillers were completely combusted.
Wielenski et al., 2019	The behaviour of copper and zinc during incineration of the digested sewage sludge	The study indicated the partial sequestration of copper and zinc into oxide mineral structures that could be possibly nanoparticulate.
Foppiano et al., 2018	The behaviour of zinc oxide in wood combustion	The study confirmed the presence of incidental zinc oxide nano-objects upon combustion of the wood nanowaste model and emphasised the possibility of the formation of secondary nanomaterials. Due to the toxicity of zinc oxide, Foppiano et al. (2018) recommended addressing the emissions of small to medium waste management plants that may lack an efficient filtering system.
Gogos et al., 2019	Transformation of cerium oxide nanoparticles in the combustion of digested sewage sludge	The study showed the reductive decomposition of cerium oxide nanoparticles and the transformation of Ce(III) into a mineralogical phase with probably allanite-like local Ce(III) coordination.
Meier et al., 2016	The morphological and chemical changes of sulphidised silver nanoparticles in sewage sludge during the incineration	The study revealed that metallic Ag-NP transformed to Ag2S-NP during wastewater treatment; however, a rapid formation of metallic Ag from Ag2S-NP was identified during sludge incineration, whereas Ag2S was absent.
Ounoughene et al., 2019	The behaviour and fate of nanosilica from polydimethylsiloxane nanocomposites during the incineration	The study results showed that due to its high melting point (\sim 1700°C), nanosilica particles were persistent in the residues, and the fumes, silicon oxycarbide SixOyCz particles were also found.
Chivas-Joly et al., 2019	The identification of Al- based nanofillers modification and related hazards during thermal degradation of industrial nanocomposites	Evaluation of cytotoxicity responses of pristine nanofillers, residual ash and soot showed that safe boehmite nanoparticles become toxic due to a chemical modification after the incineration process.

Studies by Gogos et al. (2019) and Wielinski et al. (2019, 2021) were conducted in pilot-scale facilities using samples from full-scale wastewater treatment facilities. Other studies discussed in Table 6 were carried out in a laboratory setting. The focus on specific nanomaterials was motivated by their frequent use (Meier et al., 2016; Singh et al., 2019; Tarik and Ludwig, 2020), toxicity and implications for emissions to the environment (Chivas-Joly et al., 2019; Foppiano et al., 2018; Ounoughene et al., 2019), agricultural re-use of wastes containing nanomaterials

(Wielenski et al., 2019), and growing production rates (Gogos et al., 2018; Wielinski et al., 2021).

The literature search identified only one recent study by Oischinger et al. (2019) that was conducted in an **actual waste management plant**. This study examined emission pathways of nano-titanium oxide in the waste incineration plant. It determined that most titanium dioxide was in the bottom ash, and a smaller part was detected in the products of the flue gas cleaning. In the clean gas, the presence of titanium dioxide was negligible. The researchers postulated that this was due to the high efficiency of the fabric filter employed for flue gas cleaning. The study results were similar to the findings of the previous laboratory studies. Comparing their results to other plant-based studies, the researchers highlighted the similarities in the fate of nano titanium dioxide, cerium oxide and barium sulphate (Oischinger et al., 2019). Additionally, Part et al. (2018) referred to studies carried out in commercial incineration plants by Börner et al. (2016) and Baran and Quicker (2016).

The **toxicity** of incineration residues from the combustion of waste containing nanomaterials has not been widely investigated to date; however, few studies assessing the toxicity of nanomaterial by-products under experimental conditions have been identified (Chivas-Joly et al., 2019; Stueckle et al., 2019; Vejerano et al., 2015). Vejerano et al. (2015) investigated the toxicity of particulate matter from the combustion of waste containing nanomaterials to human lung epithelial cells. The toxicity and oxidative potential of pure nanomaterials and plastic and paper waste containing nanoparticles, such as Ag, TiO₂, NiO, fullerene, Fe₂O₃ and quantum dots were assessed. The study showed that the presence of nanoparticles did not significantly modify the genotoxicity or cytotoxicity of the particulate matter and that the low concentrations of these nanomaterials in waste should not exacerbate hazards posed by particulate matter.

In the study by Stueckle et al. (2019), the toxicity of nanoclays and their by-products was examined in order to contribute to the assessment of the life cycle of these materials. The results showed that the exposure of human lung epithelial cells to pristine nanoclays caused increased cytotoxicity, acute loss of monolayer and cell death, whereas incinerated nanoclays caused cell monolayer damage and necrosis with little evidence on recovery of monolayer (Stueckle et al., 2019). The toxicity of Al-based nanocomposites was assessed by Chivas-Joly et al. (2019). The results indicated that the residual ash of Al-based nanocomposites was not cytotoxic; however, the soot was. What is more, the study drew attention to the fact that pristine nanoparticles may become cytotoxic due to modified physicochemical parameters during the incineration process (Chivas-Joly et al., 2019). Overall, these experiments were case studies of the toxicity of specific nanomaterials and under different experimental conditions. There is a need for further studies on the toxicity and cytotoxicity of nanoparticles and nanocomposites during the incineration process.

4.3 Behaviour and fate of nanomaterials in recycling

Recycling of waste includes a set of processes and technologies for collecting, re-using or reprocessing materials or products that otherwise would be disposed of. Recycling encourages extracting additional value from a material or a product (Polonsky, 2014). The WFD specifies that recycling covers any recovery operation that reprocesses waste into products, materials, or substances regardless of whether they are used for original or other purposes. However, the Directive does not include the reprocessing of materials for later use as fuels or for backfilling.

With the increasing volumes of waste combined with the environmental pollution caused by its disposal, the significance of recycling as a waste minimisation strategy has grown. The European Union set a number of targets for waste recycling in the policy documents:

• 70% of all packaging waste must be recycled by the end of 2030. By 2030 all plastics packaging on the EU market must be reused and recycled cost-effectively (European Commission, 2018a).

- 65% of municipal solid waste must be recycled by 2035 (European Commission, 2018b).
- A minimum of 55% to 80% of waste electrical and electronic equipment (depending on the type) should be recycled starting from 2018. For instance, for IT and telecommunication equipment 80% target is applied, while 55% for lighting equipment and electronic tools etc. (European Commission, 2012).

According to Eurostat (2020a) and the European Environmental Agency (2020a), 66% of packaging waste was recycled in 2018 (EU-27), 43% of municipal solid waste (EU-28, 2018), and 31% of waste electrical and electronic equipment – in 2017 (EU-28).

In 2017, Eunomia and European Environmental Bureau (Gillies et al., 2017) prepared a report and established ten leaders in recycling municipal solid waste on a global scale. The top three countries included Germany (recycling rate of 56.1%), Austria (53.8%) and South Korea (53.7%). The recycling rates were compiled from several sources and based on the specific concept of municipal solid waste, so these findings may not be comparable with the Eurostat statistics presented above.

According to Polonsky (2014), there are different recycling techniques (see Figure 7) for extracting value from products and materials.



Figure 7: Waste recycling techniques

Source: adapted from Polonsky, 2014

As shown in Figure 7, the simplest way of recycling a product is by re-using it for the same purposes by other consumers (e.g., collecting and reusing products on the second-hand markets). In other cases, the products are re-used for a different purpose. Often the end-of-life products are reprocessed to provide raw materials necessary for new ones – e.g., recycled paper or plastics. In case the product contains valuable substances or materials, recycling could be targeted at valuable component extraction. More sophisticated recycling technologies involve synergies of several industrial processes where the waste of one process is utilised as a raw material for another one (Polonsky, 2014).

Material flow analysis models show that different waste streams that contain nanomaterials are directed to recycling (see section 4.1). However, **the literature about the recycling of waste**

containing nanomaterials is scarce. The scarcity of the literature on the topic was reported in the extensive review of the behaviour and fate of nanomaterials in municipal solid waste by Part et al. (2018).

The literature search for this study identified literature reviews that report about the use of nanomaterial-containing waste for extracting non-nanomaterial substances and nanomaterials (Liu et al., 2019) and the synthesis of nanomaterials from waste that do not necessarily contain nanomaterials (or this feature of waste is not discussed or considered important), such as metal waste, battery waste and waste electrical and electronic equipment, industrial waste and sludge, sewage sludge (Dutta et al., 2018; Bhattacharya et al., 2020; Yuan & Dai, 2017). It should be noted that terminological ambiguity exists in these papers that often give different meanings to 'recovery', 'recycling' and 'synthesis'. For instance, the paper by Bhattacharya et al. (2020) focuses on "metal-oxide nanomaterials recycled from e-waste and metal industries" and sets the objective to discuss "promising routes for obtaining high-quality metal-oxide nanoparticles and nanowires", i.e., their synthesis. Similarly, Dutta et al. (2018) focus on the "recycling battery and electronic wastes for the recovery of nanomaterials" while using the terms 'synthesis'' and 'recovery' synonymously. So, in one case, the researchers discuss recycling nanomaterial containing waste (e.g., Liu et al., 2019), while in the second case, the discussion is about recycling waste that does not necessarily contain nanomaterials for the production of nanomaterials. So, the second case is out of the scope of this literature review.

Not much could be concluded from the narrative literature review by Liu et al. (2019), which is motivated by the search for ways to reuse highly polluted sludge containing nanomaterials and is mainly focused on the ways of extraction of heavy metals.

Importantly, little is known both about the behaviour and fate of nanomaterials in recycling and the effect of their presence on the recycling of waste. According to the report by the United Nations (2018, p. 10), the lack of evidence about the effects of nanomaterials on the recycling of waste can be caused by recycling processes that "involve mainly mechanical and thermal treatments rather than complex chemical transformations that could be affected by the presence of ENMs and levels of ENMs in recycled materials are at present relatively low".

4.4 Behaviour and fate of landfilled nanomaterials

Landfilling of waste is the least desired waste management option and may have many negative environmental impacts. However, a significant volume of waste produced in the European Union is still being landfilled. According to Eurostat (2020a), in 2018, 39% of all waste generated in the EU-27 was disposed of in landfills. The landfilling preferences vary significantly across the EU Member States. For instance, in 2018, only 8% of waste was landfilled in Belgium, 12% - in Italy, while in Romania, the share of landfilled waste reached 94% and in Bulgaria – 85% (Eurostat, 2020).

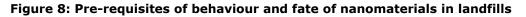
Nanomaterials arrive at landfilling sites directly as manufacturing wastes or part of the products that reached their end of life. In the latter case, waste could be treated in other facilities (e.g., incineration, wastewater treatment plants) before being landfilled (Part et al., 2018).

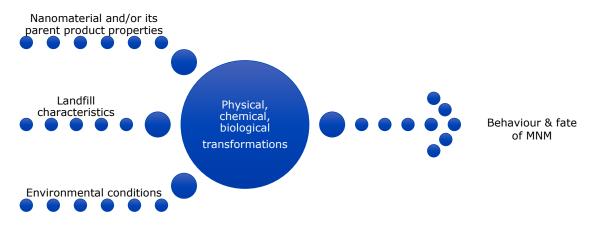
Several studies were conducted to identify the **presence** of nanomaterials in wastes disposed of in landfills. Mitrano et al. (2017) focused on the presence and mobility of the following nanomaterials: silver, titanium, zinc, copper, iron, and cerium, in the leachates of municipal solid waste incineration slags. The study analysed the simulated leachates and the leachate samples and slags collected from the Swiss landfill for municipal solid waste incineration residues. The researchers identified the presence of zinc, silver and copper in the simulated and natural leachates and indicated the abundance of titanium in the natural leachates. Hennebert et al. (2017) studied samples of non-hazardous waste landfill sludges in France and identified the moderate concentration of copper, zinc, nickel, and antimony in landfill sludge. The research

found that copper, zinc, and nickel concentrations were comparable to those in soil, compost, or sediments. Copper, zinc, and nickel were mainly in colloidal form.

The extensive literature reviews Part et al. (2018) and Lead et al. (2018) summarised major factors and processes that are crucial for understanding the **behaviour and fate of nanomaterials in landfills** (see Figure 8 overleaf).

As shown in Figure 8, first of all, the properties of a nanomaterial affect its transformation behaviour and fate. Size, shape, composition, and surface properties are essential to understand their potential transformations and related risks under various conditions. As nanomaterials are often contained in different products, therefore, it is essential to know how they are embedded in the parent products (e.g., bounded within products, in coated surfaces, dispersed in bulk products etc.). Second, the type of landfill, its age and operation peculiarities influence the transformation and fate of nanomaterials. The processed waste characteristics and leachate properties are important parameters for judging the potential transformations and routes of nanomaterials within the landfill system and the environment. And finally, each landfill operates under specific environmental conditions that could potentially affect transformations of nanomaterials (e.g., washout, weathering, etc.) (Part et al., 2018; Lead et al., 2018).





Source: Lead et al., 2018; Part et al., 2018

As an outcome of the effect of all factors, different transformations take place. According to Lead et al. (2018), they include:

- Physical transformations that cover aggregation, agglomeration, sedimentation, and deposition.
- Chemical transformations dissolution, oxidation and sulphidation, photochemical reactions and corona formation.
- Biological transformations biodegradation and biomodification.

These processes explain the mobility, persistence of nanomaterials in waste and their reactions with other substances in landfills that might lead to nanomaterial emissions, increase or decrease in their toxicity, and the impact on waste treatment processes.

This literature review identified seven case studies focused on the behaviour and fate of specific nanomaterials in landfill waste (see Table 7).

Nanomaterial	Study scope	Source
Titanium dioxide	Synthetic leachates of incinerated waste	He et al., 2017
	Leachates of the Swiss construction and demolition landfill	Kaegi et al., 2017
	Fresh municipal solid waste	Dulger et al., 2016
Zinc oxide	Landfill leachates containing heavy metals	Li et al., 2020
	Fresh municipal solid waste	Sakallioglu et al., 2016
Quantum dots	Leachates from the Austrian municipal solid waste landfills	Part et al., 2020
Silver	Releases of nanosilver from textiles at the stage of active use and landfilling	Mitrano et al., 2016

Table 7 shows that identified studies reveal a broad diversity of goals and study settings. Some of the studies were experiments that simulated landfill operations (e.g., Dulger et al., 2016; Sakallioglu et al., 2016; Mitrano et al., 2016), leachates (e.g., He et al., 2017; Li et al., 2020) or analysed leachate samples from the operating landfills (e.g., Kaegi et al., 2017; Part et al., 2020). Studies are also different in scope (see Table 4-4) and methods. For instance, Kaegi et al. (2017) and Part et al. (2020) performed long-term analysis (one year and 180 days, respectively), while Dulger et al. (2016), Sakallioglu et al. (2016) and Mitrano et al. (2016) conducted short-term experiments. We can summarise that, currently, case studies that focus on nanomaterials used in high volumes (except quantum dots) are prevalent; however, there is a lack of comparable studies covering a broader spectrum of nanomaterials to allow a systematic approach to the fate and behaviour of nanomaterials in landfills.

Li et al. (2020) studied the effect of heavy metals on the aggregation, sedimentation, and dissolution of zinc oxide in landfill leachates. According to the study, in the fresh leachate, the presence of Cr(VI) ions leads to aggregation of zinc oxide, while Cu(II) improved the concentration of the dissolved zinc from zinc oxide. The presence of Cr(III) increased the sedimentation of zinc oxide. The differences in effects were observed in fresh and aged leachates.

Dulger et al. (2016) conducted a short-term experiment to analyse the leaching potential of titanium dioxide in fresh municipal solid waste and found that most titanium dioxide remained in the waste. All components of municipal solid waste contributed to the retention of titanium dioxide. Sakallioglu et al. (2016) found that 80-93% of zinc oxide remained in the solid waste in a similar experiment.

He et al. (2017) studied the behaviour of titanium dioxide in the leachates of incinerated waste. In the study, titanium dioxide was introduced to synthetic leachate. The results demonstrated the tendency of titanium dioxide to agglomerate (depending on the ionic strength, ionic composition and pH of the leachate). Consequently, titanium dioxide is likely to remain in the landfill. The behaviour of titanium dioxide was studied by Kaegi et al. (2017). In this case, samples of leachate were collected for one year from the Swiss construction and demolition landfill. Findings demonstrated the low amount of titanium dioxide (5 g in 2014) released from the landfill to the aquatic environment. However, according to the authors, with the increasing use of titanium dioxide in construction, these numbers could grow. The effect of titanium dioxide released into the environment should also be considered in the long-term perspective and compared to the natural TiO_2 abundance in surface waters.

Part et al. (2020) investigated the fate of semiconductor quantum dots exposed to leachates from Austrian landfills that contained municipal solid and bulky wastes. The study found that the behaviour and fate of quantum dots depended on the type of particle coating, temperature, and composition of the leachate. The outcomes showed either sedimentation or degradation behaviour of the analysed quantum dots models. The researchers suggested thermal pre-treatment or supplementary leachate treatment to prevent the mobility and persistence of quantum dots in an aqueous environment. Additionally, the labelling of products containing potentially hazardous nanomaterials could be an effective solution to separate their collection and treatment.

Mitrano et al. (2016) analysed the behaviour of nanosilver in textile during their active use and landfilling. The simulation of nanosilver-containing textile washing and landfilling showed that nanosilver release mainly occurred at the stage of active textile use; however, minor releases of nanosilver were still observed at the stage of simulated landfilling. However, the experimental setting substantially differed from the real environmental conditions, challenging the transfer of the results to field-scale landfill settings.

Additionally, contemporary **landfills often use biological treatment** facilities to enhance the disposal of waste containing organic components. Examples of **solid waste that contains organic components** are food waste, food packaging (e.g., plastics, paper), textile, garden/park waste, biosolids, sewage sludge, etc. (Part et al., 2018; United Nations, 2018). Nanomaterials are present in municipal solid waste as shown in sections 3.1 and 4.1; they also could be abundant in sewage sludge (United Nations, 2018). Biological treatment is used to stabilise and/or reduce the volume of the organic constituent of waste. A substantial decrease in the waste mass could be achieved; therefore, biological treatment contributes to more sustainable waste disposal in landfills (Trulli et al., 2018). Often biological treatment facilities are installed to convert organic waste to energy (e.g., methane as an energy carrier) (Uyguner-Demirel et al., 2017).

Biological waste treatment involves the decomposition of biodegradable wastes by living microbes (bacteria, algae and/or fungi), which use biodegradable waste materials as a food source for growth and proliferation. Specific microorganisms could perform the biological treatment of waste under the presence and/or absence of oxygen (e.g., bacteria – aerobically or anaerobically; algae, fungi - aerobically). According to the main types of biological treatment conditions, one can distinguish two main classes of biological treatment of waste: aerobic – when microorganisms break down biodegradable waste in the presence of oxygen (Samer, 2015). For instance, composting is an aerobic process, so oxygen accessibility is essential. Digestion can be either aerobic or anaerobic but is more often an anaerobic process (aerobic digestion is much more energy intensive) (Kosseva, 2020).

The most extensive review on the behaviour and fate of nanomaterials in the biological treatment of municipal solid waste was performed by Part et al. (2018), who provided an overview of research publications for the last two decades. The review analysed the available research on treating waste under aerobic and anaerobic conditions. It found that the **laboratory studies that mainly focused on biodegradable polymers containing various nanomaterials (e.g., nano-silver, nanoclays, etc.) did not show any negative impact of nanomaterials on the biodegradation of waste in composting**. The contradictory results were obtained for nano-silver and its possible negative influence on the processes of organic decomposition of waste.

The studies on **the influence of nanomaterials on the biodegradation of waste under anaerobic conditions** focused on understanding the mechanisms of ecotoxicity of nanomaterials. Part et al. (2018) reported on the inhibitory effect of nano-silver, copper nanomaterials, nano zinc and titanium oxides and fullerenes on microorganisms. However, the findings of different studies varied. In the case of nanosilver and copper-based nanomaterials, the inhibitory effect was due to high solubility and manifested in an aqueous phase while it was absent in soil, sediments, or sludge. The effect of nano-silver and zinc oxides depended on their concentration, while the negative influence of titanium dioxide and fullerenes was preconditioned by the nature of biological treatment processes and environmental conditions. The review by Part et al. (2018) shows the complexity of conditions and factors that lead to adverse effects of nanomaterials on anaerobic processes. Additionally, the available research studies mechanisms of nanotoxicity under varying conditions. It is not clear if the experiments were conducted with pristine nanomaterials or those that transformed under realistic conditions; therefore, contradictory results are possible.

Several systematic literature reviews focused on the **metal/metal oxides and other conductive nanoparticles** (Chandrakant et al., 2021; Ye et al., 2021; Zhu et al., 2021; Li et al., 2021) **as additives that could improve** the efficiency of anaerobic digestion and increase the production of biogas or methane. The studies analysed both positive and negative influences of nanomaterials on anaerobic digestion and factors that could shape these outcomes.

The impact of nanomaterials on anaerobic digestion is influenced by temperature, nitrogen ratio, pH, particle size of nanomaterials, type of waste and their concentration in waste (Chandrakant et al., 2021; Ye et al., 2021). For instance, Chandrakant et al. (2021) indicated that nanosilver, zinc oxide, cerium oxide, and copper oxide could inhibit biogas production. Zhu et al. (2020) discovered the negative impact of nanosilver, nano copper, copper oxide, manganese(III) oxide and zinc oxide on the efficiency of various anaerobic digestion processes and production of biogas and/or methane.

According to Chandrakant et al. (2021), Ye et al. (2021) and Zhu et al. (2021), the concentration of nanomaterials in waste also plays an important role. For instance, with the application of copper oxide in doses of 11, 110, 330, 550 and 1100 mg/L to municipal solid waste sludge, the inhibitory effect on biogas production up to 84% was observed. However, iron oxides boosted biogas production from the municipal solid waste up to 117% (Chandrakant et al., 2021).

Ye et al. (2021) reviewed the mainly positive impact of iron nanoparticles on anaerobic digestion when adding them to food waste and domestic waste. According to Ye et al. (2021), zero-valent iron enhanced the ability of microorganisms to resist high concentrations of ammonia nitrogen; however, the applied dosage should be controlled, and safety issues should be considered. A similar positive influence on the anaerobic digestion of food waste was identified by Li et al. (2021) for iron (II, III) oxide.

The available research shows that nanomaterials could positively and negatively impact biological treatment, especially under anaerobic conditions. It provides valuable insights into the factors and conditions that shape these effects. However, the earlier research cited by Part et al. (2018) and the newest literature reviews (Chandrakant et al., 2021; Ye et al., 2021 and Zhu et al. 2020) indicated that most research was carried out at a laboratory scale under unrealistic conditions (e.g., short-duration experiments, pristine nanomaterials, artificial waste, controlled humidity, and temperature, etc.) and doses of nanomaterials.

There is a scarcity of studies on the effects of sub-standard waste management in landfills on capturing and eliminating nanomaterials from waste. The only case study on nanomaterials in the uncontrolled construction dumps was carried out by Oliveira et al. (2019); see it summarised in Table 8. However, the data by EURELCO (European Enhanced Landfill Mining Consortium) and i-Cleantech suggests that sub-standard landfills pose an acute issue. According to the estimations of the study, there are over 500,000 landfills in the European Union (EU-28). Ninety percent of these landfills does not comply with the European landfilling regulation and lack environmental protection technologies (EURELCO, 2018). A sanitary landfill differs from a dump by being an engineered structure that contains bottom liners, leachate collection and removal systems, and final covers. A dump has no barriers that would separate waste from the soil and groundwaters (Vaverková, 2019). The main pollution pathways include air, soil and water. They are also relevant for nanomaterials.

However, uncontrolled waste dumps are not the only instances of sub-standard landfill management. Additionally, the efficiency of nanowaste management in landfills depends on their overall performance. In the studies of nanomaterial emissions from landfills, specific attention has been given to the emissions of nanomaterials through leachate (Part et al., 2018). The available performance scenarios of the European landfills estimate a 95% leachate collection efficiency in 50 years of landfill management, with 5% emitted to the environment (Sauve & Acker, 2020). This data could become a starting point for addressing the issue of nanomaterials management performance in landfills. However, further research that considers the specifics of nanomaterials in landfills is required.

Table 8: An example of the fate of nanomaterials in the uncontrolled construction landfill

The study analysed the presence, composition, and solubility of nanomaterials in five uncontrolled dumps of construction wastes in the region of Porto Alegre, Brazil. Thirty-three samples of concrete slabs, concrete roofing tiles and plasterboards were collected for analysis. The researchers detected spherical nanoparticles of coal combustion fly ash, magnetite, and titanium dioxide in the waste samples. Fine powder of coal combustion fly ash was abundant in concrete waste and posed risks for population exposure. Magnetite was detected in concrete and tiles. The latter also contained spherical nan o-titanium dioxide in crystalline forms (anatase and rutile). Other detected nanoparticles included Al, As, Au, Ca, Cd, Co, Cr,

Cu, Hg, Na, Fe, K, S, Sn, Si and metal nanoparticles or metalloids in the nanoscale range (As, Co, Cr, Cu, Hg, Fe, Sn or Ta). The low solubility of all studied wastes was reported. As, Mo, Cr, W, W, and B demonstrated higher mobility with 2% of the total concentration of the elements solubilised by water and 16% leachable boron contained in plasterboard waste.

The uncontrolled dumps were open and easily accessible to the population. The researchers highlighted the following exposure pathways to nanomaterials:

- Direct exposure to nanomaterials by inhalation due to their transport by wind, traffic, or direct inhalation by accessing uncontrolled dumpsites by population. Importantly, easily accessible dumpsites could be attractive to the local poor communities for re-use of the materials.
- Migration of nanomaterials (e.g., with the rain) to aquatic systems due to the absence of landfill liners and leachate collection systems.

Source: Oliveira et al., 2019

The age of landfills is also found to affect the management and emissions of nanowaste (Part et al., 2018). Uyguner-Demirel et al. (2017) highlighted that high concentrations of high molecular weight organics, such as humic and fulvic acid, in old landfills can increase the mobility of nanomaterials. For instance, the presence of humic acid improved the mobility of single-walled carbon nanotubes.

As shown by Oliveira et al. (2019), risks of uncontrolled landfill could cover nanoemissions to the soil and groundwaters and exposure to nanomaterials by the populations that live close to the uncontrolled dumps or directly access it (see Table 8).

4.5 Behaviour and fate of nanomaterials in wastewater treatment

The increased production and the widespread application of nanomaterials in many products such as medicines, cosmetics, clothing, sunscreens, electronics, and other consumer and industrial goods cause their release into the environment, and one of the major acceptors are wastewater treatment plants (Wang & Chen, 2016). Nanomaterials can get into wastewater streams through the use or disposal of consumer products that contain nanoparticles, via direct discharges from manufacturing processes that involve nanomaterials, and through direct application of nanoparticles in wastewater treatment processes. The concentration of

nanoparticles in wastewater streams depends on the type of wastewater (domestic or industrial), the quantities of nanomaterials produced and used in the local area, the concentration of free and fixed nanoparticles in consumed commercial products, the extent of dilution, and the level of adsorption or agglomeration that occur in wastewater. Industrial effluents from manufacturing processes, especially those used to produce nanoparticles, tend to have the highest concentrations of nanomaterials (Kunhikrishnan et al., 2015).

Predictions of quantities of nanoparticles in wastewater streams have been made through MFA or environmental fate models (see Section 4.1). However, these figures are estimations that should be interpreted with caution. Although the data in the literature on realistic concentrations of nanomaterials in wastewater is limited, several studies have been conducted to investigate the presence of nanoparticles in existing conventional wastewater treatment plants (Cervantes-Aviles et al., 2019; Cervantes-Aviles et al., 2021; Choi et al., 2017; Li et al., 2016; Polesel et al., 2018). The incidence of Ag (Cervantes-Aviles et al., 2019; Cervantes-Aviles et al., 2021; Li et al., 2016; Polesel et al., 2018), Ti (Cervantes-Aviles et al., 2021; Choi et al., 2017; Polesel et al., 2018); Zi (Cervantes-Aviles et al., 2021; Choi et al., 2017), Fe, Ce, Mg, Cu, Ni, Al, Au, Co, and Cd (Cervantes-Aviles et al., 2021) have been reported in wastewater treatment plants in Norway and the US. Concentrations between 1,600 and 10,700 ng/L for metal nanoparticles such as Ti, Fe, Ce, Mg, Cu and Zn have been measured by Cervantes-Aviles et al. (2021) using single-particle inductively coupled plasma mass spectrometry (spICP-MS). However, spICP-MS cannot distinguish between manufactured, incidental and natural nanoparticles and can only detect one element at a time. Thus, composite particles (e.g., FeTiO₃) will result in multiple nanoparticles (one for Fe and one for Ti in the case of FeTiO₃). Particle sizes and concentrations from such measurements thus can only be used as indicative values. More reliable data will be generated in the near future from sp-ICP-ToF-MS where multiple elements can be detected simultaneously (Mehrabi et al., 2021).

The most investigated nanoparticles in the literature in the context of wastewater treatment were **Ag**, **ZnO**, **TiO**₂, **CeO**₂, **Cu**, **CuO**, **SiO**₂, **Al**₂**O**₃ (Huangfu et al., 2019; Kapoor et al., 2018; Park et al., 2017; Wang et al., 2016; Wang et al., 2017; Wu et al., 2018; Wu et al., 2019). Carbon-based nanoparticles, such as CNTs and fullerenes, have also been investigated (Huangfu et al., 2019; Wang et al., 2016; Wang et al., 2017; Wu et al., 2018).

When wastewater arrives at a municipal wastewater treatment plant, it goes through a suite of **treatment processes**. Typically, this consists of primary treatment (pre-treatment for particle sedimentation), secondary treatment (also called biological treatment or activated sludge process consisting of a combination of nitrification and denitrification reactors combined with a secondary clarifier), and tertiary treatment (additional process steps such as media filtration or UV disinfection used as an advanced treatment) (Samer et al., 2015; Wu et al., 2018). During the primary treatment, particles with settling velocity values higher than the reactor's critical settling velocity can be removed from the wastewater (Wu et al., 2018). Coagulation and flocculation, which are traditional wastewater treatment processes, can facilitate the removal of particles (including nanoparticulate solids) through sedimentation. Coagulants neutralise the surface charge on suspended particles, whereas the addition of flocculants encourages particles to form larger clusters through heteroaggregation, which enhances their settling properties (Punzi et al., 2020).

Dissolved organic matter and particles that are too small for sedimentation can be removed via the activated sludge process. The process uses microorganisms to transform dissolved organic matter into biomass that can be removed from the treated wastewater through a secondary sedimentation process. The activated sludge process includes anoxic/aerobic treatment (i.e., oxidation ponds, aeration lagoons, activated sludge, biological filters, etc.) and an anoxic/anaerobic treatment (anaerobic lagoons, anaerobic bioreactors). The tertiary treatment processes include media filtration, pH neutralisation, chemical precipitation, disinfection, and ion exchange (Samer et al., 2015). According to the European Environment Agency (2020b), 69% of the population in the EU-27 countries were connected to tertiary level and 13% to secondary level wastewater treatment in 2017.

Depending on the specific conditions of the primary treatment and the nanoparticles in question, suspended nanoparticles will be present in wastewater led to the secondary treatment step. The review by Wu et al. (2018), which investigated the impact of metallic and metal oxide nanoparticles (ZnO, TiO₂, CeO₂, Ag) on biological wastewater treatment, showed that **more than 80-90% of nanoparticles are removed from wastewater during biological treatment**, and less than 10% is removed through tertiary treatment processes (Wu et al., 2018), although that depends on the type of the treatment. Hence, biological treatment plays a key role in the removal of nanomaterials from wastewater in a wastewater treatment facility. Therefore, it is important to understand the transformation and behaviour of different nanoparticles at this stage of the wastewater treatment process.

Several comprehensive literature reviews have been conducted to discuss the impact of nanomaterials on biological treatment, as well as transformations, behaviour, and the fate of nanoparticles in wastewater treatment plants (Huangfu et al., 2019; Kunhikrishnan et al., 2015; Kapoor et al., 2018; Wang & Chen, 2016; Wang et al., 2017; Wu et al., 2018; Wu et al., 2019). Firstly, it is important to understand the **transformations** that nanoparticles may undergo when they move through the wastewater treatment process. Several physical and chemical transformation mechanisms can influence the behaviour and fate of nanomaterials, such as agglomeration, aggregation, sedimentation, deposition, association, dissolution, coating, reaction, decomposition, adsorption, complexation, oxidation, reduction, and sulphidation (Huangfu et al., 2019; Kunhikrishnan et al., 2015; Wu et al., 2018). According to Wu et al. (2019), aggregation, sedimentation, sulphidation, and adsorption are the most significant transformations that influence the fate of nanoparticles in wastewater treatment systems. These processes determine physicochemical properties of nanoparticles (e.g., aggregation, size, solubility, surface charge, etc.), distribution, bioavailability, uptake, transport, and toxicity (Wang et al., 2017; Wu et al., 2018). In their literature review, Wang et al. (2017) observed that the migration and transformation of nanomaterials depended on different properties of nanoparticles, environmental factors, and various properties of the exposure media (e.g., pH, ionic strength, presence of natural organic matters). Similarly, influencing factors such as ionic valence, ionic strength, pH, light, oxidation-reduction potential and dissolved oxygen were discussed by Huangfu et al. (2019).

Natural organic matters and electrolytes in wastewater can affect the surface charge of nanoparticles and their aggregation or stabilisation behaviours. Nanoparticles, such as TiO₂, ZnO, and CeO₂, tend to aggregate with larger sizes (Wu et al., 2018). This behaviour was observed by Zhou et al. (2015) in their study, where TiO₂ and ZnO nanoparticles formed 300-400 nm aggregates, which were found to be stable in wastewater matrix after 4.5h suspension due to the presence of organic matter. The addition of electrolytes, on the other hand, prevented the aggregation, but the Al₂(SO₄)₃ solution system allowed to achieve it (Zhou et al., 2015). In their experiments, Barton et al. (2015) observed a preferential accumulation of CeO₂ to biosolids through heteroaggregation. However, CeO₂ nanoparticles were not completely transformed in the wastewater treatment process. Aggregation between the same particles (homoaggregation) is most relevant in laboratory systems, where there is an absence of other particles or surfaces, whereas heteroaggregation is usually observed in real wastewater treatment facilities (Zhang et al., 2016).

Attachment of nanoparticles to biosolids is also an important and unavoidable process during the biological wastewater treatment, which inevitably causes their direct interaction with microorganisms. Over 90% of TiO2, ZnO and Ag nanoparticles were observed to be directly associated to the activated sludge (Wu et al., 2018). Puay et al. (2015) used a lab-scale sequencing batch reactor to evaluate the impact of ZnO nanoparticles on the biological wastewater treatment process and its performance. It was found that almost 100% of ZnO was removed through attachment to the activated sludge, which occurred in three phases over a long-term operation (almost 100 days) (Puay et al., 2015). Similarly, over 90% attachment to the activated sludge was observed for TiO₂ nanoparticles, which also enhanced methane production by 15% (Cervantes-Aviles et al., 2018).

The transportation of silver nanoparticles through sewerage systems transforms them into less toxic precipitates and complexes, such as silver sulphide (Ag_2S), and primary treatment processes reduce the quantity of silver nanoparticles in wastewater through heteroaggregation, adsorption, settling/sedimentation, and other mechanisms before they enter biological treatment. Hence, Ag nanoparticles would have a higher impact on biological treatment in the facility without primary treatment processes and/or sewage collection systems. Microorganisms in the suspended-growth bioreactor are more susceptible to silver nanoparticles than in the attached-growth bioreactor; however, microbial functional redundancy and adaptability towards Ag nanoparticles reduce their adverse effects on wastewater treatment (Zhang et al., 2016).

The investigation of nanoparticles incidence and behaviour in the real wastewater treatment plant revealed that the activated sludge process and reclaimed water removed 84-99% of metalbased nanoparticles from influent, except for Cd, Mg, and Ni, where removal rates ranged between 70 and 78% (Cervantes-Aviles et al., 2021). Some examples of removal efficiencies for the most common nanoparticles can be found in Table 9. Overall, wastewater treatment plants that use activated sludge can remove the most commonly occurring nanoparticles from the wastewater; however, it results in high concentrations of nanoparticles in the sludge (Cervantes-Aviles et al., 2021).

Nanoparticle	Removal rate	Source
Ag	76.3% of the colloidal Ag fraction was removed during secondary treatment, whereas 96.3% removal was achieved after tertiary treatment with ultrafiltration.	Cervantes-Aviles et al., 2019
TiO ₂	It was estimated that 92% of TiO ₂ nanoparticles were removed by anaerobic sludge, and 8% remained in the treated effluent.	Cervantes-Aviles et al., 2018
ZnO	More than 98% of nanoparticles were removed in a membrane bioreactor.	Tan et al., 2015
	ZnO nanoparticles were effectively removed (almost 100%) from wastewater, mainly through attachment to the sludge.	Puay et al., 2015

Table 9: Examples of removal rates of nanoparticles from wastewater

As discussed, because of transformation processes such as aggregation, adsorption, sequestration, or sedimentation, over 90% of nanoparticles will be **trapped in the activated sludge or biosolids,** and only a small amount will remain in the effluent. Hence, the toxic effects of nanoparticles on **biological treatment and sludge digestion performance** need to be evaluated and understood (Wu et al., 2018).

The impact of nanomaterials on biological wastewater treatment, namely **organic matter**, **nitrogen**, **and phosphorus removal**, has been extensively reviewed in the literature. For the removal of organic matter, low concentrations (e.g., TiO2 – <10 mg/L, Ag – <2 mg/L, ZnO – <5 mg/L) of nanoparticles did not negatively affect the growth of heterotrophic microorganisms, although high concentrations (e.g., TiO2 – 10-60 mg/L, Ag – 2-30 mg/L, ZnO – 5-60 mg/L) inhibited their performance. Exposure to high concentrations of nanoparticles in wastewater is not likely to occur neither regularly nor in the long term (Wu et al., 2019).

The nitrogen removal (nitrification, denitrification, anammox) is more vulnerable to the presence of nanoparticles (Wu et al., 2018). Kapoor et al. (2018) have reported that the increased levels of metal oxide nanoparticles in wastewater significantly impact nitrification, an important part of the nitrogen removal process. Similarly, Wang et al. (2017) observed adverse impacts of SiO₂ and Al_2O_3 nanoparticles on nitrification and denitrification, with TiO₂ showing some inhibitory effects on nitrifying and denitrifying bacteria. ZnO nanoparticles decreased nitrogen removal and reduced the diversity of the bacteria community in the activated sludge (Puay et al., 2015). In their experiment, Tan et al. (2015) introduced 1 and 10 mg/L of ZnO nanoparticles and observed permanently inhibited ammonia-oxidation after long-term exposure; however, nitrite-oxidation was not affected.

Furthermore, the activated sludge properties changed substantially, which caused severe membrane fouling (Tan et al., 2015). The accumulation of nanoparticles in the bacterial membrane may cause membrane damage, which can later have an adverse effect on DNA, lipoproteins, and enzymes (Kapoor et al., 2018). Moreover, the induced reactive oxygen species production can interrupt the metabolic pathways by exerting oxidative stress on bacterial structure (Wu et al., 2018). However, **acute inhibition is often noticed at the beginning of exposure to nanoparticles but does not last in the long term** (Wu et al., 2019). This can be explained by the potential capacity of microbial communities to resist or even recover from the stress caused by nanoparticles by self-adaption or shifting in the community structure (Wu et al., 2018).

Finally, no significant adverse effects have been observed in the biological removal of phosphorus in the wastewater treatment process in the presence of most nanoparticles (Wang et al., 2017; Wu et al., 2019); however, at certain concentrations, ZnO can seriously affect the phosphorus removal (Wang & Chen, 2016; Wang et al., 2017). Overall, **the impact of nanomaterials on different biological wastewater treatment processes varies and depends on several main factors such as the type of nanoparticle, dose, and exposure** (short- or long-term). Nitrogen removal appears to be more sensitive to the presence of nanoparticles in wastewater than the removal of phosphorus or organic matter. However, it is essential to emphasise that the impact and toxicity of nanoparticles to microorganisms discussed in the literature have mainly been investigated on pure cultures and have often been overestimated, and the information regarding the casual effects of nanoparticles in complex biological systems and in real wastewater are limited (Kapoor et al., 2018; Wu et al., 2019).

The primary and secondary **sludge** from the wastewater treatment plant is usually sent to anaerobic digesters for further decomposition of organic matter, biogas production and sludge stabilisation. During this process, many biological reactions such as hydrolysis, acidogenesis and methanogenesis occur (Wang & Chen, 2016). Therefore, another important factor to consider is the **impact of nanoparticles on the anaerobic digestion of waste sludge**. Similarly to wastewater treatment, the effects of nanoparticles on sludge digestion **depend on the type**, **concentration and exposure time** (Wang & Chen, 2016). Concentrations of nanoparticles in the waste sludge measured by Cervantes-Aviles et al. (2021) in the wastewater treatment plant were between 0.5 ng/L for Cd to 10,970 ng/L for Fe. However, concentrations would vary in different wastewater treatment plants depending on the factors that determine quantities of nanoparticles in wastewater streams, as discussed at the beginning of this chapter.

Typically, waste sludge is stored under anaerobic conditions for up to 10 days of hydraulic retention time, during which heteroaggregation, settling, accumulation, and potential transformation of metal-based nanoparticles takes place (Cervantes-Aviles et al., 2021). In their literature review on the influence of nanomaterials on sludge digestion, Wang and Chen (2016) discussed several main potential effects, both positive and negative. The release of metal ions from metal oxide and metallic nanoparticles appeared to be the main reason for the toxicity of nanoparticles on waste sludge digestion. For instance, the presence of nano zero-valent iron can assist in the production of hydrogen gas, which is beneficial to methanogenesis. Still, it can also release high concentrations of soluble ferrous iron, which can damage methanogens. Hence, this nanoparticle may benefit the process of hydrogen generation, cell solubilisation and acidogenesis but adversely affect methanogenesis. The studies did not find any inhibitory effects of TiO₂, Al₂O₃, and SiO₂ nanoparticles on anaerobic waste sludge digestion; however, the impact of ZnO was dose-dependent, causing the inhibition of sludge hydrolysis, acidification and methanation in short-term and hydrolysis and methanation reduction in the long-term exposure experiments (Wang & Chen, 2016). Zhu et al. (2021) made similar findings in their systematic literature review on the impact of metallic nanoparticles on anaerobic digestion, where ZnO and Co nanoparticles exhibited adverse effects on methane or biogas yields. The same review has summarised that all kinds of nano-additives with trace elements can improve the performance of anaerobic digestion at low concentrations, but the addition of non-trace elements-based metal nano-additives does not have a noticeable effect, although increased concentrations can cause negative effects on gas production rates. Multi-nano-additives can achieve better performance by increasing methane production or overcoming some negative effects (Zhu et al., 2021).

The reviewed literature has mainly discussed **the addition of nanoparticles** to anaerobic digestion. However, nanoparticles already present in the sludge may exhibit different characteristics due to transformations that they undergo throughout the wastewater transport and treatment; hence, direct conclusions on the impact of nanomaterials on the anaerobic sludge digestion and biological communities cannot be made, and further research is required. Furthermore, most studies have focused on the effect of nanoparticles on gas production but not on changes in microbial structure, the effluent (nutrient-rich digestate product) quality, or the quality of the produced gas (Zhu et al., 2021). Therefore, the effort should be made to evaluate the quality of final products from anaerobic digestion so that the assessment of the risks arising from the use of these products could be carried out.

4.6 Exposure to nanomaterials in waste management

The OECD report (2016) referred to risk assessment studies of consumer products containing nanomaterials and standalone nanomaterials. However, it concluded that there was uncertainty about nano-specific risks of manufactured nanomaterials in the waste containing nanomaterials. The study summarised the main possibilities of exposure to nanomaterials in waste recycling facilities.

Our literature search identified few studies focusing on exposure to nanomaterials in recycling, but most publications covered industrial and research facilities. Therefore, we assume that the exposure situation in manufacturing and waste management facilities could have many things in common and discuss available research on the topic.

The current research on occupational exposure to nanomaterials is inspired by safety concerns and practical needs to launch appropriate protection initiatives and offer adequate safety measures. Recent studies addressed the impact of nanomaterials on human health. For instance, in the bibliometric analysis of 641 studies published in 2008-2017, silver, titanium dioxide, silica, ceria and gold nanoparticles received attention in the research on the neurotoxicity of nanomaterials (Su et al., 2018). Wang et al. (2018) documented research focusing on the developmental and reproduction toxicity of nanomaterials. They revealed that the impacts of ten nanomaterials (with nano-silver, titanium dioxide, zinc oxide and carbon nanotubes on the top of the list) were in the focus of the researchers in 266 papers published between 2006 and 2016. In 2013, the European Commission published *Guidance on the protection of the health and safety of workers from the potential risks related to nanomaterials at work* and *Guidance for employers and health and safety practitioners* for use in a general, occupational setting (European Commission, 2013).

Occupational exposure to nanomaterials can happen through contact with liquids containing nanomaterials, airborne nanomaterials. Usually, nanomaterials enter the organism by inhalation, ingestion, or dermal routes (Pietroiusti et al., 2018). The exposure of workers to nanomaterials may occur during various mechanical, physical, and chemical waste management processes.

The literature search identified four extensive systematic literature reviews that addressed various aspects of occupational exposure to nanomaterials (see Figure 9 overleaf).

The studies were published in 2016-2018 and focused on similar issues. Basinas et al. (2018) and Ding et al. (2017) focused on the airborne nanomaterials that come into contact with

humans via inhalation, while Kuijpers et al. (2017) and Debia et al. (2016) studied various routes of exposure. Two studies – Basinas et al. (2018) and Debia et al. (2016) developed a methodology for assessing the quality of evidence provided in the publications they analysed. All studies focused on occupational exposure, mostly in industrial and research settings; however, Basinas et al. (2018) and Ding et al. (2017) included a few studies on encounters with nanomaterials in recycling facilities. Most literature reviews covered the timeframe 2000 – 2015, while one study focused on 2004-2016. As to the coverage of publications, Basinas et al. (2018) seem to be the most exhaustive overview (107 publications), although specific objectives and selection strategies in the reviews pre-conditioned the number of analysed publications.

Figure 9: Systematic reviews of the studies on occupational exposure to nanomaterials



Note: MNMs - manufactured nanomaterials

Analysis of the systematic reviews revealed that **all studies addressed the exposure to carbon-based materials, metal/metal oxide nanoparticles** (Basinas et al., 2018; Ding et al., 2017; Kuijpers et al., 2017; Debia et al., 2016). Debia et al. (2016) and Basinas et al. (2018) provided high-quality evidence on the exposure to some nanomaterials. Interestingly, although the findings of the studies have a lot in common, the evidence quality analysis contributes to differences in reporting exposures to some nanomaterials. The findings of Ding et al. (2017) and Basinas et al. (2018) are summarized in Table 10.

Activity	Nanomaterial	Activity	Nanomaterial
Ding et al., 2017 (2004-2016)		Basinas et al., 201	8 (2000-2015)
Collection, sorting & processing	Metal/metal oxides, carbon- based	Synthesis – reaction phase	Titanium dioxide, metal nanoparticles
Physical & chemical synthesis	Metal/metal oxides, carbon- based	Synthesis – collection, sorting and processing	Carbon nanotubes, carbon, nanofibres, silicon oxide, titanium dioxide, metal oxides and mixtures

Table 10: Examples of exposure to nanomaterials

Study on the Product Lifecycles, Waste Recycling and the Circular Economy for Nanomaterials

Activity	Nanomaterial	Activity	Nanomaterial
Ding et al., 2017 (2004-2016)		Basinas et al., 2018 (2000-2015)	
Weighing, transferring & mixing	Metal/metal oxides, carbon- based, ceramics powders	Feeding into a process	Carbon nanotubes, carbon nanofibres, silicon oxide, metal oxides
Machining & abrasion	Nylon 6 nanofibres, alumina fibre, carbon fibres, multiwalled carbon nanotubes	Handling & transfer of liquids	Unclear
Cleaning & maintenance	Metal/metal oxides, carbon- based	Weighing & mixing	Carbon nanotubes, carbon nanofibres, silicon oxide, titanium dioxide
Finishing	Cerium oxide, titanium dioxide, silica-iron nanomaterial, indium tin oxide, zinc oxide, silicon oxide; carbon black, multiwalled carbon nanotubes	Handling & transfer of powders	Carbon nanotubes, carbon nanofibres, titanium dioxide, metal oxides and mixtures, metal nanoparticles
Packing & bagging	Carbon black, fullerenes, carbon nanofibres, multiwalled carbon nanotubes, carbon nanodiscs/nanocones; nano- silica, titanium dioxide, silicon oxide, calcium carbonate	Extrusion/injectio n moulding	Carbon nanotubes, carbon nanofibres, titanium dioxide, metal oxides and mixtures
Sonification	Fullerenes, multiwalled carbon nanotubes, carbon black, silver oxide, cerium oxide	Machining & abrasion	Carbon nanotubes, carbon nanofibres
Testing	Cadmium-zinc/selenide quantum dots, Nylon 6 nanofibre	Spraying & finishing related processes	Carbon nanotubes, carbon nanofibres, silicon oxide, metal oxides, metal nanoparticles
Ball milling	Multiwalled carbon nanotubes	Testing & characterization	Metal nanoparticles
Feeding	Nano-silver	Packing	Carbon nanotubes, carbon nanofibres, silicon oxide, titanium dioxide, metal oxides and mixtures, metal nanoparticles
Recycling	Silicon oxide/aluminium oxide/cerium oxide, carbon nanotubes	Cleaning & maintenance	Carbon nanotubes, carbon nanofibres, silicon oxide, titanium dioxide, metal oxides and mixtures, metal nanoparticles
		Recycling	Unclear

According to Debia et al. (2016), researchers reported high-quality evidence that:

• workers were exposed to multi- and single-walled carbon nanotubes, carbon nanofibres, aluminium oxide, titanium dioxide and silver nanoparticles.

• during handling tasks, workers were exposed to micro-sized agglomerations of nanoparticles and exposure effects were reduced by engineering controls (Debia et al., 2016).

Similarly, Basinas et al. (2018) concluded that there is high-quality evidence on the exposure to carbon nanotubes, carbon nanofibres, silicon oxide, titanium dioxide, metal nanoparticles and metal oxides in various industrial/research operations. The route and form of exposure depend more on the activities and less on the type of nanomaterial. According to Basinas et al. (2018), manual activities (e.g., cleaning and maintenance, handling, spraying and finishing, etc.) increase the likelihood of inhalation and dermal exposure. Interestingly, the ability of local exposure controls (LEC) to prevent the workers' exposure varied for different types of nanomaterials. Basinas et al. (2018) found that LEC effectiveness was higher in large-scale industrial facilities. It could be attributed to the differences in experience and training in managing occupational hazards between small and large facilities. However, the literature review showed little is known on the exposure in recycling settings because quality evidence is not available in the studies (Basinas et al., 2018).

Kuijpers et al. (2017) detected the highest emissions of nanomaterials during a) the synthesis of nanoparticles at mechanical reduction and gas phase, b) handling and transfer of bulk nanomaterial powders in harvesting and dumping operations, c) processes with liquids, especially in gas and pressure spraying, sonification and brushing/rolling and e) handling of nanoparticles. In general, it is in good agreement with the findings of other studies that indicated the increased risk of exposure when manual works are performed.

In 2019, the Swedish non-profit organization, ChemSec, added **carbon nanotubes** to the socalled SIN list (SIN stands for 'Substitute-It-Now'). SIN list is a comprehensive database of chemical substances that should be banned in the EU, according to ChemSec (Hansen & Lennquist, 2020). Usually, the addition of substances to this list generates a wide political and corporate response. So, including carbon nanotubes drew the interest of the researchers of occupational exposure to carbon nanotubes. In the project *NanoExplore*, funded by the European Union, a systematic literature review on the exposure to carbon nanotubes was performed. Canu et al. (2020) identified 27 studies that included carbon nanotubes occupational exposure assessments. However, only two studies provided high-quality evidence, while 15 – moderate and 12 – low. The studies have shown that the main activities where the **exposure to higher concentrations of carbon nanotubes occurred covered non-enclosed activities**, such as sieving, harvesting, packaging, reactor clearing, extrusion, and pelletising (Canu et al., 2020). This finding corresponds to the results provided in the earlier literature reviews. Currently, there is a debate in the international community about the justification for treating carbon nanotubes as a substance of very high concern (Bergamaschi et al., 2021).

4.7 Best available techniques for managing exposure

OECD (2016) described a set of technical, organisational, and personal protection measures to safeguard workers from exposure to manufactured nanomaterials. The World Health Organisation (WHO) in the guidelines on the protection of workers from manufactured nanomaterials (2017) recommended several steps:

- Assessing health hazards of nanomaterials by using existent sources as the Globally Harmonized System (GHS) of Classification and Labelling of Chemicals and updating safety datasheets.
- Assessing exposure to nanomaterials by using occupational exposure limit (OEL) values if they are available in regulation documents or conducting assessment in place.
- Controlling exposure to nanomaterials by reducing it as much as possible using various methods to control it and introducing various hygiene measures. Personal protection measures should be considered as a last resort.

- Performing health surveillance. Due to the lack of studies, there were no recommendations for specific health surveillance programmes.
- Training and involvement of workers in control of and protection for exposure. Due to the lack of studies, no specific recommendations were provided.

Considering the approaches in OECD (2016) and in the WHO guidelines, we reviewed the available studies on occupational exposure limits, technical and personal protection measures, and training.

One way to assess the exposure of workers to nanomaterials is to rely on the existing **occupational exposure limit (OEL)** recommended by competent governmental bodies. OELs refer to a maximum tolerable level of exposure to an agent. Exceeding this level would lead to unacceptable health risks (Mihalache et al., 2017). OELs are established to protect workers from adverse health effects caused by the inhalation of nanomaterials at work. Rodriguez-Ibarra et al. (2020) analysed 17 entities in the USA, Europe, and Asia to determine regulation or relevant guidelines on OELs for manufactured nanomaterials. Such limits have been mostly established for titanium dioxide, carbon- and silver-based nanomaterials, zinc oxide and other metal oxides. The concept of OELs varies from country to country; therefore, its estimations are also different (see Table 11, Rodriguez-Ibarra et al., 2020; Mihalache et al., 2017).

Entity	Exposure limit
American Conference of Governmental Industrial Hygienists (ACGIH®; USA)	TiO ₂ : 10 mg/m3 8-h time-weighted average
National Institute for Occupational Safety and Health (NIOSH; USA)	Fine TiO ₂ : 2.4 mg/m3 10-h time-weighted average Ultrafine TiO ₂ : 0.3 mg/m3 10-h time-weighted
New Energy and Industrial Technology Development Organization (NEDO; Japan) and The Japan Ministry of Economy, Trade and Industry (Japan)	TiO ₂ : 0.6 mg/m3
Secretary of Economy (SE; Mexico)	Fine TiO ₂ : 2.4 mg/m3
Source: adapted from Rodriguez-Ibarra et al., 2020	

Table 11: Occupational exposure limits to TiO₂

Currently, the estimations are based on laboratory testing and modelling but not on the calculations made in real-life conditions (Rodriguez-Ibarra et al., 2020). Researchers and organisations employ different methods for determining the OELs. Mihalache et al. (2017) reported about two generic OELs establishment methods based on environmental limits for all nanomaterials or on the local exposure background that served as a starting point for estimating the acceptable level of exposure. Other methods were suitable for calculating OEL for the groups or individual nanomaterials.

Protection means against exposure usually cover **technical and personal protective measures**. Basing on the review of 41 studies on the exposure of workers to nanomaterials, Goede et al. (2018) estimated the effectiveness of technical and personal protective measures. The study was focused on inhalation and dermal exposure and three measures – engineering controls, respiratory equipment, and skin-protective means, such as clothing and gloves. For each protection measure, the estimated nano-specific average efficacy varied significantly:

 for engineering controls: from 76.9% for LEV (Local Exhaust Ventilation) – enclosing hoods to 99.5% for containment measures.

- for respiratory equipment: from 21.2% for unspecified nuisance masks to 100% for powered air-purifying respirators.
- for skin-protective equipment: gloves (from 88.4% for thin nitrile gloves to 100% for vinyl gloves) and clothing (from 49.6% for woven workwear to 100% for coated and ventilated/overpressure suites).

These estimations were mainly based on experimental modelling studies and comparison to measures applied to conventional substances. The lack of information about the efficacy of the discussed measures under real-life exposure conditions significantly limits the reliability of the data (Goede et al., 2018).

Important standardisation work is carried out to provide guidance about the efficiency of engineering controls for managing the exposure of workers to nanomaterials. For instance, the ISO 21083 series aims to standardise methods for determining the efficiencies of filter media against nanoparticles. So far, two standards in the series have been published:

- **ISO 21083-1:2018.** Test method to measure the efficiency of air filtration media against spherical nanomaterials Part 1: Size range from 20 nm to 500 nm.
- **ISO/TS 21083-2:2019.** Test method to measure the efficiency of air filtration media against spherical nanomaterials Part 2: Size range from 3 nm to 30 nm (ISO, http://www.iso.org/).

In their 2017 guidelines, the WHO pointed out the lack of studies on the training of workers about the hazards of nanomaterials and safety measures. A qualitative study of Danish and Swedish managers responsible for occupational safety and health by Kirkegaard et al. (2020) brought insights into **organisational protection measures** against nanomaterial exposure. The study highlighted an active position of interviewed representatives of academia and industry in managing risks and ensuring safety in their organisations. However, it also revealed insufficient and problematic communication of nanomaterials risks, insufficient and inaccessible information, and the instruction of employees. It emphasised the need to combine technical and personal safety measures with effective communication and instruction of workers.

4.8 Emission control and best available technologies (BAT)

Emissions of nanomaterials are incidental by-products created in manufacturing or waste management processes. Usually, they occur in various operations (e.g., physical, thermal, chemical processing of materials, etc.) and originate from nanomaterial-containing and nanomaterial-free products and materials (Part et al., 2018).

Currently, the main source of knowledge about the emissions at various stages of manufacturing and use, waste management of nanomaterials and to the environment are material flow analysis (MFA) models (see the discussion of examples in section 4.1) and environmental fate models (EFM). While MFA models intend to describe the routes of nanomaterials from their manufacturing, use, end-of-life processes to the environment and their emissions in various technical systems, EFMs focus on their behaviour and fate in the environmental compartments. To predict environmental concentrations, EFMs use the data of MFA as an input. It also considers some physical and chemical transformations of nanomaterials in the environment (e.g., agglomeration and dissolution). Both types of models estimate the concentration of the nanomaterials in various environmental compartments (e.g., water, soil and air). MFA models and EFMs are widely used by the regulators for various decision-making exercises considering chemical substances that are not necessarily related to nanomaterials. For nanomaterials, the models introduce specific parameters. For instance, the MFA-based decisionmaking tool EUSES, the European Union System for the Evaluation of Substances, is aimed at chemicals. It contains a module *SimpleBox*, which predicts the environmental fate of chemicals. The adaptation of this model - SimpleBox4Nano is used to predict the behaviour and fate of nanomaterials in the environment. Currently, the main limitations of MFA models and EFMs

are the lack of reliable input data and the limited inclusion and availability of thermodynamic and kinetic data on nanomaterial transformations.

The researchers are working on the development of analytical techniques allowing to detect, characterise, and quantify the concentration of nanomaterials in the environment. This work is important to develop collections of data necessary for predicting the environmental concentrations of nanomaterials based on model calculations. Additionally, such data are required for validating the results of MFA models and EFMs. However, available methods and equipment face challenges in differentiating manufactured and natural nanomaterials, characterizing nanomaterials in complex environmental media, and measuring their concentrations. Therefore, the estimations obtained by modelling exercises have not been validated yet. This and other modelling limitations do not allow a confident judgment about the concentration of nanomaterials in the environment and their impacts (Bundschuh et al., 2018; Nowack, 2017).

Emissions of nanomaterials to the environment is an important topic of discussion due to the **potential adverse effects of nanomaterials on the environment and living organisms**. The field of nanotoxicology explores these effects and the conditions in which they occur. According to Bundschuh et al. (2018), the ecotoxicity of nanomaterials is pre-conditioned by the chemical, biological and physical transformations they undergo at various stages of their lifecycle, end-of-life treatment, and the environment.

The **pathways of nanomaterials to the environment** vary depending on the properties of nanomaterials, the products and waste flows that contain them and the spectrum of waste treatment techniques applied to them. Importantly, emissions of nanomaterials also depend on the efficiency of the waste management process and available technologies.

One of the sources of emissions of nanomaterials is waste treatment operations in **incineration** plants. In waste incineration plants, waste is combusted at high temperatures. This process results in the transformation of the waste matter into flue gas containing substances that are harmful to human health and the environment. Flue gas also contains nanomaterials. To avoid emissions, an important task in waste processing is the cleaning of the flue gas. Several technologies are commonly used to remove nanoparticles from the flue gas. These include electrostatic precipitators that serve for dust removal by applying electrostatic force, fabric filters that employ temperature resistant fabric bags to filtrate flue gas constituents and wet scrubbers. The researchers also distinguish between dry and wet flue gas cleaning systems (Vehlow, 2015; Ozgen, 2015). Electrostatic precipitators and fabric bag filters are recognised as the best available technology for managing channelled air emissions. However, bag filters are much more widespread than electrostatic precipitators (Joint Research Centre, 2018; Joint Research Centre, 2019). The available studies assessed the efficacy of different technologies to prevent nanomaterial emissions from incineration plants:

- The newest study by Mertens et al. (2020) measured the emissions of nanomaterials from real-life industrial installations that employed electrostatic precipitators (ESP) and bag filters. The study included two Waste-to-Energy incineration plants with capacities of 110 MWe and 60 MWe. The results have shown high-efficiency (99% for bag filters and 96% for ESP) levels for both technologies with higher effectiveness of bag filters. Mertens et al. (2020) concluded that the level of emissions is negligible in agreement with the previous studies.
- Jones & Harrison (2016), Vehlow (2015, important to note, this review covered not only ultrafine particles), Buonanno and Morawska (2015) who reviewed the emissions of ultrafine particles (particles with the diameter less than <100 nm) reported good performance of fabric filters for removing nanoparticles. In simulation experiments, Förster et al. (2016) and Boudhan et al. (2018) concluded that fabric filters effectively collected nanoparticles. According to Boudhan et al. (2018), the efficiency of the filter in collecting nanoparticles ranged from 97.8% to 99.99%.

 Ozgen (2015) analysed the emissions of nanoparticles in a Waste-to-Energy plant that burned municipal solid waste, non-hazardous waste and some clinical waste. The research identified differences in the performance of dry and wet flue gas cleaning systems. The wet cleaning system showed higher emissions of nanomaterials than the dry one. Ozgen (2015) attributed it to the secondary formation of nanoparticles that occurred during wet cleaning.

Buonanno and Morawska (2015) carried out a literature review to evaluate the emissions of nanomaterials from waste incineration plants and their potential impact on citizens living in the surrounding area. The research identified nine studies published in 2003–2012 and concluded that the emissions of nanoparticles from waste incineration plants were lower than from other sources (e.g., transportation) that contributed to daily citizens' exposure to nanomaterials. Jones and Harrison (2016) reviewed the studies that measured emissions from municipal waste incineration plants in 2000–2016 and identified seventeen studies. This review reached the same conclusions as Buonanno and Morawska (2015).

Despite a very high efficiency in capturing nanomaterials by the current cleaning installations in waste incinerators, Mertens et al. (2020) warn that the mechanism of emissions has not been fully understood. The researchers refer to **secondary formation of nanoparticles** that occur after the cleaned gas has left the chimney and cooled and diluted in the air. The mechanisms of such emissions have not been fully understood (Mertens et al., 2020).

Wastewater treatment plants can remove most nanoparticles from wastewater, with close to 100 per cent efficiency (Cervantes-Aviles et al., 2021; Tan et al., 2015; Puay et al., 2015: for details, see section 4.5). Effluents are then discharged into the surface waters. However, high concentrations of nanoparticles stay in the sludge, which is treated in the anaerobic digesters. For example, Cervantes-Aviles et al. (2021) reported concentrations ranging from 10-400 ng/L for Cd, Au, Ag, Al and Co-based nanoparticles to 4600-39,900 ng/L for Ni, Cu, Mn, Zn, Ce, Mg, Fe and Ti-based nanoparticles in the anaerobic sludge from the existing wastewater treatment plant.

In Europe, dumping of sewage sludge into the sea is prohibited by existing regulations (EU Directive 91/271/EEC); therefore, the sludge is often used for agricultural soil amendments, which creates a pathway for nanoparticles, if present, to be transferred to the surface waters with surface runoff. Furthermore, sludge can also be sent to landfills, where nanoparticles can enter the aquatic environment by leaching (McGillicuddy et al., 2017). EU-27 countries produced almost 7 million tonnes of sewage sludge in 2016, 33% was used for agricultural applications, and 8.7% was sent to landfills; however, these figures vary significantly for different countries. For example, countries like the Netherlands, Malta and Slovakia did not use sludge in agricultural applications in 2016 (Eurostat, 2021).

Other sources of potential emissions of nanomaterials are **landfills**. They are used for the disposal of nanomaterials contained in manufacturing wastes or residues of waste treatment. In landfills, nanomaterials can be released because of chemical or mechanical processes through liquids, gas emission, and wind erosion (Part et al., 2018). Several studies explored the possibility of the release of nanomaterials through clay liners of landfills. All studies were simulation experiments. Kim et al. (2020) concluded that colloidal fullerene (C_{60}) cannot pass the clay liners; a similar conclusion was reached in the study considering silver nanoparticles (Lee et al., 2021). However, under the effect of increasing temperature (with the maximum at 50 Celsius), Yang et al. (2018) found the growing mobility of nano zinc oxide that under experiment conditions permeated the geosynthetic clay liner.

Estimations of the release of nanomaterials to the environment and **quantitative risk assessment** were performed in two studies (Wigger et al., 2020; Kjølholt et al., 2015). They used predicted environmental concentrations (PEC) estimated in the modelling studies on the fate of nanomaterials and calculated **risk characterisation ratio** (RCR) or **risk quotient**. RCR is a proportion of the predicted environmental concentration (PEC) and predicted no-effect

environmental concentration (PNEC). PEC and PNEC are used to perform the environmental risk assessment of chemical substances under REACH (ECHA, 2016a).

Wigger et al. (2020) carried out a meta-analysis of 35 papers published in 2008-2019 that modelled the flows of nanomaterials to and fate in the environment. According to the study, none of the analysed nanomaterials posed risks to the environment because the risk characterisation ratio (RCR) did not reach the value of 1. Wigger et al. (2020) estimated risk ratios for 11 nanomaterials and provided several highlights:

- For emissions of nanomaterials to **surface waters**, the highest value of risk characterisation ratio was for zinc oxide (0.09), with titanium dioxide and nano-silver showing values above 0.01. Values for titanium dioxide varied from 0.004 to 0.03, depending on the nanoform that pre-conditioned different toxicity. However, the studies did not consider fate processes (e.g., agglomeration, sedimentation, dissolution, etc.) and local concentrations of nanomaterials in different regions.
- For emissions of nanomaterials to **sludge-treated soils**, the highest risk characterisation ratio was for titanium dioxide (0.3). This value was the highest of all reported ratios and indicated potential risks. However, it was derived from the study of 2009 that could reduce its reliability.
- For nanomaterials in **sediments**, only risk characterisation ratios for carbon nanotubes were available, and the highest value was 0.3.

Following a similar approach, Kjølholt et al. (2015) conducted the risk assessment for 9 nanomaterials in the effluents from wastewater treatment plants and fresh waters in Denmark. The researchers calculated the most probable and the highest risk quotients. It appeared that risk quotients for **most nanomaterials did not exceed 1**, meaning that environmental risk is controlled. The most probable values of risk quotients were higher than 1 for copper oxide and carbon black. However, it was assumed that all copper-based preservation of wood was done with nano-copper, which was not the case at the time of research. Furthermore, the study assumed that carbon black products consisted exclusively of nanoparticles, which is not necessarily the case in real-life situations. According to researchers, these assumptions could have influenced the results of the study.

However, it should be noted that in scholarly literature, quantitative risk assessments are often based on projections with a high level of uncertainties in data. For instance, the estimated PECs vary significantly in different models, the uncertainty in data increases in the studies with the broader geographical scope (e.g., Europe, world). For instance, Wigger et al. (2020) compared PEC values in 35 nanomaterial modelling studies (that used MFA or EFM models) published in 2008-2019 and found that "depending on the models and their assumptions considered, the PEC results vary across several orders of magnitude" (see Wigger et al., 2020: p. 14). Schwirn et al. (2020) highlighted that despite substantial scientific progress, robust PNECs estimations are still absent due to knowledge gaps in the studies about the toxicity of nanomaterials (e.g., the focus on the acute toxicity of nanomaterials in studies, limited availability of long-term toxicity studies, lack of information on the actual exposure to nanomaterials during the test, etc.) (Schwirn et al., 2020). Furthermore, the methodology for PNEC is still based on approaches derived for dissolved chemicals and may therefore not be directly transferable to nanomaterials (Baun et al., 2009). Kjølholt et al. (2015) mentioned this as a major source of uncertainty in the PNEC estimations based on the assessment factor approach that was used in their risk predictions.

The nanotoxicity studies cannot give a straightforward quantifiable answer to the question of the **impact of nanomaterials on the environmental compartments** they enter. The literature review has shown several reasons for it. First, the nanotoxicity studies aim to provide a general view of the toxicity mechanisms but **do not connect nanotoxicity to the specific geographical contexts and quantitative measures**. This is because in order to make risk assessment, toxicity is understood as an intrinsic property, fully separated from the exposure of

that nanomaterial. Hence, the nanotoxicity studies are performed in laboratory in standard conditions. Many nanotoxicity literature reviews are qualitative (e.g., see Bundschuh et al., 2018; Kabir et al., 2018; Spurgeon et al., 2020). Often, they use flow or fate models of nanomaterials as a general reference point to justify the relevance of the study, without considering the geographical and other specific aspects in these models (e.g., see Courtois et al., 2019; Tan et al., 2018). This does not allow us to judge if/how the discussed effects work under real-life conditions. Second, as Wigger et al. (2020) observed, **studies often apply high doses of nanomaterials to the studied samples**. Methodologies for studying the toxicity of nanomaterials also significantly vary. For instance, see the summary of parameters of the studies on nanosilver toxicity from the literature review by Courtois et al. (2019) in Table 12.

Parameters	Direct exposure (strains/enrichment)	Direct exposure (substrate/soil)	Application of sewage sludge
	Effects of nano-silve	r on microorganisms	
No. of studies	7	15	9
Concentration range	0.05 – 50 mg.L ⁻¹	0.001 - 5590 mg.kg ⁻¹	0.56 – 706 mg.kg ⁻¹
Duration range	-	-	-
Effects of nano-silver on plants			
No. of studies	25	8	2
Concentration range	0.001 – 10000 mg.L ⁻¹	0.0015 - 5000 mg.kg ⁻¹	0.14 - 400 mg.kg ⁻¹
Duration range	24 h – 10 weeks	8 days – 72 weeks	28 - 50 days
Effects of nano-silver on soil invertebrates			
No. of studies	13	20	3
Concentration range	0.05 – 1000 mg.L ⁻¹	0.0003 - 4400 mg.kg ⁻¹	4 – 78 mg.kg ⁻¹
Duration range	24 h – 56 days	1 day – 52 weeks	14 – 28 days
Source: adapted from Courtois et al., 2019			

To conclude, a closer connection between the studies on nanotoxicology and the fate of nanomaterials in managed waste facilities and the environment should be established. Reliable quantitative measures of nanotoxicity effects related to the environmental concentrations, which should be established based on pilot and field-scale experiments, are needed to judge the impact of nanomaterials on the environment.

4.9 Regulatory, technical and practical concerns related to nanomaterials in waste management

The discussion of the behaviour and fate of nanomaterials in waste management processes has shown that nanomaterials experience physical and chemical transformations and can be released to the environment at various stages of their treatment, including final disposal or incorporation of nanomaterials into secondary products. It can generate various risks of adverse effects of the released nanomaterials on human health and the environment. Thus, regulatory concerns in waste treatment processes relate to the ability to make sound regulatory decisions to ensure the safety of waste treatment processes and prevent environmental threats that are caused by their outcomes. Technical and practical concerns cover the development of appropriate aids and tools to support the implementation of regulatory requirements.

In general, the integration of nanomaterials into legislative systems worldwide was recognised as an important long-term task and a challenge. Under the Strategic Approach to International Chemicals Management (SAICM) policy framework, gaps in knowledge about the end-of-life of manufactured nanomaterials were considered a significant barrier for the inclusion of the latter into regulatory data requirements (United Nations, 2020). Despite the recent progress in regulatory developments on nanomaterials in the EU, there are **specific regulatory uncertainties in the management of nanowaste** (Ricardo Energy & Environment et al., 2016; United Nations, 2018).

In the EU, general principles and rules for defining and managing waste are set in the Waste Framework Directive (2008/98/EC). WFD is a key legislative act that defines waste and sets out the main measures to protect human health and the environment by preventing and reducing the generation of waste and proper management of waste (European Parliament, 2008). It is transposed in the legislation of the EU Member States through separate legal acts (European Commission, 2018).

One of the key decision domains in waste management under WFD is the classification of waste as hazardous or non-hazardous. The outcomes of waste classification determine obligations in managing waste. **Under WDF, hazardous waste is subject to certain obligations on monitoring and tracking, packaging and labelling, and treatment to protect human health and the environment**. Classifying waste as hazardous is based on the properties listed in Annex III of the WFD. Further guidance for waste classification is provided in the List of Waste (Commission Decision 2014/955/EU) that lists waste categorised according to its hazards (European Commission, 2018). Classification, Labelling and Packaging Regulation (CLP Regulation, 1272/2008) principles are applied in the European List of Waste (European Commission, 2018).

Currently, **nanomaterials are not addressed in the Waste Framework Directive (WFD)** (Ricardo Energy & Environment et al., 2016). The analysis of WFD shows that situation has not changed since 2016, and, currently, there are no nanomaterial-specific provisions. Additionally, nanowaste or waste-containing nanomaterials is not defined or distinguished as a specific waste category.

In the review of the EU legislation applying to nanomaterials, it was concluded that the WFD did not set any specific requirements for the identification and management of nanomaterials in waste. It was highlighted that the classification of waste as hazardous or non-hazardous relied on the principles adapted from the CLP Regulation, which did not include any nano-specific provisions as well (Ricardo Energy & Environment et al., 2016). The question about the regulatory uncertainty in the classification of waste was raised in the report of the Open-ended Working Group of Basel Convention as well (United Nations, 2018). Currently, there is an ongoing discussion about the **applicability of classification criteria outlined in the CLP Regulation** (and, in general, in the Global Harmonised System (GHS), on which CLP Regulation is based) to nanomaterials. It has been claimed that GHS and consequently CLP were developed for bulk chemicals; therefore, its appropriateness to nanomaterials should be checked (German

Environmental Agency, 2020). The issue of applicability of GHS classification criteria to nanomaterials was explored by the United Nations Sub-Committee on the GHS Classification and Labelling of Chemicals (SCEGHS) and by the Nanomaterials Expert Group of the ECHA (SCEGHS, 2018). An important contribution to this discussion is the research performed for the Nordic Chemical Group at the Nordic Council of Ministers (Larsen et al., 2019). The study evaluated the applicability of GHS classification criteria to selected nanomaterials that included single-walled carbon nanotubes, nano silicon dioxide, nanosilver and nano zinc oxide. The nanomaterials selection aimed to cover diverse parameters in terms of chemical composition, shapes, water solubility, surface area and density. The study concluded that, in general, GHS classification criteria were applicable for the characteristics on the selected nanomaterials, although some specific aspects should be additionally considered in the testing of voluminous nanomaterials, i.e., those with relatively high specific surface areas and low pour density (Larsen et al., 2019). However, the issue of applicability of GHS classification criteria to nanomaterials has not been solved yet and is still on the agenda of the UN SCEGHS (TDG-GHS, 2020). As a result, there is not yet a consensus on which nano-specific provisions (if any) should be introduced in the current EU waste management legislation for the classification of waste.

A **technical issue** relevant to the implementation of regulatory requirements in the classification of waste containing nanomaterials and taking appropriate management decisions is **detection**, **characterisation**, **and quantification of nanomaterials in waste**. Despite substantial progress in this field, the lack of mature and standardised analytical tools in detection, characterisation, and quantification of nanomaterials in waste and, in general, in complex environmental media is indicated in grey literature reports (United Nations, 2018; United Nations, 2020) and research publications (Part et al., 2015; Laborda et al., 2016; Bundschuh et al., 2018; Miernicki et al., 2019; Saleh, 2020). Good results have been achieved in the detection, characterisation and quantification of inorganic nanomaterials and many analytical techniques for qualitative characterisation and quantitative measurements of nanomaterials are available (Laborda et al., 2016; Bundschuh et al., 2018; Saleh, 2020). An important work in standardisation and guidance of analytical techniques has been conducted by international standardisation bodies (see examples of relevant documents in Table 13) and by the OECD Working Party on Manufactured Nanomaterials (WPMN) (Halamoda-Kenzaoui et al., 2018; Rasmussen et al., 2019).

Title	Scope		
International Standardisation Organisation (ISO)			
ISO/TR 14187:2020 Surface chemical analysis – Characterization of nanostructured materials	Surface characterisation methods		
ISO/TR 16196:2016 Compilation and description of sample preparation and dosing methods for engineered and manufactured nanomaterials	Sample preparation, dosing methods		
ISO/TR 18196:2016 Measurement technique matrix for the characterization of nano-objects	Available measurement methods/techniques/instruments		
ISO/TS 17200:2013 Nanoparticles in powder form – Characteristics and measurements	Material specifications and the methods to measure these characteristics		
ISO/TR 13014:2012 Guidance on physicochemical characterization of engineered nanoscale materials for toxicological assessment	Physicochemical characterisation		

Table 13: Examples of ISO and CEN documents in detection, identification and characterisation of nanomaterials in the environmental media

Title	Scope	
The European Committee for Standardisation (CEN)		
CEN/TS 17273:2018 Nanotechnologies. Guidance on detection and identification of nano-objects in complex matrices	Guidance on analytical methods based on a combination of size classification and chemical composition analysis	
CEN/TS 17010:2016 Nanotechnologies—Guidance on measurands for characterizing nano-objects and materials that contain them	Characterisation of nano-objects and materials containing nano-objects	
CEN ISO/TS 19590:2019 Nanotechnologies - Size distribution and concentration of inorganic nanoparticles in aqueous media via single-particle inductively coupled plasma mass spectrometry (ISO/TS 19590:2017)	Detection of nanoparticles in aqueous suspensions, characterization of the particle number, particle mass concentration and the number-based size distribution	
Sources: Halamoda-Kenzaoui et al., 2018; CEN (http://www.cen.eu/); ISO (http://www.iso.org/)		

However, differentiation between manufactured and natural nanomaterials in complex environmental media (Part et al., 2015; Bundschuh et al., 2018), developing effective characterisation and measurement techniques for organic nanomaterials (Miernicki et al., 2019), achieving appropriate sensitivity in existent tools for low concentrations of nanomaterials (Saleh, 2020) is still challenging.

On the practical side, guidance for adopting appropriate waste management practices for waste streams containing nanomaterials is crucial to implement the existing legislation. The need for standardisation in the management of nanowaste was recognised in scholarly publications (e.g., see Faunce & Kolodziejczyk, 2017). An important achievement in this field is CEN/TS 17275 Nanotechnologies - Guidelines for the management and disposal of waste from the manufacturing and processing of manufactured nano-objects (The European Committee for Standardisation, 2019). The technical specification provides guidance for all waste management activities associated with the manufacturing and processing of manufactured nanomaterials and covers the management of process waste, residues, and emissions of manufactured nanomaterials. Importantly, the guidance recognises the existence of uncertainties in the impacts of nanomaterials on human health and the environment. For situations with incomplete knowledge about hazards of manufactured nanomaterials, a precautionary approach is recommended (European Committee for Standardisation, 2019). The literature search also identified the guidance on managing waste containing nanomaterials developed by the German Chemical Industry Association (VCI, 2019). However, there were no other examples of industrial, national or international guidance in managing nanowaste.

To summarise, currently, knowledge gaps about the fate and behaviour of diverse nanomaterials cause uncertainties about introducing nano-specific provisions in waste legislation. Thus, the management of waste containing nanomaterials should follow the general provisions laid out in waste legal acts. The lack of information about the composition of waste (especially comprising end-of-life products, see the discussion in section 3.3) and limitations in detection, characterisation, and quantification of nanomaterials in waste streams posed by the current analytical tools and techniques can complicate classification of waste according to the European Waste List. Guidance on managing waste containing nanomaterials is lacking, although there are initial steps in advice on managing manufacturing waste.

5. Nanomaterials in the Circular Economy

The section **aims** to analyse how nanomaterials could contribute to reaching the goals of the circular economy and provides preliminary thoughts on the benefits and challenges that arise in this context. Contextual information and the definitions of circular economy and related fields in nanomaterial research are provided at first. Different nanomaterial research fields may have a role to play in the circular economy, including green synthesis of nanomaterials, recovery of rare-earth elements and waste recycling. A case study on the application of nanomaterials in wastewater treatment is provided in Annex 5.

It should be noted that the literature search identified publications focusing on nanomaterial solutions that were thought to refer to specific objectives of the circular economy. However, as detailed below, circularity is not necessarily the outcome of such applications.

5.1 Context and definitions

In contemporary societies, the use of global natural resources (biomass, fossil fuels, metals and non-metallic minerals) has grown dramatically. According to the Global Resource Outlook (Oberle et al., 2019), since 1970, the use of:

- Biomass increased 2.7 times, with 24 billion tonnes extracted in 2017.
- Metals increased 3.5 times, with 9.1 billion tonnes extracted in 2017.
- Fossil fuels grew 2.5 times, with 15 billion tonnes extracted in 2017.
- Non-metallic minerals increased 4.9 times, with 44 billion tonnes extracted in 2017.

High rates of waste production accompany the expanding extraction and consumption of global resources. According to the World Bank data, 0.74 kg of waste per capita is generated daily on the global scale, with a national variation from 0.11 to 4.54 kg of waste per capita. In 2016, an estimated total volume of collected municipal solid waste reached 2.01 billion tonnes (Kaza et al., 2018).

The increase in waste streams and the rates of natural resources extraction has led to natural resource exhaustion and environmental degradation, climate change and pollution. These trends pose a global challenge. Therefore, solutions that minimise the use of natural resources, maximise the re-use of products and recovery of valuable resources and energy from waste are necessary. One of these solutions is the circular economy (Velenturf et al., 2019).

In the context of materials, the **circular economy** is a closed-loop system that aims to minimise resource input and output by applying various strategies and solutions at different stages of material manufacturing, use, distribution, and disposal. Such strategies include product lifetime extension – manufacturing materials and products to maximise their lifetime and increase the potential for their reuse, re-manufacturing, redistribution, and recycling – using waste for creating new valuable products and materials, and minimisation of waste streams (Council of Europe, 2017).

In the EU, the introduction of the circular economy strategies was inspired by understanding the pressures associated with raw materials. With time, these initial considerations have grown into a policy covering the whole economic cycle of products and materials and resulted in the **Circular Economy Action Plan** announced in 2015 (Ellen McArthur Foundation, 2020). The Action Plan aimed at **boosting the competitiveness of the EU economy and sustainability** by "the transition to a more circular economy, where the value of products, materials and resources is maintained in the economy as long as possible, and the generation of waste minimised". It introduced 54 actions, addressing different stages of production, consumption, repair and remanufacturing, waste management and recycling, recovery of raw materials. The

implementation of the Action Plan was supported by cross-cutting measures to encourage innovation and investments (European Commission, 2015; Ellen McArthur Foundation, 2020). The plan resulted in over 10 billion Eur investment in circular economy research, innovation and other transition activities, reviewing waste legislation, adoption of sectoral strategies to increase circularity and many other initiatives (European Commission, 2019).

The Circular Economy Action Plan laid the ground for other strategic developments. In 2019, the new strategy for the European growth – the European Green Deal – outlined the ambitious aim "to transform the EU into fair and prosperous society, with a modern, resource-efficient and competitive economy where there are no net emissions of greenhouse gases in 2050 and where economic growth is decoupled from resource use" (European Commission, 2019). Three documents – the New Circular Economy Action Plan (European Commission, 2020), the European Industrial Strategy (European Commission, 2020a) and the European Chemicals Strategy (European Commission, 2020b) were adopted to support the implementation of the circular economy objectives outlined in the European Green Deal.

The New Circular Economy Action Plan (CEAP) launched a sustainable product policy framework that focused on **making the products more circular** and increasing their durability, repairability, upgradability, and enabling high-quality recycling. The CEAP emphasised the circularity developments in the sectors with high consumption of resources, such as electronics and ICT, batteries and vehicles, packaging, plastics, textiles, construction and buildings, food, water and nutrients. **Waste prevention and reduction**, as well as decreasing the **presence of hazardous substances**, were addressed as well (European Commission, 2020).

In turn, the **European Industrial Strategy** that was introduced in 2020 and reviewed in 2021 to address COVID-19 pandemics issues supported the **transition of the industry to a more sustainable and green circular economy**. The Strategy outlined key enabling technologies that are vital for the future development of Europe. It mentioned **nanotechnology** among several other enabling technologies (European Commission, 2020a; European Commission, 2021).

Finally, the **European Chemicals Strategy** (2020b) recognised the significant role of chemicals in daily life and activities as well as building blocks for various goods and addressed the **green transition of the chemical industry** and effective response to challenges posed by hazardous chemicals. The Strategy emphasised transition to **chemicals that are safe by design** ensuring that both **primary and secondary materials and products are safe**.

The use of nanomaterials can offer many benefits for the environment (e.g., application of nanomaterials in water treatment, recovery of various substances and precious metals) and the circular economy (e.g., application of nanomaterials in the recycling of waste); however, nanomaterials could also be hazardous to human health and the environment. Currently, improving the sustainability of the nanomaterials at the stages of manufacturing, use and end-of-life of nanomaterial-containing products has been a focus of **green nanotechnology**. Green nanotechnology addresses not only a clean and sustainable synthesis of nanomaterials but also the application of nanomaterials in the synthesis of various materials, recycling and other waste management processes (Gottardo et al., 2021).

In order to address the safety and sustainability of nanomaterials, the Safe by Design (SbD) concept has also been applied to nanomaterials in recent years. The EU policies on the circular economy have addressed SbD (European Commission, 2020). SbD is a set of guiding principles for the product design aimed at identifying, estimating and eliminating/minimising risks and uncertainties to humans and the environment throughout the life cycle of the material/product and along the entire value chain (Jimenez et al., 2020). These guiding principles involve several aspects:

• the safety of the product/material by minimising possible hazardous properties while maintaining its functions;

- safe production, which ensures occupational, process, and environmental safety (e.g., using green synthesis for the manufacturing of nanomaterials);
- safe use and end-of-life of a nanomaterial, including recycling and disposal (OECD, 2020).

While these principles help promote a more sustainable way of manufacturing nanomaterials, several other factors will need to be accounted for to increase sustainability. If the guiding principles are followed, resulting in safer materials and manufacturing, this will support a circular economy.

5.2 Green synthesis of nanomaterials

Researchers have drawn substantial attention to the green synthesis of nanomaterials in the last several decades. Usually, a search for alternative approaches has been grounded by disadvantages of some of the conventional synthesis methods, such as the creation of by-products, the use of expensive or hazardous chemicals as reagents (Patwardhan et al., 2018; Wang et al., 2019; Khalaj et al., 2020).

Green manufacturing of nanomaterials, or green nano synthesis, is a promising field that proposes greener and more sustainable ways to synthesise nanomaterials. The **green synthesis** of nanomaterials has attracted a lot of academic interest over the last couple of decades. Khalaj et al. (2020) carried out a comprehensive scientometric assessment to highlight advancements and scientific progress in this field. The study established that the ultrasonic irradiation (UI) and microwave-assisted methods were the first green production techniques for the synthesis of nanomaterials in the nineties; however, **biosynthesis** has become a highly explored, studied, and promoted green synthesis method over the last couple of decades (Khalaj et al., 2020).

Since 2015, attention to the green synthesis of nanomaterials in compliance with the twelve principles of **"green chemistry"** has grown. Green chemistry, also known as "sustainable chemistry", is the design of chemical products and processes that reduce or eliminate the use or generation of hazardous substances. The principles of green chemistry can be applied throughout the life cycle of the product (Khalaj et al., 2020). The European Green Deal, a new European Commission's Action Plan for a Circular Economy, and the European Industrial Strategy and the Chemicals Strategy for Sustainability launched in October 2020, in line with the United Nations Sustainable Development Goals 2030, require that all new products and materials are not only cost-effective and functional but also safe and sustainable, so that the compliance with regulation and acceptance by customers could be achieved. Therefore, the application of green chemistry principles in nanotechnology is pivotal for enabling a **circular economy** in this sector (Gottardo et al., 2021).

The biological production of nanoparticles is a bottom-up mode of synthesis¹, in which atoms are assembled to form materials in the range of 1-100nm (Rana et al., 2020). Several insightful literature reviews have discussed methods of green synthesis of nanomaterials using **biological agents** such as fungi, bacteria, actinomycetes, yeasts, viruses, algae, plants, and biomolecules (Gour & Jain, 2019; Rana et al., 2020; Salem & Fouda, 2020; Saratale et al., 2018a; Singh et al., 2020). The use of waste biomass and biopolymers has also been reported (Saratale et al., 2018b). These organisms are used as major sources of metabolites that can work as reducing, stabilising, and capping agents during the synthesis (Ishak et al., 2019; Saratale et al., 2018a; Singh et al., 2020). Using different bio-reducing agents for biosynthesis produces nanoparticles that have distinct sizes, shapes, and bioactivity (Saratale et al., 2018b).

Nanoparticles can be synthesised both intracellularly and extracellularly, the latter method being preferred since it does not require a downstream process to recover nanoparticles from

¹ Arrangement of smaller components into more complex assemblies by chemical forces (Rana et al., 2020).

organisms (Singh et al., 2020). Depending on nanoparticles to be synthesised, the biosynthesis process can be classified into metal, metal oxide, quantum dot and magnetic nanoparticles synthesis (Saratale et al., 2018b). The biosynthesis of **metallic nanoparticles** has been the most common process mentioned in the literature, with **silver** and **gold** nanoparticles receiving the most attention. Silver nanoparticles have antibacterial, antifungal, anticancer, antiviral, anti-inflammatory, and antioxidant properties (Abdelghany et al., 2017; Ahmad et al., 2019). Similarly, gold possesses anticancer, antibacterial, antioxidant and catalytic features and is remarkably biocompatible (Akintelu et al., 2020; Teimuri-Mofrad et al., 2017). Table 14 provides a list of nanoparticles discussed in the literature reviews.

Nanoparticle	Sources
Gold (Au)	Gour & Jain, 2019; Ishak et al., 2020; Rana et al., 2020; Salem & Fouda, 2020; Saratale et al., 2018a; Singh et al., 2020; Yadi et al., 2018
Silver (Ag)	Gour & Jain, 2019; Ishak et al., 2020; Rana et al., 2020; Salem & Fouda, 2020; Saratale et al., 2018a; Singh et al., 2020; Yadi et al., 2018
Zinc/zinc oxide (Zn/ZnO)	Gour & Jain, 2019; Ishak et al., 2020; Salem & Fouda, 2020; Saratale et al., 2018a; Singh et al., 2020; Yadi et al., 2018
Titanium dioxide (TiO ₂)	Ishak et al., 2020; Rana et al., 2020; Salem & Fouda, 2020; Saratale et al., 2018a; Singh et al., 2020;
Iron/iron oxide or magnetite (Fe/Fe ₃ O ₄)	Ishak et al., 2020; Rana et al., 2020; Salem & Fouda, 2020; Saratale et al., 2018a; Singh et al., 2020
Palladium (Pd)	Ishak et al., 2020; Rana et al., 2020; Salem & Fouda, 2020; Singh et al., 2020; Yadi et al., 2018
Platinum (Pt)	Ishak et al., 2020; Rana et al., 2020; Salem & Fouda, 2020; Saratale et al., 2018a
Cerium/cerium oxide (Ce/CeO ₂)	Gour & Jain, 2019; Ishak et al., 2020; Rana et al., 2020; Saratale et al., 2018a; Yadi et al., 2018
Copper/copper oxide (Cu/CuO)	Ishak et al., 2020; Gour & Jain, 2019; Salem & Fouda, 2020; Saratale et al., 2018a; Yadi et al., 2018
Selenium (Se)	Rana et al., 2020; Saratale et al., 2018a; Singh et al., 2020
Zirconium dioxide (ZrO ₂)	Rana et al., 2020; Salem & Fouda, 2020; Saratale et al., 2018a
Silicon/Silicon dioxide (Si/SiO ₂)	Rana et al., 2020; Salem & Fouda, 2020
Cadmium/cadmium sulphide (Cd/CdS)	Gour & Jain, 2019; Saratale et al., 2018a
Nickel (Ni)	Salem & Fouda, 2020
Quantum dots	Rana et al., 2020
Uraninite	Rana et al., 2020

Table 14: Nanoparticles produced using biosynthesis

Nanoparticle	Sources
Tellurium (Te)	Singh et al., 2020a

Metal and metal oxide nanoparticles are highly promising materials for the unique application in different sectors such as biomedicine (biosensing, cancer treatment, antibacterial, antiviral, drug delivery), agriculture (crop protection, nanopesticides, nanofertilisers, nanofungicides) (Salem & Fouda, 2020; Saratale et al., 2018a), cosmetics industry (antiaging creams, moisturisers, skin wound disinfection, etc.) (Saratale et al., 2018a), food industry (e.g., antifouling agent) (Rana et al., 2020; Salem & Fouda, 2020), catalysis (Rana et al., 2020), environmental field (e.g., bioremediation) (Gour & Jain, 2019; Rana et al., 2020; Salem & Fouda, 2020), textile industry and wastewater treatment (Salem & Fouda, 2020).

For instance, biologically produced nanoparticles showed excellent inhibition against several pathogenic microorganisms, and some of them even killed various microbial species with high resistance to drugs. Hence, these biogenic nanoparticles can successfully replace drugs against which the bacteria developed resistance (Singh et al., 2020a). A systematic review by Foko et al. (2019) revealed the antiplasmodial potential of nanoparticles fabricated via biosynthesis methods highlighting their usefulness as a promising source for the development of new anti-malarial drugs. However, further detailed studies on the safety of available nanoparticles are necessary prior to their use in humans (Foko et al., 2019).

The reuse of the available resources, such as waste, to synthesise nanomaterials has also been investigated in the academic literature. Xu et al. (2019) and Ravi and Vadukumpully (2016) reviewed developments in the use of biowaste for the green synthesis of nanomaterials, mainly carbon bases nanoparticles such as carbon dots, carbon nanotubes, nanocomposites (see Table 15).

Waste sources	Nanomaterial	Application examples
Biowaste (cowhide, goatskin, pig bristles, oil palm leaves), waste tyres	Nanocarbons and nanocomposites	Fillers in composites and hybrids, chemical- and biosensing in medicine, supercapacitor electrodes, bioelectronics platforms, enhanced supports for precious-metal- based catalysts, plant growth promoters
Biowaste (fruit peels, fish scales, rice husk, goose feathers, natural hair)	Carbon dots	Biosensing, bioimaging, drug delivery, photocatalysis, photovoltaic devices, and optoelectronics
Biowaste (sugar cane bagasse, waste corn residue), scrap tyre chips, plastic waste	Carbon nanotubes	Single-molecular transistors, scanning probe microscope tips, gas and electrochemical storage, molecular computing elements, molecular filtration membranes, sensors
Biowaste (goldfish scale, chicken eggshell membrane, cherry calyces, corncob sponge, waste sawdust, rice husk, banana fibres, peanut shells, waste coffee grounds, sugarcane bagasse), mixed waste plastics	Porous carbon nanomaterials	Large-scale energy storage, high- performance supercapacitors, batteries, adsorbents for wastewater treatment, energy storage

Table 15: Use of waste for the synthesis

Waste sources	Nanomaterial	Application examples		
Biowaste (red-grape pomace, chicken eggshells, mango seeds, rice husks, Orchis mascula, fish scales, wine dregs)	(silver, gold,	Biosensing, catalysis, optics, antimicrobial activity, computer components, electrometers		
Sources: Ravi & Vadukumpully, 2016; Xu et al., 2019				

Waste can serve a starting material or serve as a reducing, capping or stabilising agent in the production of nanomaterials (Xu et al., 2019). Potential applications for these nanoparticles include environmental remediation, renewable energy, biomedical, electronics, energy storage, and others (Ravi & Vadukumpully, 2016; Xu et al., 2019). The use of various wastes to derive nanomaterials can also provide a potential solution for managing increasing streams of waste and a safe and eco-friendly alternative to conventional ways of nanomaterial production. However, many methods of synthesis/recovery of nanomaterials from waste are in the early stages of development and not commercialised. Therefore, a lot of work to convert the proposed technologies into commercially viable, safe and publicly acceptable solutions would need to be done.

Green synthesis methods are efficient, cost-effective, environmentally friendly, and relatively simple (Singh et al., 2020; Ishak et al., 2020). Other **advantages** are the use of non-toxic reagents, easy scale-up, enhanced stability, biocompatibility, and low energy requirements (Rana et al., 2020). Ishak et al. (2020) reported that plant extracts enable the control of nanoparticles synthesis to achieve well-defined morphologies and sizes in a single-step synthesis with high yields and provide the ability to produce nanoparticles on a large scale (Ishak et al., 2020). Despite promising advantages, there are several constraints to this technology.

The use of biosynthesis still **requires more optimisation of factors** such as pH, temperature, reaction time, growth medium, to make the process more effective and to achieve the desired size, shape and monodispersity of nanoparticles (Rana et al., 2020). In addition, more studies are required on the production of nanomaterials with specific physiochemical characteristics, especially in the field of biomedicine (Salem & Fouda, 2020).

Furthermore, the assessment of the toxicity and biocompatibility of biosynthesised nanoparticles to human health and the environment needs to be addressed, as it has not been well investigated (Ishak et al., 2019). The release of nanoparticles into the environment may prompt or trigger unpredictable behaviour; hence, this area needs further research (Rana et al., 2020). However, the biosafety of metallic nanoparticles used as anticancer agents has been explored. In the systematic review, Hanan et al. (2018) discussed the cytotoxicity of biologically synthesised nanoparticles. It was revealed that most of the plantmediated syntheses of metallic nanoparticles demonstrated cytotoxicity to various cancer cells, and silver nanoparticles had higher cytotoxicity than gold nanoparticles when synthesised by the same plants irrespective of the cancer cell type. However, most biosynthesised metallic nanoparticles had a narrow range of doses for their therapeutic index, which shows that even minor differences in dose or blood concentration can lead to severe adverse drug reactions and/or therapeutic failure that can be life-threatening. Most research studies compared the cytotoxicity of nanoparticles to human cancer cells and non-human cells, therefore, the therapeutic index could change when studies progress from *in vitro* to animal safety to human safety (Hanan et al., 2018). Hence, the use of biosynthesised metallic nanoparticles for cancer treatment needs more research that can provide strong evidence on the safety and efficacy of this technology.

Finally, **the supply of natural agents for biosynthesis is not sufficient for industrial production**, which is important for the commercialisation of nanoparticles. However, synthetic analogues are being sought, and bio-inspired synthesis methods are designed. Most initiatives

are still performed on a laboratory scale, and there is a lack of knowledge necessary to design a product with desirable properties and assess the availability of necessary resources and cost-effectiveness of the production (Patwardhan et al., 2018).

Despite the previously mentioned wide range of applications of nanomaterials, the **technology transfer from lab to real applications is still very limited** (Khalaj et al., 2020), and scaling up the production of nanoparticles using green technology is considered challenging, which makes commercialisation difficult (Salem & Fouda, 2020). Therefore, comprehensive investigations are necessary to operationalise the industrial-scale production of green nanoparticles (Rana et al., 2020).

Furthermore, as reported by Khalaj et al. (2020), the green synthesis reported in the literature cannot meet the objectives of sustainable development that requires high quality (i.e., efficient), environmentally friendly, economically and socially acceptable products because the main emphasis has been placed on technical conditions of the green synthesis and the intended application of produced nanoparticles, and not on economic issues that may undermine the production of such materials. In addition, the research literature has not adequately addressed the environmental impact of the developed methods and their social acceptability (Khalaj et al., 2020). Hence, further research of biologically synthesised nanoparticles for sustainable development is necessary to establish whether this technology is viable for commercialisation and meets circular economy principles. Finally, green synthesis does not address the circularity of produced nanomaterials, which means that, although potentially safer, such nanomaterials will not last after their use and become waste.

5.3 Nanomaterials for the recovery of rare-earth elements

The application of nanomaterials for solving the issues of supply of rare-earth elements (REE) has been actively explored in recent publications (Kegl et al., 2020; Cardoso et al., 2019; Rahman et al., 2020). In this research, nanomaterials are agents that facilitate the recovery of rare-earth elements. Researchers consider such applications of nanomaterials as a contribution to the circular economy objectives by advancing the recovery of natural resources and optimisation of waste governance (Velenturf et al., 2019). Rare-earth elements are 17 elements, with 15 of them belonging to the group of lanthanides plus yttrium and scandium. These elements are moderately abundant, however, not concentrated enough for easy commercial exploitation (El Latunussa et al., 2020). There is a high demand for rare-earth elements in nuclear energy, medicine, digital technologies and electronic goods, while extraction is restricted to several large mining districts. It increases the interest of policymakers, scientists and industry to provide alternative ways of supply by using available resources, as for instance, waste.

In the European Union, rare-earth elements are **critical raw materials**, i.e., those that are important to the EU economy and where the supply could be disrupted. REEs are important to reach the climate neutral economy goals with the manufacturing of high-tech, low-carbon products (e.g., electric vehicles, wind turbines, batteries and energy-efficient light bulbs). Various sectors, including electric and electronic equipment, batteries, the automotive sector, renewable energy and others extensively use rare-earth elements (El Latunussa et al., 2020).

However, **the European Union depends on importing REE**, mainly from China (42% of imported REE) and the Russian Federation (36% of imported REE). In 2008, the European Commission launched *The Raw Materials Initiative* that aimed to secure the sustainable supply of the critical raw materials in Europe and encouraged their **supply through recycling** (Joint Research Centre, 2020a). The promotion of secondary raw materials on the EU market is one of the important priorities of the Circular Economy Action Plan (European Commission, 2020).

According to the Joint Research Centre analysis (Gislev & Grohol, 2017), three main sectors could be **potential sources of secondary raw materials** (among them – rare-earth elements):

- Mining waste there is still no data about extracted or extractable rare-earth materials from mining waste.
- Landfills dispose of waste electronic equipment and industrial wastes that can become a source of rare-earth elements. According to the JRC (Gislev & Grohol, 2017) estimations, some of the rare-earth elements are annually added to the landfill stock: yttrium (approx. 1000 tonnes), europium (about 100 tonnes) and terbium (about 100 tonnes).
- Sectors where critical raw materials are mostly used, i.e., electrical and electronic equipment (terbium, europium, gadolinium, erbium, and yttrium), batteries (lanthanum and cerium), automotive sector (neodymium, praseodymium, dysprosium and terbium), renewable energy (neodymium, praseodymium, and dysprosium), defence industry (dysprosium, neodymium, and praseodymium and limited application of REE), chemicals and fertilisers (cerium, neodymium, and praseodymium) (Gislev & Grohov, 2017).

REE are known for very **low recycling input rates** ranging from 6% to 7%, and the absence of recycling practices for some REEs (e.g., scandium). Recycling of REEs is difficult because they are small components in complex items, and the recycling requires sophisticated procedures and high energy input (Gislev & Grohol, 2017).

The literature search identified three recent review studies (Ambaye et al., 2020; Kegl et al., 2020; Cardoso et al., 2019) that focused on analysing the previous scientific knowledge on the **use of nanomaterials to recover** REE from wastewater and/or e-waste and one laboratory experiment (Rahman et al., 2020). Table 16 summarises recovered REEs, nanomaterials used, recovery methods applied, and sources of waste.

Recovered REE	Nanomaterial used in the recovery	Recovery method	Waste stream	Source
Ytterbium	Composite hybrid nanomaterial	Solid-liquid separation	Fabricated waste sample	Rahman et al., 2020
Lanthanum, cerium, praseodymium, neodymium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, lutetium, yttrium, scandium	Silicon dioxide, titanium dioxide, carbon, magnetite, maghemite, zero-valent iron Graphene oxide composites, carbon nanotubes, activated carbon, fullerene, carbon dots, carbon black, mesoporous carbon, carbon nanofibres	Physical/chemical adsorption and desorption Solid-phase extraction (sorption)	Wastewater Wastewater, e- waste	Kegl et al., 2020 Cardoso et al., 2019
Europium, cerium, gadolinium, scandium, yttrium, lanthanum, and neodymium	Graphene oxide composites, carbon nanotubes, carbon black, mesoporous carbon, fullerenes, carbon nanofibres, activated carbon	Solid-phase extraction	E-waste	Ambaye et al., 2020

Table 16: Use of nanomaterials in the recovery of REE

Kegl et al. (2020) reviewed recent studies on using **nanomaterials** for recovering rare-earth elements from **wastewater** and showed that non-magnetic nanomaterials based on silica, carbon and titanium dioxide were mostly used in the recovery processes. Magnetic

nanomaterials, such as magnetite, maghemite and zero-valent iron, have also been used. Nonmagnetic nanomaterials showed great efficiency, selectivity for REE ion adsorption and excellent yield, whereas magnetic nanomaterials showed a potential for reuse without the loss of efficiency because of the possibility of magnetic separation. According to the review, magnetic nanomaterials with functional groups that react preferentially with REE ions showed the most effective adsorption capacity. The adsorption process was usually endothermic and spontaneous, and dominant mechanisms were surface complexation and ion exchange (Kegl et al., 2020).

Cardoso et al. (2019) and Ambaye et al. (2020) focused on previous studies that used carbonbased (graphene oxide, carbon nanotubes, carbon dots, carbon nanofibres, etc.) nanomaterials to recover rare-earth elements from wastewater (Cardoso et al., 2019) and **e-waste** (Cardoso et al., 2019; Ambaye et al., 2020) by solid-phase extraction. According to Cardoso et al. (2019), the advantages of sorption over other commonly used recovery methods include easy installation and operation, low maintenance costs and high removal efficiency. However, several factors, such as the metal ion to be recovered, the typology of the sorbent, and experimental parameters (pH, temperature, the dose of sorbent, REE concentration, stirring speed) can influence the removal efficiency. In addition, the presence of other metal ions can also affect the recovery of REE, which needs to be taken into consideration when dealing with real effluents (Cardoso et al., 2019).

The reported adsorption efficiencies varied depending on experimental conditions and the type of nanomaterial used. Kegl et al. (2020) had also looked at the desorption of REE ions from nanomaterials and found that the agent, its concentration, and experimental conditions influenced the separation process. These factors affected the recovery and reusability of both REEs and nanomaterials used. Magnetic nanomaterials were the most suitable for reuse as a repeated process of the adsorption/desorption cycle did not significantly reduce the adsorption efficiency (Kegl et al., 2020).

Table 17: Example of using nanomaterials for REE recovery

The EURARE project (2013-2017, <u>http://www.eurare.org/</u>), funded under the EU 7th Framework Programme for Research and Technological Development, focused on the sustainable use of the REE in Europe. Among other activities, the project team aimed to develop procedures for the separation and extraction of REE. Several partners worked on the different extraction methods. The Swedish University of Agricultural Sciences (Sveriges Lantbruksuniversitet, SLU) developed the technology to recover dysprosium, neodymium, yttrium, and lanthanum using magnetic silica nanoparticles functionalised by various organic ligands. The major advantage of the technology was the green process of extraction that took place in aqueous media.

Source: Balomenos et al., 2017

Currently, most studies have been carried out in a laboratory setting, and there is a lack of costeffectiveness, safety and other analysis for their industry-scale implementation (Cardoso et al., 2019). Low concentration of rare-earth elements in wastewater and gaps in knowledge about the potential harm of nanomaterials to the environment and living organisms complicate the recovery processes (Kegl et al., 2020).

5.4 Nanomaterials for recycling of waste

Nanomaterials may also increase the effectiveness of recycling of other end-of-life materials and products (e.g., see Lopez de Dicastillo et al. (2020) for recycling of food packaging). Nanomaterials act as additives that enable recycling of various types of waste into secondary products without a decrease in their functional properties. Some literature reviews and studies have been identified, focusing on the application of nanomaterials in the recycling of demolition and construction, plastic waste and other products (see Table 18).

Secondary product / Examples	Nanomaterial used in recycling	Source	
Concrete	Nano silicon dioxide, nano calcium carbonate, nano aluminium oxide, nano titanium dioxide, carbon nanotubes, nano- clay, zinc oxide, zinc peroxide, iron oxide	Herath et al., 2020; Jindal & Sharma, 2020; Luo et al., 2019; Moro et al., 2020; Vishvakarma et al., 2018; Younis & Mustafa, 2018	
Plastics (PET, PS, PE, HDPE, PP, bioplastics) and plastic-based products (polymer blends, food packaging, radiation shielding)	nanocellulose, zinc oxide, titanium dioxide, silicon dioxide, nanoclay, calcium carbonate, carbon black, bismuth oxide,	Distaso, 2020; Avazverdi et al., 2016; Zdiri et al., 2018; Lopez de Dicastillo et al., 2020; Mahmoud et al., 2018; More et al., 2021; Amin et al., 2019	
Paper	Silicon dioxide, nanofibrillated cellulose, cellulose nanocrystals	Sabazoodkhiz et al., 2017; Viana et al., 2018; Lenze et al. 2016	
Epoxy-based composites	Nano-magnetic iron oxide	Irez et al. 2018	
Zn-Al alloy	Boron nitride, silicon carbide	Yawer et al. 2021	
Lithium-sulphur batteries	Graphene oxide sheets	Zhang et al., 2017	

Table 18: Use of nanomaterials in recycling

To solve the problem of increasing volumes of **demolition and construction waste**, researchers investigate its recycling opportunities. Recycled concrete shows poorer properties than its "virgin" counterpart, such as low compressive, tensile, and flexural strength, higher water absorption, porosity. Therefore, scientists explore the potential of nanomaterials for strengthening the mechanical properties of **recycled aggregate concrete** (RAC). Several studies discussed the addition of silicon dioxide (Herath et al., 2020; Jindal & Sharma, 2020; Luo et al., 2019; Vishvakarma et al., 2018; Younis & Mustafa, 2018) and titanium dioxide (Jindal & Sharma, 2020; Luo et al., 2019; Luo et al., 2019; Moro et al., 2020; Vishvakarma et al., 2020; Luo et al., 2018), but there is also a potential for other nanomaterials such as calcium carbonate (Herath et al., 2020; Luo et al., 2019; Vishvakarma et al., 2018), aluminium oxide (Jindal & Sharma, 2020; Vishvakarma et al., 2018), carbon nanotubes, nano clay (Jindal & Sharma, 2020), zinc oxide, zinc peroxide and iron oxide nanoparticles (Vishvakarma et al., 2018).

Nanoparticles can act as fillers or activators when added to recycled aggregate concrete (Vishvakarma et al., 2018). Nano-strengthened recycled concrete showed enhanced mechanical properties, durability, and strength (Luo et al., 2019; Moro et al., 2020; Vishvakarma et al., 2018; Younis & Mustafa, 2018) and dense microstructure (Luo et al., 2019; Vishvakarma et al., 2018; Younis & Mustafa, 2018). In addition, nanoparticles reduced porosity in cement blends, increased particle packing density and homogenous qualities (Moro et al., 2020), promoted hydration process (Vishvakarma et al., 2018), and reduced absorption and permeability problems, hence controlling degradation issues related to aquatic environments (Vishvakarma et al., 2018; Younis & Mustafa, 2018). Furthermore, some nanoparticles (titanium dioxide, zinc oxide) can decrease contamination levels and break down organic pollutants and bacterial membranes due to their antibacterial and antifungal properties (Moro et al., 2020; Vishvakarma et al., 2018). Nevertheless, several studies reported decreased workability due to the addition of some nanoparticles (e.g., titanium dioxide, nano clay, aluminium oxide), which imposes some disadvantages in the application of nanomaterials to recycled aggregate concrete (Jindal &

Sharma, 2020; Luo et al., 2019; Vishvakarma et al., 2018). Table 19 (see overleaf) provides the example of the commercial application of recycled concrete using nanofillers.

The environmental impact of the addition of titanium dioxide to concrete pavements was investigated by Baral et al. (2018). According to the study, incorporating this nanoparticle in concrete decreased environmental impact by reducing ecotoxicity, acidification, eutrophication, smog formation, human health degradation factors, and respiratory effects because of photocatalytic removal of NO_x, SO_x and toluene, and white pavements were more effective in removing NO_x than grey (Baral et al., 2018). However, protection measures are required when working with photocatalytic cement. Batsungnoen et al. (2019) analysed aerosolised particles size distributions and concentration in titanium dioxide-based photocatalytic and regular concrete. The study revealed that photocatalytic concrete contained 18.5 times more airborne nano-titanium dioxide than regular bagged concrete powder. Aerosolised photocatalytic concrete showed significantly smaller particle size distribution and greater particle concentration comparing to regular concrete (Batsungnoen et al., 2019). This might have negative implications on occupational exposure as titanium dioxide is a suspected carcinogenic to humans.

Table 19: An example of commercial use of nanomaterials in recycling concrete

Czech company ERC-TECH developed and patented the technology for manufacturing concrete (ercconcrete[®]) from construction and demolition waste, e.g., concrete, bricks, paving, ceramics, sanitary products, mixtures – concrete/bricks, roof tiles and ceramic products, mortar, etc. Ercconcrete[®] is produced 100 per cent from recycled material. The unique patented technology uses nanofillers to improve the recycled concrete properties, which are comparable to concrete made of natural aggregate. Ercconcrete[®] possesses lower thermal conductivity and volume density and a longer life cycle than its virgin counterpart. These features contribute to its competitive potential in the market.

In 2019, ERC-TECH received honourable mention in the report "Deloitte Technology Fast 50 in Central Europe" for reducing the extraction of raw materials and decreasing the disposal of construction and demolition waste by its re-use in new concrete products. The green impact of ercconcrete[®] is comparable to removing about 8.7 million passenger vehicles off the road due to the potential of re-using approximately 2 billion tonnes of construction and demolition waste per year with about 200 kg savings in CO_2 emissions per tonne.

Sources: ERC-TECH, n.d.; Deloitte, 2019

Another popular material that creates high volume of waste is plastics, abundantly used in food packaging and in many other applications. Recycled polymers lose their original mechanical, optical, thermal and barrier properties. The use of nanomaterials allows the improvement of polymer properties and an increase in their useful life.

Nanoparticles can be used as additives, which can be classified as organic and inorganic (Distaso, 2020). The most mentioned organic nanoparticles in the literature were graphene (Distaso, 2020; Lopez de Dicastillo et al., 2020), carbon nanotubes (Zdiri et al., 2018; Distaso, 2020; Lopez de Dicastillo et al., 2020) and nanocellulose (Distaso, 2020; Lopez de Dicastillo et al., 2020). Among the inorganic nano-additives were nano clays (Avazverdi et al., 2016; Zdiri et al., 2018; Distaso, 2020; Lopez de Dicastillo et al., 2020), zinc oxide, silicon dioxide (Distaso, 2020; Zdiri et al., 2018), and titanium dioxide (Matxinandiarena et al., 2019; Distaso, 2020). Nanoparticles, used as additives for nano-reinforcement of recycled plastics, improved mechanical properties (Distaso, 2020; Zdiri et al., 2018; Lopez de Dicastillo et al., 2020), thermal properties, and rheological behaviour (Zdiri et al., 2018). The use of nanoclay as an additive effectively increased yields, stress, modulus of tension, hardness, rigidity, and resistance to humidity (Distaso, 2020). Nano clays seem to be a promising nanofiller due to their platelet form, which is suitable for inhibiting migration in food packaging, low cost, and great mechanical enhancements (Lopez de Dicastillo et al., 2020). However, Avazverdi et al. (2016) reported that the composite was more brittle, and the impact strength decreased for PE when reinforced with nano clay.

Amin et al. (2019) compared the performance of starch and composite bioplastics reinforced by titanium dioxide. Although both products showed good physical, mechanical and thermal properties, the composite bioplastics were remarkable for a more consistent surface (less prone to holes and cracks) and higher heat stability. Both products were highly biodegradable, although starch bioplastic showed better performance. Due to the antimicrobial properties of titanium dioxide, composite bioplastics could be considered suitable for food packaging and the pharmaceutical industry (Amin et al., 2019).

Nanoparticles can also be used as nano-pigments to provide an optical response such as colour, which can be enhanced, intensified, or modified. Nanomaterials have been applied as a catalyst for the depolymerisation of plastics with a possibility to recover catalysts; however, this application is still at the lab scale and requires further research (Distaso et al., 2020).

An important trend in the current research is the exploration of the synthesis of nanostructured polymer materials and their application for radiation shields (Mahmoud et al., 2018). More et al. (2021) provided a literature review of the experimental studies in the field. Recycled polymer materials reinforced by metal oxides, graphitic nanofibres etc., demonstrate efficient protection against gamma radiation while being lower in weight than traditionally used lead materials. The addition of nanofillers enhances the strength, hardness, and radiation absorption abilities of the synthesised composite. These novel materials are much better shielding options against radioactive sources, and they are environmentally sound and non-toxic. Polymer composite materials have a high potential for application in the nuclear industry, medical diagnostics, and nuclear research organisations. However, further comprehensive studies are necessary to establish the radiation attenuation/absorption properties of nanoparticles against different types of radiation (More et al., 2021).

The impact of nanomaterials reinforced recycled plastic on the environment and human health is still unclear. It is crucial to ensure that nanoparticles remain enclosed in plastic material and are not released into the environment because they can have a potential direct risk for living organisms and an indirect threat to human health because of the accumulation of non-degradable nanoparticles in the environment (Distaso, 2020). A better understanding of the recyclability and migration of substances from reinforced materials to food in food packaging applications is still an issue and requires further research (Lopez de Dicastillo et al., 2020).

Another waste stream that could benefit from nanotechnology is **paper** (see Table 5-2). Although recycled paper can become a primary or secondary source of raw material to produce paper, recycled fibres have inferior resistance properties and are morphologically different from virgin ones due to lower hydration capacity, shorter average length, less flexibility, and lower capability to form inter-fibre bonds (Viana et al., 2018). Therefore, recently the research has been focusing on adding certain nanoparticles to improve the properties of the paper produced from recycled fibres. Nanoparticles such as silicon dioxide (Lenze et al. 2016; Sabazoodkhiz et al., 2017), nanofibrillated cellulose (Viana et al., 2018), and cellulose nanocrystals (Lenze et al. 2016) have been used as additives for recycled waste office pulp, recycled cardboard, and paper (printing, writing, newspaper) and recycled copy paper.

The **addition of nanoparticles to recycled paper** improved mechanical and physical properties such as density, tensile, burst and tear resistance when compared to regular paper (Sabazoodkhiz et al., 2017; Viana et al., 2018). During the production process, nanoparticles also helped to promote dewatering, paper uniformity (Lenze et al. 2016), and fine-particle retention (Lenze et al. 2016; Sabazoodkhiz et al., 2017), reduce paper thickness (Viana et al., 2018), and improve drainage (Sabazoodkhiz et al., 2017). According to Viana et al. (2018), the improvement in mechanical properties of recycled paper made with nanofibrillated cellulose is related to the increase of hydrogen bonds between fibres. Nanoparticles form a dense network resulting in greater surface area of the nanoparticle.

Zhang et al. (2017) reported a unique and innovative way to produce low-cost, environmentally friendly, high-performance lithium-sulphur (Li-S) batteries from recycled paper and graphene

oxide sheets via capillary adsorption method. The assembled battery showed a superior life span of 620 cycles with a great capacity retention rate of 60.5%. This novel method of designing and fabricating Li-S batteries could contribute towards tackling global deforestation and fossil fuel depletion by recycling bio-mass materials for energy storage devices (Zhang et al., 2017). However, the process is relatively new and requires further research.

The application of **nanomaterials for recycling other waste streams**, for instance, metal waste and rubber:

- Yawer et al. (2021) reported on Zn-Al alloy reinforced by boron nitride and silicon carbide nanoparticles. Such reinforcement resulted in enhanced mechanical properties of the composite with uniformly dispersed particles and improved compression properties (Yawer et al., 2021).
- Irez et al. (2021) analysed the reinforcement of the recycled and devulcanised rubber by nano-magnetic iron oxide and developing modified epoxy composites, which could provide a solution for manufacturing cost-efficient, lightweight materials for industrial applications such as aeronautical and automotive engineering. Tough and low-cost materials with good mechanical properties and magnetic permeability were obtained during the process (Irez et al., 2018).

Overall, the use of nanomaterials as additives and fillers for reinforcement of recycled aggregate concrete, plastic, alloy Zn-Al alloy and epoxy-based composites, as well as for improvements of recycled paper properties, have been extensively researched. Hence, nanotechnology has the potential to contribute to increasing recycling rates of waste and the quality of the recycled products. However, the environmental and human health impact of nanoparticles has not yet been fully investigated; reports about the recyclability of nano-enhanced secondary products and materials are absent. Therefore, the potential contribution of nanomaterials as enablers of the circularity of waste is unclear.

6. Findings of the Expert Consultation

Twenty-one interviews with stakeholders were conducted, each interview lasting around one hour. Interviewees were from academia, national authorities, non-profit organisations, industry associations and enterprises, and from various countries, mainly the EU, but also the US, Canada, and India (see Annex 4 for the list of respondents). The respondents were asked to rate their confidence level in making judgements on the topics of the interview as high (constant work/research related to the topics, following the updates), medium (occasional work/research related to the topics), and basic (general knowledge about the topic with limited research/practical work experience). Most respondents rated their confidence in the topics they discussed as medium to high, with only one respondent indicated confidence as low. The interview recordings were transcribed, and a thematic analysis was carried out to highlight the main topics that emerged.

During data analysis, patterns of responses to the topical discussions and relations between topics were noted (see Figure 10, overleaf).

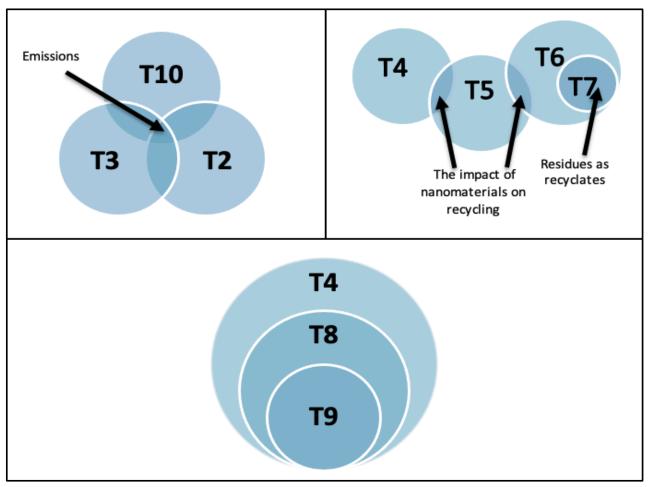


Figure 10: Patterns in the interviewee responses to discussions on various topics

Note: Topic 1 – sources of waste containing nanomaterials; topic 2 – behaviour and fate of nanomaterials in waste; topic 3 – occupational exposure of waste treatment staff to nanomaterials; topic 4 – benefits and challenges of nanomaterials for the circular economy; topic 5 – the impact of nanomaterials on recycling; topic 6 – recyclate streams; topic 7 – abatement systems residues containing nanomaterials; topic 8 – the impact of nanomaterials on waste management and recycling; topic 9 – nanomaterials in reducing waste streams and substituting hazardous substances; topic 10 – emissions, emission control and best available techniques

As Figure 10 shows, some topics were closely interrelated:

- Topic 2 (fate and behaviour of nanomaterials), topic 3 (occupational exposure of waste treatment staff to nanomaterials) and topic 10 (emissions, emission control and BAT) shared the theme of nanomaterial emissions. Emissions of nanomaterials are one manifestation of behaviour and fate in different waste treatment processes, while exposure of workers to nanomaterials occurs because of their emissions. So, respondents who were invited to discuss topic 2 inevitably commented on topics 3 and 10.
- Topic 4 (benefits and challenges of nanomaterials to the circular economy), topic 5 (impacts of the nanomaterials on recycling and subsequent need for regulation/technical solutions) and topic 6 (recyclate streams) shared the theme of the impact of nanomaterials on recycling. So, there were overlaps in discussions on topics 4, 5 and 6. Topic 7 was mainly discussed under topic 6 because recyclates that originate from the residues of abatement systems are an outcome of waste recycling.
- Much information on topic 8 (impact of the nanomaterials on waste management and recycling) and on topic 9 (the role of nanomaterials in reducing waste and as potential

substitutes for hazardous substances) was covered in discussions of topic 4, as benefits of nanomaterials for the circular economy include waste management applications.

Based on these observations, the interview data analysis strategy was adjusted and monitored to reach enough responses on each topic, irrespective of which topics were originally under discussion. Stakeholders who declared their competency in various topics during the expert poll were encouraged to discuss several topics with us. Two experts sent us extensive written comments on several topics following their interviews.

Data collection resulted in a different number of responses to each topic (see Table 20). For analysis, the interrelated topics were integrated into one theme (e.g., topics 4/8/9 and topics 6/7).

Topic of discussion	Number of respondents
Topic 1	10
Topic 2	8
Topic 3	8
Topic 4/8/9	7
Topic 5	6
Topic 6/7	6
Topic 10	10

Table 20: Responses to the topics of interviews

Table 20 shows that three topics – 1, 3 and 10 received the most responses, while topics 5 and topics 6/7 – less. However, it is important to note that some questions from topics 6/7 were covered in topic 5. All topics received no less than six responses.

In the following sections, the thematic analysis of each topic is presented, with the interrelated topics grouped under one heading. If issues relevant to a specific topic were already covered in another topic, a comment is provided. Each section contains a map of thematic categories that emerged in discussions and their interpretation illustrated by quotes from the respondents.

6.1 Topic 1: Sources of nanomaterials in waste

Topic 1 was aimed at gaining information about the main sources of nanomaterials in waste. In the discussions, respondents were asked to identify:

- the main types of waste that contain nanomaterials,
- the predominant nanomaterials present in the identified waste streams,
- why the identified streams of waste and/or nanomaterials should be considered.

Figure 11 summarises the main topics and sub-topics mentioned by the interviewees.

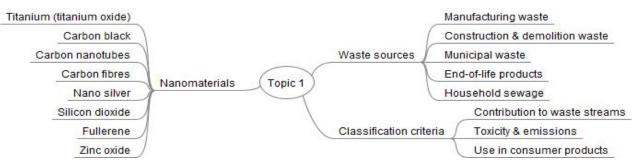


Figure 11: Thematic categories in topic 1

As shown in Figure 11, the interviewees mentioned several main **sources of waste** – manufacturing waste, municipal waste and construction & demolition waste, household sewage. For instance:

- "I think, probably, most nanomaterials in waste will either be from industrial processes or the use of nanomaterials in the production of goods or from domestic activities."
- "Home waste, including products and/or their packaging."
- "Home dirty water."
- "Construction and demolition waste is, you know, a big stream to check."

Many interviewees spoke about **end-of-life consumer products** as a significant source of waste. These products can also enter construction, demolition, and municipal waste streams. For instance, "products will probably reach the end of life via the consumer and not much via the industry, one source is the end-of-life stage of products, and they will go into certain routes". Many examples of such products containing specific nanomaterials were mentioned: "sports equipment", "vehicles", "textile", "cosmetics", "e-waste". Several interviewees discussed an interesting example of a new waste stream containing medical personal protections from COVID-19:

"So recently, we have been looking a little at the presence of nanomaterials in biocides and their use in COVID protection material. <...> And then, of course, I am thinking of the face masks that came onto the market <...> and might be another waste stream that would be worth looking at".

Interviewees mentioned **eight types of nanomaterials** (see Figure 10) occurring in waste. Most nanomaterials were carbon-based (e.g., carbon black, carbon nanotubes or nanofibres, fullerene). Usually, the interviewees focused on a specific nanomaterial and associated it with a typical manufacturing sector or consumer product, e.g.: "nowadays, silver is used a lot in cosmetics and, I would say, also in clothing; carbon fibres are used in different sport applications".

The experts discussed specific nanomaterials because of several reasons:

- Their contribution to waste streams. E.g., "some studies looked at what ends up in waste, and I would probably name silver, titanium dioxide and carbon-related nanoparticles".
- Concerns about their toxicity and emissions. E.g., "safety and emissions risks should be considered when talking about nanomaterials in waste".
- Wide use in consumer products. E.g., "if we focus on the quantities, it is titanium dioxide and silicon dioxide. They are everywhere in consumer products and food".

Many interviewees mentioned the presence of nanomaterials in consumer products as an indicator of their potential contribution to waste streams. There were only two mentions that the safety and toxicity of nanomaterials should be considered when ranking their significance in waste streams.

6.2 Topic 2: Behaviour and fate of nanomaterials in waste processes

In topic 2 interviews, interviewees were asked to identify waste treatment facilities, factors that influence the behaviour and fate of nanomaterials and their treatment effectiveness, and gaps in knowledge in the field. Interviewees commented on four major topics that are summarised in Figure 12.

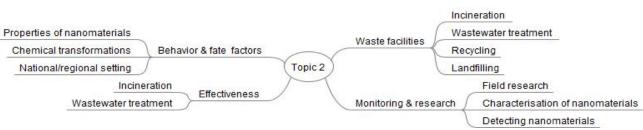


Figure 12: Thematic categories in topic 2

Interviewees mentioned **four waste treatment facilities** – incineration, wastewater treatment, recycling, and landfilling. However, in further discussions, most of them were more comfortable talking about incineration. Usually, interviewees commented on the routes of specific nanomaterials or products containing them to certain waste management facilities, e.g.: "titanium dioxide is used a lot in the construction and demolition, a lot of it will end up in recycling; silver, as I mentioned, is used a lot in cosmetics and clothing; so, the main route will be wastewater treatment plants; incineration – medical devices, plastics, and tyres".

The experts mentioned three factors that shape the behaviour and fate of nanomaterials in waste treatment. They covered **properties of nanomaterials**, **chemical transformations** of nanomaterials in waste treatment processes and **national or regional settings**, especially legislation, that impacts how waste treatment residues are used.

Interviewees highlighted **two types of properties of nanomaterials** – features of pristine nanomaterials and the matrixes where they are present. **Features of pristine nanomaterials** could influence their behaviour in environmental compartments, e.g., "the long-living metal nanoparticles that are antibacterial give the bacteria enough time to develop a modular resistance, and it is a big concern". According to the interviewees, nanomaterials are often embedded in **complex matrices**, and it may affect their transformations in the processes of waste treatment:

- "Some polymers, for example, act protective, which means that they protect the carbon nanotubes from being oxidised, so, they have emitted, at least in our setup".
- "Nanoparticles are not destroyed but chemically modified, and it is related to the degradation of the matrix".

The experts recognised that **chemical transformations** of nanomaterials taking place in waste treatment processes are critical factors for their behaviour and fate. For instance:

- "Chemistry has the biggest effect on the treatment of nanomaterials".
- "Matrix, the size of the particles, the chemistry of the particles are important. At the beginning of incineration, nanocomposites can be toxic and afterwards not, and vice versa".

When speaking about the gaps in knowledge, most interviewees focused on state-of-the-art **monitoring and research of nanomaterials** in waste treatment processes. They mentioned three gaps – the lack of protocols for **characterisation of nanomaterials**, **the lack of field research** with currently predominant laboratory studies and the lack of analytical techniques for **detecting nanomaterials**, especially distinguishing between manufactured, incidental, and natural nanomaterials.

The lack of harmonised techniques for **characterisation of nanomaterials** complicates the studies of transformations of nanomaterials, e.g.:

"We tried to mix different nanoparticles to study how they degrade because there is a mixture of nanoparticles and matrixes in waste. We try to understand how to access and characterise these kinds of modifications. <...> It is not so easy to extract such nanomaterial parameters in various media; there is a lack of protocol to extract such parameters."

Interviewees also pointed out that many studies take place in a laboratory, but **field research** is crucial to understand the mechanisms of transformations of nanomaterials in industrial waste management processes and facilities:

- "The field research is missing, the field research with waste incineration plants. For instance, now there are [studies on – author comment] cerium oxide and titanium. But there are many other nanoparticles and especially those that are a bit more dynamic than these two. The same is with [the research of – author note] wastewater treatment plants".
- "You can do a small-scale lab study, resembling waste incineration, but that is a stable process and does not at all resemble what happens in the waste incineration plants because we have experience of working with those as well".

Interviewees discussed **detecting manufactured nanomaterials** because many incidental nanomaterials may form in waste treatment processes:

- "The major problem is, of course, the incidental and natural nanoparticles. You can measure nanoparticles in wastewater treatment plants, and you will find many. But how to know which of them are engineered?"
- "I think there is one thing that is so complex. I mean, you can measure nanoparticles. But how to distinguish engineered nanoparticles from those occurring naturally?"

Techniques that would allow a distinction between manufactured and incidental nanoparticles would facilitate studying the fate of nanomaterials in waste processes and the environment.

Interviewees were asked to focus on those waste treatment processes they know the best. Most interviewees were more comfortable speaking about the **effectiveness of incineration** processes. The temperature was mentioned as the most crucial effectiveness criterion. For instance, they mentioned:

- "I think you can safely assume it [nanomaterial author comment] is gone if incineration is done according to the state-of-the-art [procedures author comment] or in some sort of modern facility ensuring about 850 degrees for diagnosing destruction."
- "If waste incineration is not done properly, then it is a source of pollution. We know this since the 90s. <...> So, the first thing that you must do is having proper combustion. For example, you should foresee that a specific temperature is reached."

A comment on **wastewater treatment** was also provided. According to the interviewee, the presence of nanomaterials can affect the efficiency of the treatment, e.g., "the addition of a nano form to the product could modify waste treatment efficiency (see, for example, nanosilver reports for water treatment)".

6.3 Topic 3: Exposure of workers to nanomaterials at waste treatment facilities

In the interviews on topic 3, interviewees were asked about waste management facilities and processes during which the exposure of workers to nanomaterials occurs. Figure 13 summarises the key themes that emerged.

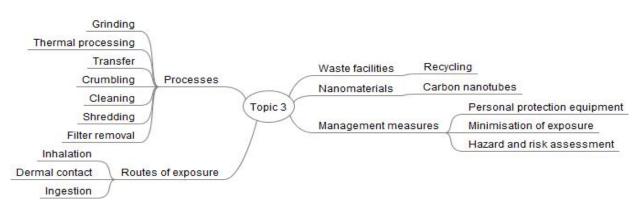


Figure 13: Thematic categories in topic 3

Figure 12 reveals that the interviewees focused on **five topics** in the discussion. Most respondents mentioned **recycling facilities** as a prominent source of occupational exposure to nanomaterials. The respondents also focused on specific **processes** rather than facilities. They highlighted major **routes of exposure** and **management measures** to mitigate the exposure problems. Interestingly, the interviewees preferred to speak about **nanomaterials abstractly**, without mentioning specific types of them. Only one comment was received on exposure to carbon nanotubes.

The only waste management facility specified straightforwardly was **recycling**. E.g.:

- "I think we identified that one of the exposure routes with the highest risk was recycling as it often involves some sort of grinding and comminution."
- "Normally, recycling involves shredding, and of course, shredding produces dust. <...> During shredding, you need to take care of the dust."

Otherwise, interviewees preferred to speak about specific waste management **processes** when occupational exposure may occur. However, they considered various waste management facilities. E.g., "if waste treatment includes combustion or any other high energy process, cutting, grinding and other steps, then you can get occupational health problems". Some processes, e.g., cleaning, could apply to many waste management facilities: "the line between worker and wastewater worker is blurry: what is missing are the clean-up people". Other mentioned processes included grinding and shredding, crumbling, removing filters and transferring waste, thermal processing operations, e.g.:

- "Handling equipment to remove this material [i.e., nanomaterials author comment], then the activity to remove filters. If the residue is from electrostatic precipitators, it is going to be quite a high-risk process."
- "Environmental release through the shredder and there is a huge cloud of dust that could contain nanomaterials. For occupational health, you need to take care of the particles."
- "When we talk about recycling, you know, there could be different processes, e.g., remelting of materials. It could be plastic remelting, where the temperature would go up to 200-300 degrees, and there could be volatilization of some compounds."

Most interviewees focused on the **inhalation route** of occupational exposure. Most of them were speaking about "dust" and "airborne" or "inhaled" nanomaterials. One interviewee mentioned

dermal contact and digestion as other routes of occupational exposure. However, the inhalation route was predominant, e.g.:

"They are so small that during base treatment or any kind of end-of-life [treatment – author comment], there would be a very high risk that they become airborne and would be inhaled. There is a special toxicity mechanism with inhalation. So, nanoparticles are usually much more toxic when inhaled compared to any other route of exposure."

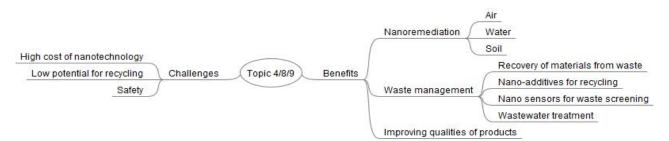
Practices and measures to manage occupational exposure were briefly mentioned by many respondents. They included decision-making processes (e.g., minimisation of exposure or hazard and risk assessment), the use of personal protection equipment. e.g.:

- "We created a matrix of how we handle nanomaterials based on their properties. So, we look at the nanomaterial and assess its characteristics: is it solid bound in a matrix? Is it in a suspension? Is it dry? And then we determine how to handle a nanomaterial."
- "If it is a material that is prone to create a lot of dust, that's where exposure could happen. So, one of our earlier recommendations was to try to minimise this situation.
 <...> We also looked at how effective the personal protection equipment could be and, I think, in most cases, we could have quite a high efficiency."

6.4 Topics 4/8/9: Benefits and challenges of nanomaterials for the circular economy (including waste management)

In the interviews focused on topic 4, questions were asked to highlight the positive and negative impact of nanomaterials on reaching any circular economy goals. To avoid bias, the task of defining a circular economy was left to the interviewees. Topics 8 and 9 addressed the positive roles of nanomaterials in waste management and the reduction of waste streams. The section covers these issues as well. The respondents raised three benefits and the same number of challenges of nanomaterials for the circular economy. Figure 14 summarises the main discussion themes.

Figure 14: Thematic categories in topics 4/8/9



As shown in Figure 14, **three benefits of nanomaterials for the circular economy** were raised: nanoremediation, i.e., purification of air, water and soil, multiple benefits for waste management and improving the qualities of products. Benefits for waste management included the insights from the discussions on topics 8 and 9.

Interviewees mentioned the use of nanotechnology for the "preservation of primary resources" by **cleaning water, air and soil**. E.g., "since over 10 years ago, nanotechnologies are applied to treat air, soil, and water; see many publications. They were early applied on water, then on-air and more recently – on soils. Some of them are commercialised".

Many interviewees indicated **various benefits for waste management**. Instances included the recovery of valuable nanomaterials from waste, the facilitation of recycling waste by incorporating nano-additives in secondary products, wastewater treatment and using nanosensors for screening and ranking the streams of waste. For instance, one interviewee referred to the example of the recovery of nanomaterials from the mining waste: "they have a lot of waste products from mining <...>, and they are looking how they could use that waste. They are trying to extract metals in ionic forms and to make nanoparticles that could be used, for instance, as catalysts". Other respondents highlighted the roles of nanomaterials as additives that enable recycling waste into secondary products, e.g., "plastic, tyres, building materials – facilitation of the recycling of product without losing their properties"". The interviewees mentioned wastewater treatment, e.g., "nanoparticles act as adsorbents" [in wastewater treatment – author comment]; "Hong Kong Polytechnic University has developed a polymeric nano sorbent that has been successfully applied in wastewater treatment by the Dunwell Group". A comment was received on the potential of nanomaterials to serve in monitoring waste streams:

"Today the need for cheap sensors is growing (big data, data mining, internet of things, numerical tweens, prediction, control). The market is driven by air and water quality. The circular economy could benefit from these techniques shortly – for waste screening and ranking."

And finally, the last benefit addressed the application of **nanomaterials as additives to various products** (not necessarily recycled from waste) to improve their longevity and properties:

- "We have already shown that if you use the [nano author comment] additive, its [product – author comment] life cycle would be much longer. If we talk about the battery durability, I am just giving an example, in five years, it could suddenly last 15 years, and it will keep 100% capacity it can deliver."
- "The positive impact on the circular economy would be that there will be potential [product – author comment] lifetime extension."

Interviewees highlighted **three challenges of nanomaterials** for the circular economy. The first challenge – the **high cost of nanotechnology** could limit its application for the benefit of the circular economy. E.g., "the cost of materials and manufacturing, however, may prevent nanotechnology from being used right away. This technology is still in its infancy. Large-scale fabrication of nanotech, especially carbon nanotubes, is possible and already implemented in some industries. This technology is more expensive and less tested than other, more traditional solutions, but it holds promise". The second challenge addressed the **low potential for recycling** nanomaterials for various reasons, such as small amounts of nanomaterials in waste streams, low economic feasibility for recycling. E.g.:

- "Nanoparticles could not work for the circular economy because of the small fraction that could be removed from waste."
- "From a material point of view, nanomaterials are seldom clean. If you would think to reuse them, for example, for new metals, it is nearly impossible because they always have this core structure."

The third challenge refers to the **safety of nanomaterials** to human beings and the environment. Interviewees addressed the potential for the accumulation of nanomaterials in the human body and their adverse effects on the environment if they are applied to water, soil, or other treatment. One reason for concern is unknowns about the safety of nanomaterials. E.g.:

- "The major challenge is to assess safety during their [nanomaterials author comment] use and to develop methods to evaluate the performance but also the ageing of these new materials."
- "With water, it works both ways as a means for water purification, but also antibacterial nanomaterial effect could be negative."
- "As well in the nonmedical applications, they [nanomaterials author comment] are cleared out, or in some cases, they never leave the body. So, there are some issues with the long-term effects of inert nanoparticles in the body. There are post-mortem studies

that show the enrichment of silica, aluminium, oxide, and other inert nanoparticles in the liver or the kidney, surrounded by inflammatory cells that are trying to eat them."

It could be seen in the examples that some benefits have opposing challenges. For instance, the recycling of nanomaterials has been explored as an option; however, there are doubts about its economic feasibility and even possibility. These opposing statements appeared because the discussion covered the general (and, quite abstract) issues and did not focus on the benefits of specific nanomaterials.

6.5 Topic 5: Impacts of nanomaterials on recycling

In discussions on topic 5, interviewees were asked to outline the main negative effects of the presence of nanomaterials in waste on recycling and elaborate on the necessity of technical or regulatory measures to cope with these negative impacts. Most interviewees treated this topic as partly coinciding with topic 4, where they also addressed the negative effects of nanomaterials on recycling.

There were two dominant themes in the discussions – the **impacts of nanomaterials** and the **measures** to handle them. Figure 15 summarises the key themes and sub-themes. This discussion raised uncertainty and concerns about the lack of knowledge on nanomaterials, and suggestions of specific technical and regulatory measures were not well developed. However, the experts emphasised the gaps in knowledge.

Figure 15: Thematic categories in topic 5

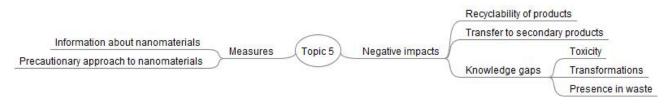


Figure 15 shows that the most well-developed part of the discussion on topic 5 covered the **knowledge gaps that prevent taking specific decisions or actions on nanomaterials**. As one participant put it, the situation with a lot of unknowns and debates stimulates us to take the approaches informed by the previous experience:

"So, the way we think about it is informed by the experience of material recycling of other products, mostly plastics, where it has been demonstrated by tests that the recycling process concentrates toxins. It concentrates POPs in recycled plastic. The issue that we have been looking at is not directly related to nanomaterials. But the impact of waste quality on recycling processes is the risk of seeing toxic substances and materials being reintroduced into the material flow and creating new ranges of exposure. <...>There are still several questions about the toxicity of nano substances and whether they survive and in what form, what kind of transformation they go through the recycling process, both the mechanical and chemical. I do not have that much information, and my understanding is that there are still a lot of unknowns, and there are still quite a lot of debates relating to the transformation."

Similarly, other interviewees addressed the lack of knowledge on the effects of nanomaterials in recycling, mostly their toxicity. e.g.:

• "We do not know the effects of nanomaterials. We are using them, and they give some benefits, but we do not know the disadvantages or negative impact. For example, to compare: if there is a possibility that in plastic material, there are chemicals that can be hazardous for health and the environment, they should not be circulated."

 "I would not dare to say that this specific nanomaterial is supposed to be regulated or not; I think it still needs to be investigated. But if, for example, there are some obvious materials, for instance, fibres, stable types of particles, of course, those, perhaps, should not be entering the normal waste flow. Perhaps, they should be taken care of in facilities which have a higher temperature. From my perspective, it is not an issue that we cannot handle. I think it could be handled, and we need to understand which materials may cause a risk and avoid them. But if the benefit of using them is being [big – author comment] enough, then we need to make sure that we safely handle them."

Additionally, a comment was provided on the **lack of information on the presence of nanomaterials in waste streams**: for recyclers and the recycling streams in general, there is a lack of information about what products nanomaterials can be found in and in what form. One of the key elements that we learned to work on a recycling stream and processes is that to adjust their processes, recyclers need to know what sort of material they are dealing with.

As in the discussion on topic 4, concerns about **recyclability of nanomaterials** present in waste were mentioned, e.g., "when nanomaterials are entering to recycling processes, they might reduce the recycling efficiency; the presence of some material may modify the properties of other materials, and it may require different recycling process (temperature, mechanical processing etc.)". Interviewees shared assumptions about the **transfer of nanomaterials to the secondary products**:

- "I feel it could be the same as with the issue of heavy metals and additives. So, the issue is that you have an involuntary transfer of materials to new products, where they should not be."
- "Look at the combined effect of the waste materials, where it ends up and look at the specific handling steps today, but also think about the future steps and how materials might affect these handling steps and risks of mixing nanomaterials into recycled polymers, for example, and then an uncontrolled spread, somehow."

To summarise, the discussion of the negative impacts of nanomaterials was heavily based on analogies with bulk materials (mostly plastics) and assumptions. It could suggest a high level of uncertainty about the risks that nanomaterials bring. These concerns were also quite straightforwardly voiced by the experts.

Considering the gaps in knowledge about the effects of nanomaterials on recycling, few suggestions on the regulatory measures addressed the **availability of information about the presence of nanomaterials in products** and **precautionary approaches to nanomaterials**. Instances of the first measure included labelling of products and 'digital passports' for products containing nanomaterials:

- "So, the question is how we can identify that there is a nanomaterial. The Commission
 has been working on the digital product passport. <...> I think this is something that can
 help us to identify the nanomaterial."
- "The first rule there should be transparency measures, recyclers should know what materials they are dealing with. Some sort of labelling, material database, product inventory. It would not completely guarantee but provide some necessary information to recyclers."

One comment was provided on the precautionary approach and designing safe nanomaterials: "better implementation of the precautionary system – ensuring that what comes to the market is safe and not toxic".

6.6 Topics 6 and 7: Recyclate streams/abatement systems residues containing nanomaterials

In the interviews addressing topic 6, questions were about recyclates that contain nanomaterials, the origin of nanomaterials in them and the role of nanomaterials in recycling. The third question was addressed in topics 4 and 5. It was noted that in topic 6 discussions, interviewees also covered the incorporation of abatement systems residues that contain nanomaterials into secondary products. Due to this, the analysis of topic 6 and topic 7 were integrated.

The main outcomes of topics 6 and 7 were the overview of the recyclate streams containing nanomaterials and the recycling of abatement systems residues. Figure 16 (overleaf) provides a summary of the key themes.

Figure 16: Thematic categories in topics 6 and 7



Mostly, respondents made assumptions about the **presence of nanomaterials in the recyclate streams** based on the availability of nanomaterials in products that undergo recycling. It was clear from the explanations of the origin of nanomaterials in the recyclates: "paper and cardboard because of the inks; we may also find some nanomaterials in the recycled plastics; functional nano-additives to the product, e.g., anti-fungal additives".

One comment mentioned that **presence of nanomaterials in the recyclate streams is negligible**: "many of them [nanomaterials – author comment] are removed through recycling, and not going into the recycled products. <...> It is small contamination that is removed through recycling. Metal recycling, steel recycling – you may investigate that, but it is a minor contribution."

Respondents reported about the usage of various abatement systems residues, such as slags, fly and bottom ash for construction or backfilling and agricultural use of sludge. Some interviewees indicated that the use of bottom/fly ash is already regulated due to the presence of hazardous substances:

- "A quite extensive discussion is on using bottom ash from waste incineration for ground construction work. The limiting factor is certain forms of zinc and copper. So, it is not related to nanomaterials."
- "Normally, fly ash is not used in specific recovery applications; it ends up in a hazardous landfill or is recovered in salt mines. In very rare cases, it can be used as asphalt filler. However, then it must pass additional environmental requirements and checks from the local legislation to make sure that this is okay."

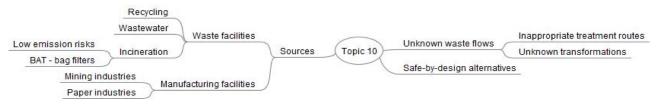
One comment was provided on the general use of sludge in agriculture: "it should be prohibited to use the sludge for soil application".

There was not much information on topics 6 and 7, and the discussion was mainly based on assumptions and parallels with other chemical substances.

6.7 Topic 10: Emissions, emission control and best available techniques

In the discussion on topic 10, respondents were asked to explain situations when emissions of nanomaterials in waste management occur, consider the common quality issues and/or substandard practices that lead to emissions, and discuss the best available techniques (BAT). This topic is closely related to topics 2 and 3, where respondents described general factors enabling the behaviour and fate of nanomaterials, including emissions and occupational exposure to nanomaterials. Three major themes emerged in the discussion (see Figure 17).

Figure 17: Thematic categories in topic 10



The interviewees identified **sources of emissions** and discussed **gaps in knowledge about the composition of waste streams** and a possible **precautionary approach to the use of nanotechnology** to prevent the occurrence of hazardous substances in waste.

The major sources of emissions are **waste treatment** and **manufacturing facilities**. Interviewees referred to recycling, wastewater treatment and incineration facilities as potential sources of emissions. E.g., "wastewater both industrial (manufacturers) and municipal (household and personal care products); there was something about the release in the recycling operations"; "incineration is only an option in relatively rich countries because if waste incineration is not done properly, then it is a source of pollution". Two interviewees pointed out the possibility of releases of nanomaterials in manufacturing facilities and provided examples of mining and paper industries:

- "My concerns would be at the point of discharge into the river, whether they are an industrial waste treatment plant or a municipal waste treatment plant. I would identify the paper industry as the industry that has been least considered in all these discussions and having the highest use of nanomaterials."
- "I would think that there are some problems with the levels of zinc in some river systems. I do not know whether the amount that would get used here would make a significant difference to the amount of zinc that enters the environment from many years of extractive industries in our country [the name of the country removed to prevent identification of the respondent – author comment]. But it is just another area, as people are much more aware."

There were several reflections about **incineration** where risks from emissions are low. E.g.:

- "Let us start with incineration; I think from what we reviewed if the facility is operated and built according to the state-of-the-art, the risk of release was relatively low."
- "Incineration plants have the best installations to clean the air from nanomaterials."

Most interviewees considered that **incineration plants** are well equipped to reduce the release of nanomaterials substantially. Many experts commented on **bag filters** as efficient equipment to prevent the release of nanomaterials to the environment. E.g.:

 "Most waste incineration plants have a bag filter. This is normally the best way to trap dust and all small materials. If you go into waste incineration, after you find ranges of emissions of dust from these plants, you will see that they are normally almost close to zero because of the filters that work well."

- "Filtering we have in our country [the name of the country removed to prevent identification of the respondent author comment] at incineration facilities could capture nanoparticles as well."
- "In the flue gas cleaning system, nanomaterials will be trapped if it is good. Studies show that most micro-size or nano-size dust is trapped."

Two experts commented on challenges raised by the **unknown composition of waste**, including uncertainties about the presence of a mix of nanomaterials. According to experts, this knowledge gap could lead to assigning inappropriate treatment methods or uncertainties about the transformation of waste in its treatment process. E.g.:

- "Currently, I am writing about the lack of input data to know the [composition of author comment] waste flow to make it more representative in our lab test. Our latest project focuses on the mixture [of substances – author comment] and its impact on the presence of nanoparticles in aerosol or residues, and the evolution of the chemical nature of collected nanoparticles."
- "I think it is a problem probably everywhere in our country [the name of the country removed to prevent identification of the respondent – author comment] and the EU where waste is not necessarily correctly consigned. So, I think the actual risk is the fact that you could have some nanomaterials potentially entering inappropriate waste treatments."

One expert commented on the alternative approach that would focus on **safe-by-design nanomaterials** to prevent any issues in waste management: "our latest projects were focused on the development of safe material, knowing that ultimately their end of life is incineration. So, they are safer by design, knowing the behaviour of all components of a nanocomposite."

7. Conclusions and Recommendations

CONCLUSION 1. Currently, it is not possible to give a sound evidence-based conclusion about the quantities of nanomaterials on the European market and in waste streams. To date, comprehensive quantitative information on the manufacturing volumes of nanomaterials in Europe is absent. National registries that collect information about nanomaterials are present in few European countries – Belgium, Denmark, France, Norway, and Sweden (Pavlicek et al., 2020). With amendments to the REACH Regulation, since 1 January 2020, manufacturers and importers of nanomaterials have to report specific information under the revised annexes to the REACH Regulation. However, the information on the quantity manufactured or imported per year may not be specific to the nanoforms of a chemical substance. Under REACH, the obligation to register nanoforms is triggered by the total manufactured or imported volume of both non-nanoforms and nanoforms of the same substance (ECHA, 2019). Analysis of the research and grey literature has shown that the quality of cited data on the production volumes of nanomaterials varies substantially, so they may not accurately reflect the state-of-the-art in production of nanomaterials in European countries.

To identify which nanomaterials are present in waste streams and in what quantities, both production volumes and data on the use of nanomaterials in industries and goods are needed (e.g., see multiple publications using mass flow analysis models, e.g., Adam et al., 2021; Zheng & Nowack, 2021; Rajkovic et al., 2020 to cite a few). Nanomaterials in waste originate from industrial (e.g., waste originating from manufacturing nanomaterials and goods containing them or using nanomaterials in specific industrial processes) or consumer (e.g., waste from end-of-life consumer goods) activities. The literature search did not identify research or grey literature publications estimating types and quantities of manufacturing waste containing nanomaterials. Data on the presence of nanomaterials in consumer products can be obtained by using public databases on nanomaterials, such as, for instance, PEN CPI, NanoData, NanoDB, NPD. However, the existing databases do not provide sound quantitative data on nanomaterials in the EU consumer products due to several reasons: a) the scope of databases is wider (e.g., NPD) or

narrower (e.g., PEN CPI) than the European Union; b) the methodology for identification of nanomaterials in products, data collection and verification is not presented or has reliability issues; c) in some databases, data are not updated anymore or renewed occasionally; d) data about quantities of nanomaterials in products are not available.

In the literature and databases that were consulted in this study, titanium dioxide, silicon dioxide, nanosilver, zinc oxide, carbon-based nanomaterials were cited as often used in products. Examples of the application of titanium dioxide, silicon dioxide and nanosilver in products include cosmetics, construction goods, automotive products, textile. Similar views on nanomaterials in products, and consequently, waste streams, were voiced in the expert consultation.

The absence of quantitative data about nanomaterials on the EU market and in consumer products complicates the identification of the predominant waste streams containing nanomaterials. The current research suggests that nanomaterials could be present in all major sources of waste generated in the EU, such as construction and demolition waste, manufacturing waste, municipal solid waste, wastewater, and sludge. However, the available research provides qualitative data about presence of nanomaterials, e.g., by analysing samples from waste management facilities (see analysis of samples of sewage sludge by Gogos et al., 2020; Liu et al., 2019; Hennebert et al., 2017)), studying samples of water near waste management facilities (Phalyvong et al., 2020; Mehrabi et al., 2021), developing the databases of products that later become waste (e.g., Jones et al., 2016) and consulting industry experts (Hincapie et al., 2015). So, while there is qualitative evidence about the presence of nanomaterials in waste streams, there is no means to give a quantitative evaluation of their presence and concentration. Importantly, waste managers can get useful information about the presence of substances of very high concern (possibly – in a nanoform) in waste streams, under the general provisions of REACH and the Waste Framework Directive.

CONCLUSION 2. Public information about nanomaterials is important to waste managers, scientists, regulatory bodies, and consumers. Despite deficiencies in the quantification of nanomaterials in waste, public information sources provide valuable information to waste managers for determining the composition of waste and its classification to fulfil obligations under the Waste Framework Directive and related waste legislation. These sources of information are widely used by scientists who make estimations of flows of nanomaterials to waste management facilities and their fate in the environment. The estimations of nanomaterial mass flows are used in models that predict the environmental fate of nanomaterials. Some of these models, e.g., *SimpleBox4Nano*, can support the decision-making of regulatory bodies in the assessment of risks of nanomaterials (Nowack, 2017). And finally, public data sources about nanomaterials in products allow consumers to make informed decisions about specific goods.

RECOMMENDATION 1. The development of public datasets containing information about nanomaterials and their presence in products could be promoted for practical and regulatory decision-making and the advancement of scientific research.

CONCLUSION 3. Research on behaviour and fate of nanomaterials focuses on specific nanomaterials in certain waste management facilities and is mostly conducted in a laboratory setting. The reviewed publications focused on some of the most common nanomaterials, including titanium dioxide, nanosilver, zinc oxide and some carbon-based nanomaterials. Most studies were conducted in a laboratory setting with few field studies. Laboratory studies were criticised for analysing the behaviour and fate of nanomaterials under unrealistic conditions (e.g., see Chandrakant et al., 2021; Ye et al., 2021 and Zhu et al. 2020 for studies of nanomaterials under anaerobic conditions; Kapoor et al., 2018; Wu et al., 2019 for studies of nanomaterials in wastewater treatment, etc.).

In the studies of nanomaterials in landfills, laboratory-scale experiments prevailed. The predominance of laboratory studies was observed in incineration, although a few studies in pilot facilities and real waste incineration plants (e.g., see Oischinger et al., 2019; Börner et al., 2016; Baran & Quicker, 2016) were identified. The situation was similar in the research on the fate and behaviour of nanomaterials in wastewater treatment. A few studies were conducted in full-scale

wastewater treatment plants (see, e.g., Cervantes-Aviles et al., 2019; Cervantes-Aviles et al., 2021; Dong et al., 2017; Polesel et al., 2018). The lack of field research was highlighted in the expert consultation.

Studies on nanomaterials in different waste treatment processes varied in number. Wastewater treatment was the most studied field compared to other waste treatment processes, with several literature reviews available (e.g., see Huangfu et al., 2019; Kunhikrishnan et al., 2015; Kapoor et al., 2018; Wang & Chen, 2016; Wang et al., 2017; Wu et al., 2018; Wu et al., 2019). For landfilling and incineration, only case studies that focused on specific nanomaterials were identified. Landfilling and incineration were also covered by only one broad literature review (see Part et al., 2018). The literature search did not find studies on the recycling of manufactured nanomaterials published in the last six years (2015-2020).

CONCLUSION 4. Generic mass flow models or fate models have been widely used to provide a general overview of the distribution of specific nanomaterials in the environment. The literature review has shown an increasing number of research publications that use material flow analysis models or environmental fate models (e.g., see Adam et al., 2021; Zheng & Nowack, 2021; Rajkovic et al., 2020). Wigger et al. (2020) identified 35 publications using such model calculations in 2008-2019. Due to their capacity to transform large volumes of data into meaningful behaviour and fate patterns and ability to provide generalised data (e.g., for entire regions and periods), these models are useful for researchers, professionals, and regulators. The prediction accuracy and precision of models are, however, substantially limited by the poor quality of the input data on the production volumes of nanomaterials per year and the presence of nanomaterials in consumer products (Nowack, 2017). Furthermore, multimedia nanomaterial fate models have been developed but not yet widely used. Both of these model concepts contribute with valuable, but different estimates that are useful for researchers, professionals and regulators.

CONCLUSION 5. Substantial progress has been made in developing analytical tools for the characterisation and measurement of nanomaterials. Available tools can provide qualitative and quantitative information about nanomaterials (Saleh et al., 2020). Guidance documents have been developed to advise on the application of analytical tools (e.g., see CEN/TS 17273:2018). Achievements have been observed in detection, characterisation and quantification of inorganic nanomaterials (Laborda et al., 2016; Bundschuh et al., 2018). However, challenges in distinguishing between natural, incidental and manufactured nanomaterials, characterisation of nanomaterials in complex media and specific quantification issues remain (Part et al., 2015; Bundschuh et al., 2018, Saleh, 2020). These challenges were also highlighted in the expert consultation.

RECOMMENDATION 2. Predictions from model calculations should be compared to field-scale experiments to assess the quality (precision and accuracy) of the calculations. Measurement and characterisation of nanomaterials in a real-life setting allow checking the accuracy of predictions provided by current tools for modelling the behaviour and fate of nanomaterials. With the predominance of laboratory-scale studies, field studies of the behaviour and fate of manufactured and incidental nanomaterials in waste treatment and recycling plants are required. Moreover, work on improving detection, characterisation and quantification of nanomaterials should be continued.

CONCLUSION 6. No studies about workers' exposure to nanomaterials in waste management facilities were identified; however, existing studies focusing on manufacturing and research sites indicate that workers are exposed to nanomaterials mainly through inhalation during manual activities. Few mentions of case studies of the workers' exposure to nanomaterials in recycling were identified; however, they were rated as providing low-quality evidence (see Basinas et al., 2018). However, a lot of studies about occupational exposure to nanomaterials in manufacturing and research sites were available. These studies focused on activities that are also relevant to waste facilities, e.g., handling, cleaning, grinding, etc. According to the available studies, manual activities such as handling,

cleaning, finishing, transferring, are likely to stimulate exposure to airborne nanomaterials. Exposure by inhalation was predominant in the studies and emphasised by the experts as an important route of nanomaterials to the human body. Most studies addressed the exposure to carbon-based, metal and metal oxide nanoparticles (Basinas et al., 2018; Kuijpers et al., 2017; Ding et al., 2017; Debia et al., 2016).

RECOMMENDATION 3. Field research on the exposure to manufactured and incidental nanomaterials in waste management and recycling facilities should be performed. Due to the lack of research on the exposure to nanomaterials in waste management facilities, there is no solid evidence of the major threats to the workers. Analysis of the occupational exposure at waste management facilities would be helpful to understand what activities pose the highest risk of exposure to manufactured nanomaterials contained in waste or incidental nanomaterials formed in waste treatment operations. Such knowledge will allow comparisons with other industrial facilities and evaluation of how to apply the available experience of managing occupational exposure in waste treatment processes.

CONCLUSION 7. The available research shows the high efficiency of incineration and wastewater treatment (for TiO₂, ZnO, CeO₂, Ag, Au, Al, Ce, Co, Cu, Fe, Ti, Zn, Mn) in limiting emissions of nanomaterials to the environment. Several studies in real waste incineration plants (Mertens et al., 2020; Ozgen et al., 2015) and experiments that simulated incineration (Forster et al., 2016; Boudhan et al., 2018) and studied the emissions of ultrafine particles (with a diameter less than 100 nm) showed the high efficiency (close to 100% as reported by some studies) of bag filters for preventing nanomaterials emission into the air. Similarly, high efficiency of bag filters in waste incinerators was reported in the literature reviews by Buonanno and Morawska (2015) and Jones & Harrison (2016) that referred to earlier studies conducted in 2000-2016. Similarly, the high efficiency of removing nanoparticles was shown in the literature reviews of the studies of wastewater treatment that claimed 76 to almost 100% removal rates for different nanomaterials at diverse stages of treatment (see, Wu et al., 2018 -ZnO, TiO₂, CeO₂ and Ag; Cervantes-Aviles et al., 2021 – a study of metal-based nanoparticles – Al, Ce, Co, Cu, Fe, Ti, Zn, Ag, Mn and Au; Tan et al., 2015 – ZnO; Puay et al., 2015 – ZnO). The efficiency of landfilling systems has not been addressed systematically, with only a few simulation experiments addressing the release of different nanomaterials through landfill liners.

CONCLUSION 8. Management of nanomaterials in waste is regulated by the general provisions; however, nano-specific guidance is emerging. The analysis of grey literature and legislation have shown that the definition of nanowaste and specific provisions to nanomaterials are absent in the Waste Framework Directive (Ricardo Energy & Environment et al., 2016). Outcomes of the current discussion about the applicability of the Globally Harmonised System (GHS) to nanomaterials can potentially trigger changes in the EU waste management legislation, as classification of waste is based on the CLP Regulation that adopts the GHS principles. However, so far, there is no evidence on the need for such changes. Standardisation activities have been observed in developing guidance about analytical tools for the detection, characterisation, and quantification of nanomaterials. Advice on the management of waste containing nanomaterials is largely absent. In this context, guidance on managing waste from manufacturing and processing of nanomaterials would be an important step to facilitate practical activities in managing nanowaste.

CONCLUSION 9. The research has been focused on several potential contributions of nanomaterials to the circular economy; however, there is no evidence of the circularity, economic feasibility, and environmental safety of the proposed applications. The analysis of literature identified several areas of research where it was thought that nanomaterials could contribute to the circular economy. These areas covered green synthesis of nanomaterials, including synthesis of nanomaterials from biowaste; using nano-additives in the recycling of plastics, construction and demolition waste; facilitating the recovery of rare-earth elements from waste by using nanomaterials and application of nanomaterials in wastewater treatment. Similar areas, also including nanoremediation, were identified in the stakeholder consultation.

Following the circular economy policies (European Commission, 2015; European Commission, 2020), the circular solutions/applications should be capable to restore, revitalise or renew sources of energy and materials and produce as little waste as possible. However, the circularity of the solutions proposed in the literature is questionable. For instance:

- The research in green synthesis of nanomaterials focused on biosynthesis, where biological agents were used in the production of nanomaterials (Gour & Jain, 2019; Rana et al., 2020; Salem & Fouda, 2020; Saratale et al., 2018a; Singh et al., 2020), and manufacturing of nanomaterials from biowaste (Xu et al., 2019; Ravi et al., 2016). However, the researchers highlighted that the supply of biological agents could not be sufficient for the industrial production of nanomaterials (Patwardhan et al., 2018). The use of biological agents means the increased use of natural resources for industrial needs that does not align with the principles of the circular economy. Alternatively, biowaste could become a resource for the production of nanomaterials. However, the safety of green synthesis and its outcomes, as well as the opportunities for commercialisation, have not been addressed yet (Ishak et al., 2019; Khalaj et al., 2020). At this point in time, all concerns expressed above make it highly uncertain that green synthesis of nanomaterials.
- The research also focused on the role of nano-additives that help to improve the mechanical properties of products recycled from plastic and construction and demolition waste. The use of nano-additives facilitates the recycling of plastics and construction and demolition waste that otherwise would be landfilled or incinerated. However, some studies show that the properties of recycled concrete may get worse due to the addition of nanomaterials (Jindal & Sharma, 2020; Luo et al., 2019; Vishvakarma et al., 2018). So, it is not clear if nano-additives have the potential to increase the circularity of construction and demolition waste. No systematic investigations of the effects of nano-additives in the goods from the recycled waste were identified.
- Abundant publications are dedicated to the application of nanomaterials for wastewater treatment (see Case Study II, Annex 5). However, most of the proposed applications are in the stage of laboratory research. There is high uncertainty and a lack of systematic assessment of the environmental impact and economic feasibility of the proposed applications. For some applications, as the use of nanomaterials for membranes, a high ecological footprint during their manufacturing process was reported (Anjum et al., 2019; Jiang et al., 2018; Erkan et al., 2021). High costs were reported for several applications, such as the use of nanomaterials in photocatalysis (Erkan et al., 2021) and nano-adsorbents (Jiang et al., 2018).

Similarly, although the use of nanomaterials in the recovery of rare-earth elements is widely discussed, the research of economic feasibility and potential safety of such applications is not available (Kegl et al., 2020).

This discussion allows to conclude that research on the applications of nanomaterials in the circular economy is, at the moment, purely theoretical. Most publications are case studies that exclusively focus on proposing and characterising specific methods of nanomaterial application. The status of the commercial application of the proposed solutions is unknown. The systematic analysis of the economic viability of the proposed methods, along with the evaluation of safety concerns, is absent.

RECOMMENDATION 4. The systematisation of current research and evaluation of the economic, environmental, and social impact of the proposed applications of nanomaterials in the circular economy should be supported. It implies interdisciplinary collaboration between different researchers, including representatives of social sciences. Closer collaboration and exchange of ideas between the researchers and the industry is necessary to conclude on the needs for nanotechnology solutions and launch appropriate research initiatives.

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Annex 1. Highest Ranked Keywords and Phrases by Research Topics

TextRank algorithm	RAKE algorithm	Keywords & weights	Combinations of words				
Sources of nanomaterials in waste (topic 1)							
released	application	product 0.295	health effect				
products	products	exposure 0.274	fresh water				
environmental	nano	nanomaterials 0.253	sustainable agriculture				
water	materials	nano 0.206	oxidative stress				
environ	environ	potential 0.168	waste water				
environment	sci	used 0.164	carbon nanotubes				
environments	waste	available 0.16	agricultural control				
risks		nanomaterial 0.131	engineered NMs				
concentration		hazard 0.126	precipitated silica				
nanomaterials		environmental 0.118	silica concentrations				
Behaviour and	fate of nanomate	erials in waste treatment emissions (topic 10)	processes (topic 2), including				
Enm*	waste	waste 0.463	landfill leachates				
Environ*	product	products 0.318	transfer coefficients				
production	ENMs	ENMs 0.309	mixed municipal waste				
Recycl*	recycling	nano 0.276	waste management process				
nano	data	ENM 0.167	waste treatment processes				
Assess*	Environ	release 0.153	separate collection				
data	Nano	paper 0.131	solid waste				
Model*	Europ*	number 0.124	municipal solid waste				
	high	product 0.123	waste streams				
	used	analysis 0.119	product categories				
	products	particle 0.108	waste management				
	rate	material 0.104	probability distributions				
		nanoproducts 0.102	site treatment				

Table 21: Highest-ranked keywords and phrases by research topics

Study on the Product Lifecycles, Waste Recycling and the Circular Economy for Nanomaterials

TextRank algorithm	RAKE algorithm	Keywords & weights	Combinations of words
Nanoma	aterials in recycli	ng and waste manageme	nt (topics 5, 6, 7, 8, 9)
material	Water	nano 0.802	multiwalled carbon nanotubes
Chemical*	Nanomaterials	se 0.361	wastewater treatment
Oxid*	Chemical	toxicity 0.192	visible light irradiation
process		mg 0.113	persistent organic pollutants
research		nanoparticles 0.098	water treatment
environment		surface 0.083	nano metal oxides
technology		figure 0.083	wastes obtained
mechanical		water 0.08	heavy metal ions
studies		organic 0.08	nanometal oxides
carbon		nm 0.08	adsorption photocatalytic
Nano*		size 0.074	graphene-based materials
control		concentration 0.062	daphnia magna
removal		toxic 0.059	photocatalytic degradation
composites		humic 0.059	photocatalytic activity
composition		zhang 0.053	environmental pollutants
Ion*		like 0.053	antibacterial activity
polymers		fate 0.053	heavy metals
metals		using 0.05	food produced
		particles 0.05	magnetic nanoparticles
		dissolution 0.05	photocatalytic degradation
Wast	te management v	vorkers' exposure to nand	materials (topic 3)
particle	identification	environmental 0.452	Airborne engineered nanomaterials
Release*	Nano*	hazardous 0.33	hazardous materials
Exposur*	assessment	ENMs 0.203	chemical safety assessment
Product*	Exposur*	ENM 0.175	carbon nanofibers
Nanoparticle*	release	science 0.172	carbon nanotubes
Inform*	information	nano 0.172	risk assessment
Stud*	importance	engineered 0.164	control banding

Study on the Product Lifecycles, Waste Recycling and the Circular Economy for Nanomaterials

TextRank algorithm	RAKE algorithm	Keywords & weights	Combinations of words
	health	health 0.162	worker exposure
	important	nanomaterials 0.159	risk assessment
	model	release 0.155	hazard assessment
	review	Nowack 0.155	exposure assessment
		environment 0.135	nanomaterial production
Benefits	and challenges o	f nanomaterials in the circ	cular economy (topic 4)
Environ*	water	nanocomposites 0.344	lithium-ion batteries
water	materials	properties 0.301	effects
Approach*	Nano*	surface 0.185	waste streams
Application*		nanomaterials 0.172	environmental safety
based		waste 0.165	direct cost
solution		nanoparticles 0.161	activated carbon
Oxid*		circularity 0.146	environmental remediation
assess		used 0.144	energy storage
Treatment		based 0.125	carbon nanoparticles
Nanomaterial*		high 0.123	nanoparticles carbon
Organic		packaging 0.118	industrial wastes
technology		mechanical 0.112	silver nanoparticles
Natur*		clay 0.101	derived nanomaterials
chemical		process 0.097	nanotechnological solutions

Annex 2. Expert Poll Statistics

In this Annex, statistical data of the responses to a short expert poll is provided. Graphs show the data for 32 responses received from the poll participants.

Figure 18 provides a summary of the countries the respondents of the poll represented.

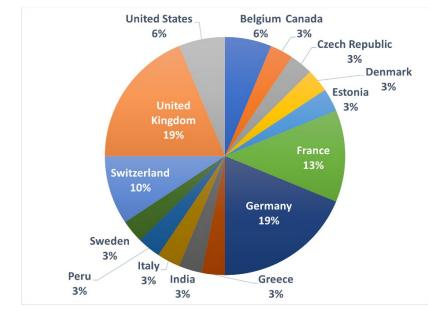


Figure 18: Location of respondents

As Figure 18 shows, most respondents originated from the European countries, with few experts representing United States, Canada, Peru, and India.

Figure 19 summarises different categories of respondents by organisations.

Figure 19: Stakeholder category by organisations

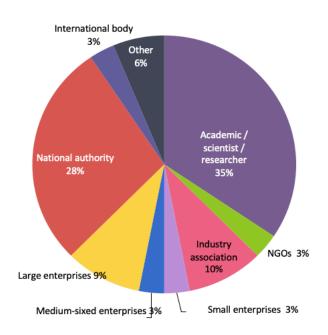


Figure 19 shows that most respondents were scientists working for academic organisations and representatives of national authorities. The third substantial respondents' group were businesses from large to small enterprises.

Table 22 shows that most respondents agreed to be contacted for the study.

Table 22: Are you happy to be contacted for any clarification, a follow-up interview, and further updates on the study?

Value	Percent	Count
Yes	87.5%	28
No	12.5%	4
	Totals	32

Table 23 summarises different contributions that the respondents agreed to deliver to the study. These contributions were showed separately for each of the 10 research topics outlined for the study. Categories included sharing information, papers, taking part in a focus group, etc.

Торіс		e mation is topic	I can p you to scientii papers grey literatu publica	fic and ıre	I'd like part of focus g on this	a Jroup	I can s experts this top	s on	No infor avail	mation able	Total Checks
	N	%	N	%	N	%	N	%	N	%	Total N
1. SOURCES	8	16.7%	12	25%	15	31.3%	8	16.7%	5	10.4%	48
2. BEHAVIOUR & FATE IN WASTE PROCESSES	9	18.8%	12	25%	8	16.7%	9	18.8%	10	20.8%	48
3. WASTE MANAGEMENT WORKERS' EXPOSURE -	5	13.9%	3	8.3%	4	11.1%	6	16.7%	18	50%	36
4. BENEFITS & CHALLENGES FOR THE CIRCULAR ECONOMY	8	20.5%	5	12.8%	9	23.1%	3	7.7%	14	35.9%	39
5. IMPACTS ON RECYCLING	8	21.1%	5	13.2%	8	21.1%	5	13.2%	12	31.6%	38
6. RECYCLATE STREAMS	4	11.1%	6	16.7%	8	22.2%	2	5.6%	16	44.4%	36
7. ABATEMENT SYSTEM RESIDUES	5	12.5%	6	15%	5	12.5%	6	15%	18	45%	40
8. WASTE MANAGEMENT AND RECYCLING APPLICATIONS	4	10.8%	5	13.5%	7	18.9%	2	5.4%	19	51.4%	37
9. SUBSTITUTION	2	5.4%	3	8.1%	7	18.9%	5	13.5%	20	54.1%	37

Торіс		e nation is topic	I can p you to scientif papers grey literatu publica	fic and ire	I'd like part of focus g on this	a roup	I can s experts this top	s on	No inforr availa	mation able	Total Checks
10. EMISSIONS, EMISSION CONTROL AND BATs -	5	13.5%	6	16.2%	3	8.1%	5	13.5%	18	48.6%	37
Total Checks	58		63		74		51		150		396
% of Total N	14.6 %		15.9%		18.7%		12.9%		37.9 %		100%
Note: "N" refers to the	Note: "N" refers to the number of responses, "%" refers to the percentages of responses										

Table 23 shows that many experts stated they could contribute to the study on topics 1, 2, 4 and 5; while few of them pointed out the possibility of contributing with their expertise on topic 9.

Annex 3. Expert Interview Template

Table 24: Interview template: introduction, general and thematic questions

Interview for the "Study on the Product Lifecycles, Waste Recycling and the Circular Economy for Nanomaterials"

Thank you for agreeing to participate in the interviews and share your knowledge about [topic X, topic Y]. This interview is part of the "Study on the Product Lifecycles, Waste Recycling and the Circular Economy for Nanomaterials", commissioned by the European Chemicals Agency. The study aims to collect available evidence on nanomaterials in the context of the circular economy and, in particular, on their behaviour and fate when they reach the waste stage of their product lifecycles. It will update and expand on the 2016 literature review Nanomaterials in Waste Streams – Current Knowledge on Risks and Impacts by the OECD.

This interview will help us to enrich information we found in the research literature with relevant examples, case studies and expert knowledge. Note that we will keep your answers anonymous and confidential. In the analysis of interview findings, we will present only anonymised answers of all interviewees, so it will not be possible to identify an individual expert or link her/his answers with any personal information. Interview materials will be kept safe and available only to our researchers involved in the interview data analysis. We will destroy all interview materials after the study has been completed.

Please, indicate if you agree with the following:

- to list my first and last name, affiliation in the annex list of all persons that were interviewed in this study;
- to allow us making a record of the interview for data analysis.

Thank you for sharing your knowledge and expertise with us!

[Introductory questions]

Could you briefly introduce us to how your professional/research experience are related to [topic X, topic Y]? Could you highlight the relevant experiences, such as participation in projects, working group, discussions, your daily work relates to the topics we are going to discuss? [Adjust the domains of expertise depending on the main topics of the interview].

How would you rate your confidence level in making judgements on the topics we are going to discuss? Rate for each topic: high (constant focus on the topics, work/research related to the topics, following the updates), medium (occasional work/research related to the topics, occasionally checking for updates), basic (general knowledge about the topic with limited research/practical work experience).

- ...[thematic questions]
- [Closing question]

Is there any other important information we have not discussed that would help us to answer the research questions? Could you recommend any relevant experts, reports, case studies on the topics we have discussed? You are welcome to share anything that you find relevant by email: zinaida.manzuch@rpa-europe.eu

Thank you for participating in the interview!

Topic 1 – Sources. The research question: "What is currently known regarding the major sources contributing to nanomaterials in waste, in terms of substances or uses/processes? "

- When asked about the presence of nanomaterials in waste, what types of waste immediately come to your mind? Please list as many types as possible. How do nanomaterials occur in this type of waste? What are the sources they come from? [Repeat these questions for all types of waste listed].
- If you need to rank these types of waste, which of them could be ranked as the three top sources of nanomaterials? First, what waste is on the top of the ranking? Why do you think it is the most important source of nanomaterials? [Repeat these questions for the second/third most important types of waste sources of nanomaterials].
- Now when we discussed the top sources of waste that contain nanomaterials, what are the predominant nanomaterials in these top-three types of waste? Please list from 3 to 5 prevalent nanomaterials in these types of waste. Why do you think these nanomaterials are predominant in the top-three waste streams? Could you briefly explain the criteria/arguments that allow you to rank them as predominant in waste?

Topic 2 – Behaviour and fate in waste processes. Research questions: "Are there studies assessing the effectiveness of real scale operations such as actual plants or pilot plants incorporating all stages of waste treatment processes and using actual waste products? What is the status of the knowledge of NMs' fate in anaerobic denitrification processes of wastewater treatment, in flue gas treatment of incinerators, in recycling facilities and landfills? ""

- When asked about the presence of nanomaterials in waste, what nanomaterials come to your mind immediately? Please list from 3 to 5 examples. Why do you think they should be mentioned? In what types of waste manufacturing (industrial) or generated by other business or household activities are they usually found?
- What waste treatment facilities are treating waste containing the mentioned nanomaterials? What waste treatment facilities do they enter? Are they managed in common commercial treatment facilities or are they treated in-house? What happens after this stage of treatment, what facility becomes the final resort of their disposal? [Repeat for all mentioned nanomaterials].
- To your knowledge, what could be the main factors that influence the effectiveness of the treatment of nanomaterials contained in waste? Let's speak about the actual waste management plants and in-house waste management facilities. Focus on the types of waste and their treatment processes you know the best. [Ask questions about all types of facilities that were mentioned in answering the previous question]. List up to 5 main factors. Could you refer us to any studies that attempted to assess the effectiveness of nanomaterials' treatment in actual waste management plants?
- Could you give us any examples of waste treatment plants or in-house waste management facilities that treat waste containing nanomaterials and developed best practices to handle them? Could you list any of such plants or/and refer us to any representatives of these plants or case study publications? What type of waste is managed in these plants? What nanomaterials are treated?
- Could you comment about the fate of manufactured nanomaterials in any of these processes: anaerobic denitrification processes of wastewater treatment, in-house treatment of industrial process effluents, flue gas treatment of incinerators, recycling facilities and landfills? How the presence of nanomaterials in waste could influence the outcomes of these processes? Could you provide any examples of specific nanomaterials and their behaviour in any of these processes? Could you refer us to available studies on any of these topics? Could you refer us to any research organisations and universities that collaborate on the above issues with the industry?
- What are the major gaps in knowledge about the fate of nanomaterials in waste treatment processes? Why it is important to fill in these knowledge gaps? Could you refer us to any persons, working groups or discussions that raise these questions? Could you refer us to any research organisations and universities that collaborate on the above issues with the industry?

Topic 3 – Waste management workers' exposure. What information is available on the exposure of workers operating in recycling/waste management facilities to (specific) nanomaterials?

- When at recycling/waste management facilities, the workers could be typically exposed to nanomaterials? In your opinion, for which waste treatment processes and waste streams the risk of exposure is the highest? Why do you think so?
- Could you give us any examples of specific nanomaterials the workers of waste management facilities could be typically exposed to? Why do you think there is a risk of exposure to these nanomaterials? What nanomaterials could bring the most significant harm to the workers during exposure in waste management?
- Could you give us any examples of waste treatment facilities (in the absence of those

 manufacturing facilities) that developed policies to manage the workers' exposure
 to nanomaterials? If none, could you recommend any case studies about best practices in
 managing occupational exposure to nanomaterials? Could you recommend any industry
 representatives with practical expertise on the topic?

Topic 4 – Benefits and challenges for the circular economy. Does the use of nanomaterials create any particular benefits or challenges for the circular economy? Note: it also answers part of topic 6 "how do nanomaterials behave in the circular economy".

- Could you give us any examples of a positive application of manufactured nanomaterials for serving any goal of the circular economy? [Ask about the following goals if the interviewee does not mention them: prolonging the useful life of the products, using less or substituting raw materials for producing goods, reducing the quantities of consumables due to increased effectiveness, reducing the quantities of waste, recycling products]. Which of these examples are already applied in the industry? Where possible, refer to real-life companies. Which of the examples are at the stage of research/testing and have a high potential for application in future?
- What could be the negative effect of manufactured nanomaterials on reaching any of the discussed goals of the circular economy? In what ways the current uses or production of manufactured nanomaterials undermines the achievement of these goals? Could you think about any examples of such uses in the industry? Are there any other obstacles that prevent the use of nanomaterials for the benefit of the circular economy?

Topic 5 – Impacts on recycling. Does the presence of nanomaterials in waste streams of materials hinder or bring detrimental impacts on recycling from technical and regulatory perspectives? (e.g., due to specific hazards, or leading to classify certain waste streams as more hazardous)?

- What are the negative impacts of the presence of nanomaterials in waste on its recycling? Could you provide any examples of <u>specific nanomaterials</u> that brought a detrimental impact on waste recycling? Could you explain how the presence of each specific nanomaterial resulted in a negative outcome?
- What technical measures are necessary to eliminate or otherwise control these negative impacts of nanomaterials on waste recycling? Please think about examples of potentially effective technical measures. Do they refer to specific nanomaterials or their groups? Are any of the measures you mentioned applied in practice? Could you give any examples?
- What legal regulation is necessary to eliminate or otherwise control these negative impacts of nanomaterials on waste recycling? Think of the technical measures that you have just mentioned. To implement them effectively, how technical measures should be supported by regulation? Has the possibility of such regulation been publicly discussed? Could you refer us to any documents, publications or presentations covering these discussions?

Topic 6 – Recyclate streams. What are the main nanomaterial-containing recyclate streams and how do nanomaterials behave in the circular economy? Note: the second part of the question is covered in topic 4.

- What are the main recyclate streams that contain nanomaterials? Please give us the top 3-5. What are the reasons or arguments to consider them the main recyclate streams? What nanomaterials do these recyclates usually contain?
- **How nanomaterials occur in these recyclates?** In the examples you mentioned, are nanomaterials added intentionally or occur unintentionally? At what stage? (e.g., industrial processes and/or product manufacturing, product use, waste collection, waste sorting, disassembling stage, during recycling, transport, storage)
- Is the presence of nanomaterials detrimental or advantageous for recycling itself and the quality of the target materials? Could you think of advantages or disadvantages concerning:

- ease/difficulty in the recycling process,
- o decrease/increase of the recycling costs,
- \circ increase/decrease of recyclability of the materials,
- improving/worsening quality of the target products?

Topic 7 – Abatement system residues. What issues arise from the incorporation of abatement system residues containing nanomaterials in residue-based secondary products? What is the impact of the agricultural application of sludge containing NMs?

- What are the typical examples of abatement system residues that contain nanomaterials getting incorporate in secondary products? Please consider residues from disposing of different kinds of waste (e.g., those generated in industrial processes or other activities by businesses and households). Could you describe how these secondary products are typically used? Please consider both industrial and consumer secondary products or infrastructures.
- What issues could arise from the use of the secondary products that you have just mentioned? Are there any risks to human health and/or the environment? Clarify for each example of secondary products.
- What could be the impact of the agricultural application of sludge containing nanomaterials on the environment or human health? Ask if not covered by the previous questions.

Topic 8 – Waste management and recycling applications. What positive applications/impacts do nanomaterials have on waste management and recycling? (e.g., different nanomaterial-based technologies for water remediation, application of nanomaterials at various stages of an in-house treatment of industrial waste and other waste treatments, and the challenges faced by these technologies).

- Could you describe the most important positive applications of nanomaterials for managing waste? Which of them has been already applied in waste management plants or inhouse industrial treatment systems? Could you give us any examples of case studies in real waste management plants or refer us to experts who could speak about them?
- What are promising applications of nanomaterials for managing waste that are not yet adopted in plants? Why do you think they are important? What are the challenges faced by these technologies? Could you indicate their technological readiness level (TRL)?

Topic 9 – Substitution. Is there evidence that the use of nanomaterials could lead to a reduction in other waste streams (e.g., the substitution of harmful materials problematic in waste treatment by nanomaterial-containing materials)?

- Could you give us any examples showing that nanomaterials (alone or as a component of other materials) could be used as a substitute for materials that are problematic in waste treatment? Could you refer us to the relevant research studies on this topic? What types of nanomaterials and their uses are most visible in the current research?
- Could you give us examples of any other research or discussions about the role of nanomaterials in reducing the streams of other waste? Is this topic considered important and visible enough in research and/or waste management/environment protection communities?

Topic 10 – Emissions, emisson control and BATs. What is the effectiveness of BAT waste treatment technologies in retaining or eliminating NMs and protecting workers from exposure to NMs? What is the effectiveness of sub-standard waste treatment technologies (e.g., incinerators with inadequate flue gas treatment, clay liners in older landfills or uncontrolled landfills)? Are there other measures to effectively capture, divert or eliminate NMs from waste streams and residual waste? What is the effectiveness of landfills in serving as a final sink for NMs? Are there potential risks of secondary materials that contain NMs? [present in the questions of topic 7]

- At what stages of waste treatment emissions of nanomaterials could occur? Let's speak about the possible emissions of nanomaterials in waste treatment facilities covering wastewater management, incineration plants, landfills, biological treatment facilities and various in-house facilities for treating industrial waste. First, what types of facilities you know the best and could confidently speak about? Speak about those treatment facilities you know the best. [If there is more than one facility to discuss repeat the question for each of them].
- What are the common quality issues at waste treatment facilities that could lead to a higher level of emissions of nanomaterials? Think about the situation in countries with moderate to high income (e.g., the European Union Member States). Focus on the facilities you

know the best. List as many quality issues as you can. Explain, how each quality issue leads to emissions of nanomaterials during waste treatment. What are the most significant issues that could negatively impact human health and the environment?

- Could you list any examples of sub-standard waste treatment practices and technologies that contribute to a higher level of emissions of nanomaterials? Could you refer us to the relevant case studies (e.g., such as uncontrolled landfills, inadequate flue gas treatment at incinerators, etc.) or persons who could inform us about the current state-of-the-art in nanomaterial emissions and sub-standard waste treatment?
- What are the best available technologies that are used for eliminating and avoiding the emissions of nanomaterials in waste treatment facilities we have just discussed? Give as many examples as possible and briefly describe the stages of waste treatment they are used at and the purposes they are used for.
- Which technologies for emission control and workers' protection are the most effective? Why do you think these technologies are more effective than others? Could you refer us to any case studies or actual waste management plants that apply these technologies? [If several waste treatment facilities are discussed, repeat the question for each of them].
- What are promising technologies that could help to achieve better results in the elimination or capture of nanomaterials in waste treatment and protection against occupational exposure than it is possible now? Think about the technologies that are not on the market yet but are developed in the research/laboratory setting. Could you link us to the relevant discussion groups, persons, or research publications about such technologies?

Annex 4. Interviewed Experts

Only details of the experts who agreed to be listed in the annexes of this study are provided in Table 26.

Table	25:	The	list	of	interviewed	experts
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First name, last name	Organisation	Country
David Azoulay	Center for International Environmental Law (CIEL)	Switzerland
Chirag Bhimani	Independent expert	India
Allessio Boldrin	Technical University of Denmark	Denmark
Carine Chivas-Joly	Laboratoire national de métrologie et d'essais (LNE)	France
Emeric Frejafon	French Geological Survey (BRGM)	France
Richard Hawkins	Environment Agency	United Kingdom
Yolanda Hedberg	University of Western Ontario	Canada
Gunther Van Kerckhove	OCSiAl Europe Sarl	Switzerland
Fred Klaessig	Pennsylvania Bio Nano Systems, LLC	United States
Mikhel Krusberg	Ministry of the Environment of Estonia	Estonia
Clare Longuet	PCH C2MA IMT Mines Ales	France
Bernd Nowack	EMPA	Switzerland
Stig Olsen	Technical University of Denmark	Denmark
Guido Premoli	LabAnalysis	Italy
Naheed Rehman	Tronox Pigment UK, Ltd	United Kingdom
Jenny Rissler	RISE Research Institutes of Sweden	Sweden
Ara Samonte	Infineum UK	United Kingdom
Gregor Schneider	RAS AG	Germany
Lighea Speziale	Confederation of European Waste-to-Energy Plants (CEWEP)	Belgium

Annex 5. Case Studies

Case Study I: RAS AG – recycling of manufacturing waste

This case study aims to illustrate the recycling of nanomaterials in the manufacturing setting. The case study was prepared with input from Gregor Schneider of RAS AG.

RAS AG is a German SME that manufactures silver nanoparticles that are incorporated into numerous products, focusing specifically on utilising the biocidal activities of silver to achieve innovative and optimal product characteristics and properties. The silver nanoparticles are used by downstream formulators in a range of products, e.g., cloths for professional cleaning, in glass-fibre reinforced polymers for refrigerated transportation (e.g., vaccines), and many more.

RAS AG utilises a batch production process where powdered silver nitrate arrives at the production site. The silver nitrate powder is dispersed in water in a reaction vessel, where an inhouse-developed protocol applies to create silver nanoparticles according to the desired size and properties. The silver nanoparticles are manufactured and always contained in dispersion in the closed reaction vessel during the batch manufacturing process. In the manufacturing room workers are wearing overalls, gloves, goggles and masks to minimise the risk of exposure. Reaction by-products (Nitrogen, etc.) are suctioned. Once the nanoparticles formulation process is concluded, the dispersion containing the silver nanoparticles is transferred to bottles and containers in volumes according to the desired requirements of the client (\leq 5 kg, to remain CLP compliant).

During the manufacturing process, no silver nitrate or silver nanoparticles are discarded into drains. During the quality control testing during the manufacturing process, small volumes (several mL) are extracted from the reaction vessel and tested in the on-site laboratory. After QC testing, any waste from the QC is collected in dedicated waste containers. These waste containers are regularly collected by a dedicated hazardous waste handler that brings the containers to a dedicated waste disposal facility that operates under German regulations and all the collected silver is brought to a precious metals refiner to be recycled.

Following the end of the manufacturing process, the reaction vessel is cleaned with paper towels that are collected and sent to a silver processing facility for recycling into metallic silver. If accidental spills occur these are also cleaned with paper towels which are sent for recycling of the silver.

The manufacturing of silver nanoparticles is performed in closed containers with very low exposure to workers and silver particles are not discarded via drains.

When the nanoparticles are sent to the clients and downstream users, information is provided with regard to how to manage and handle them as a material safety data sheet. Information is also provided with advice on how clients and downstream users should ensure relevant information is passed along the supply chain to the final users how e.g., to dispose of the final products incorporating the low levels of silver nanomaterials. RAS AG is even offering all the clients and downstream users the possibility to recycle their silver waste at the silver refinery accordingly.

Case Study II: Nanomaterials for wastewater treatment

Nanomaterial applications for wastewater treatment is a widely researched topic. In a recent scientometric analysis, Davarazar et al. (2021) identified 6,539 papers on the application of nanomaterials in wastewater treatment published from 1995. Therefore, in this case study, the focus is on wastewater treatment as a prominent instance of the application of nanomaterials for enhancing the treatment of waste.

Nanomaterials are actively applied in water and wastewater treatment because of their improved catalysis, adsorption properties and high reactivity. In a bibliometric study on nanomaterials in wastewater treatment (in 1997-2016, 2393 publications), Jiang et al. (2018) noted that at the earlier stages, titanium dioxide and nanocomposites were in the focus of the researchers, while in **the newer publications – carbon nanotubes, titanium dioxide nanotubes, silver nanoparticles, graphene oxide, graphene and magnetic nanoparticles are among mostly cited nanomaterials**. Although various nanomaterials are quoted to have potential in wastewater treatment, most are still not applied on an industrial scale.

The latest comprehensive literature reviews on nanomaterials utilisation for wastewater treatment distinguish **several application fields: adsorption, membrane processes, photocatalysis, disinfection and sensing, detection and monitoring** (Anjum et al., 2019; Jiang et al., 2018; Bishoge et al., 2018; Erkan et al., 2021; Thines et al., 2017; Teow et al. 2019). Each application and its features are discussed in detail below. Table 28 summarises nanomaterials in wastewater treatment.

Examples of nanomaterials	Application status	Sources						
Adsorption								
Carbon aerogels, carbon nanotubes, graphene, and their hybridization states, chitosan-based adsorbents and graphene oxides, titanium dioxide, magnetic nanoparticles, metal oxides, silica-based nanostructures, fullerene, nanoporous activated carbon	Rare in a commercial application, not likely to be viable to replace conventional water treatment fully	Jiang et al., 2018; Bishoge et al., 2018; Erkan et al., 2021; Thines et al., 2017; Anjum et al., 2019						
Membra	ane processes							
Carbon nanotubes, titanium dioxide, nano- zeolites, aquaporin, nano-magnetite, silver nanoparticles, copper oxides, silver nanoparticles/cysteamine, multi-walled CNTs/silver nanoparticles, and graphene oxides/silver nanoparticles, aluminium oxides, zerovalent iron, zirconia, silica oxides, gold, palladium	Limited application in waste treatment facilities	Jiang et al., 2018; Bishoge et al., 2018; Erkan et al., 2021; Thines et al., 2017;						
Phot	tocatalysis							
Carbon nanotubes, titanium dioxide, nano- zeolites, aquaporin, nano-magnetite, silver nanoparticles, copper oxides, silver nanoparticles/cysteamine, multi-walled CNTs, graphene oxides, silver nanoparticles, aluminium, and titanium oxides, zerovalent iron, zirconia, silica oxides, gold, palladium	Research laboratory level, upscaling to industrial level is challenging	Bishoge et al., 2018; Erkan et al., 2021; Anjum et al., 2019						

Table 26: Nanomaterials in wastewater treatment

Examples of nanomaterials	Application status	Sources
Dis	infection	
Zinc oxides, titanium dioxides, magnesium oxides, calcium oxides, copper, copper oxides, aluminium, quantum dots, carbon nanotubes, fullerenes, nanosilver, magnesium oxides, graphene	Applied in several commercial products	Bishoge et al., 2018; Erkan et al., 2021; Thines et al., 2017; Teow et al., 2019
Sensing, det	ection, monitoring	
Carbon nanotubes, nanotube arrays, quantum dots, graphene oxide, silica, manganese dioxide, zinc oxide, copper oxide, chromium trioxide	Considerable theoretical and practical research has been done to date with positive results	Jiang et al., 2018; Bishoge et al., 2018; Teow et al., 2019

Adsorption is a process in which liquid or gas solutes are attracted and accumulated on the adsorbent, which is usually a solid (Thines et al., 2017). Adsorption is a preferred choice over other water treatment strategies due to its universality for common organic and inorganic compounds, simplicity in operation, excellent performance for heavy metals removal (Jiang et al., 2018) and dye removal (Bishoge et al., 2018). Nano-adsorbents include metallic nanoparticles, nanostructured mixed oxides, metallic oxide nanoparticles, magnetic nanoparticles, and carbon-based nanoparticles, see Table 5-4 for examples (Anjum et al., 2019; Bishoge et al., 2018; Erkan et al., 2021). Besides, various types of silicon nanomaterials can be used as nano-absorbents, such as silicon nanoparticles, nanotubes and nanosheets. Nano clays, nanofibres, polymer-based nanomaterials, and aerogels can be used for the adsorption of heavy metals from wastewater (Anjum et al., 2019). There are several disadvantages to this technology, such as high costs and the need for large quantities of nanoparticles (Erkan et al., 2021). In addition, the production and purification steps can introduce contaminants and impurities, which can cause structure degradation (Jiang et al., 2018). Hybrid treatment applications that combine high surface areas of nanoparticles or nanostructured materials with the conventional treatment methods may provide higher contaminants removal and treatment efficiencies (Erkan et al., 2021).

A **membrane** is a material with a porous, thin-layered structure, which allows water molecules to pass through but prevents the passage of other particles such as metals, salts, bacteria, or viruses (Bishoge et al., 2018). Membrane filtration technology fabricated by nanomaterials is considered to be one of the most effective methods among current advanced wastewater treatment techniques (Anjum et al., 2019). Nanoparticles can be used to produce different membranes such as **nanocomposite**, **nanofibre**, and **thin-film nanocomposite** (see Table 28) membranes (Erkan et al., 2021; Jiang et al., 2018). The nanomembrane technology is highly economical, and straightforward in design, and it enables new functionality such as high permeability, catalytic reactivity, and fouling resistance. This technology provides effective disinfection and low space requirements for a plant (Anjum et al., 2019). The nanomembrane process can be used for the effective removal of heavy metals, dyes, and other organic and inorganic contaminants from water and wastewater (Erkan et al., 2021; Anjum et al., 2019). The technology has some disadvantages, such as membrane fouling, which can cause high energy consumption and filtration failure, as well as require frequent chemical and physical cleaning, which reduces the lifetime of the membrane. However, some nanomaterials are ideal candidates for anti-membrane biofouling and can improve its properties, for example, zeolites, silver nanoparticles, titanium dioxide, carbon nanotubes, silver oxides, silica oxides, etc. (Bishoge et al., 2018). Another disadvantage of this technology is the high ecological footprint during their manufacturing process (Anjum et al., 2019; Jiang et al., 2018; Erkan et al., 2021).

Photocatalysis is one of the advanced oxidation processes for degrading trace pollutants and microbial pathogens (Erkan et al., 2021). Nanoparticle photocatalytic reactions are based on interactions of light energy with a catalyst, which are effective in producing radicals that degrade various pollutants. Typically, photocatalysts are composed of **semiconductor metals** that can degrade various persistent organic pollutants such as detergents, dyes, pesticides, and volatile organic compounds. **Metal/metal oxide nanoparticles** (see Table 5-4) are effective in the treatment of organic contaminants (Anjum et al., 2019; Erkan et al., 2021). Photocatalysis is also highly effective in degrading PCPP, halogenated and non-halogenated organic contaminants and is used for pre-treatment to enhance the biodegradability of non-biodegradable and hazardous pollutants. Compared with conventional treatments, shorter oxidation times, removal of target recalcitrant compounds, and the ability to transform waste into valuable by-products are some advantages of this technology. However, because of several disadvantages, such as high cost and the need to deliver light and the catalyst, the application of this technology is very limited (Erkan et al., 2021).

Disinfection plays an important role in water and wastewater treatment, and the development of nanotechnology has facilitated the use of nanomaterials in this process. Several nanoparticles can be used for antibacterial purposes, such as **nanosilver**, **metal oxides**, **quantum dots**, **carbon nanotubes**, **fullerenes**, see Table 5-4 for examples (Bishoge et al., 2018). Disinfection using nanomaterials has several advantages, such as elimination of pathogens, antibacterial activity, antibiotic control, and anti-biofouling (Erkan et al., 2021; Bishoge et al., 2018). The process is safe and has low human toxicity and does not produce any harmful disinfection by-products (Thines et al., 2017; Teow et al., 2019). There have been none significant disadvantages reported; however, some problems, such as the interaction between graphene and deposited nanomaterials, for example, still need to be resolved (Bishoge et al., 2018). Disinfection with nanomaterials has been applied in several commercial products (Erkan et al., 2021).

Nano-sensors have been increasingly used to monitor water contaminants as they show three to four times higher sensitivity than the thin film-based sensors, and they can provide timely detection due to the high signal-to-noise ratio (Bishoge et al., 2018). Application of metal nanoparticles, dye-doped silica nanoparticles, carbon-based nanoparticles, magnetic nanoparticles, nanocomposites, and nano-biosensors (see Table 5-4) has been suggested for these purposes (Jiang et al., 2018; Bishoge et al., 2018; Teow et al., 2019). They are excellent absorbents; hence they can concentrate pollution to meet the detection threshold. They are good at tracing insecticides, herbicides, pathogens and viruses (Jiang et al., 2018). Gold nanoparticles show high potential for application in sensing and detection because of their stability, miniaturisation, easy surface functionalisation, and compatibility with the aqueous medium. They can also detect poisonous metal ions and enhance analytical signals. When used with nanowires, carbon nanotubes present an excellent and measurable signal in small concentrations of aimed pollutants (Bishoge et al., 2018). Eliminating false detection of pathogens and viruses in complex wastewater samples remains a challenge (Jiang et al., 2018). Considerable theoretical and practical research has been done to date with positive results in using nanomaterials for sensing and detection of heavy metals, pathogenic substances in woods, identification of biological molecules, organic contaminants, industrial contaminants, etc. (Bishoge et al., 2018).

In judging the **applicability of nanomaterials in wastewater treatment**, various criteria should be considered. According to the results of the expert interviews by Kamali et al. (2019), health and safety, treatment efficiency, operating costs and process stability are the most important criteria to be considered. One or a combination of these criteria and technological 'lock-in' due to capital investment cycles and timing of BAT etc. often become an obstacle for the widespread application of the discussed nanomaterials in wastewater treatment. Sustainability, efficiency and economic aspects of nanomaterials' application in wastewater treatment treatment were also addressed in the recent large-scale scientometric study of 6,539 publications on the applications of manufactured nanomaterials in wastewater treatment by Davarazar et al. (2021).

In particular, Davarazar et al. (2021) highlighted the poor connection between research and industry in the application of nanomaterials in wastewater treatment. Despite the overwhelming number of research publications, the reports of industrial application of nanomaterials for wastewater treatment are lacking.

Laboratory-scale research abundantly documents the efficiency of nanomaterials to treat industrial wastewater, as reported by Kamali et al. (2019). The research discussed various properties of nanomaterials that can affect their efficiency in wastewater treatment and also the mechanisms for degradation and removal of specific pollutants (Kamali et al., 2019). However, as highlighted by Davarazar et al. (2021), only a few examples of case studies of toxicity and properties of effluents treated with the application of nanomaterials have been published in several decades of research.

Economic aspects of the proposed applications of nanomaterials for wastewater treatment are rarely mentioned in research publications. For instance, as a part of their scientometric study on nanomaterials in wastewater treatment, Davarazar et al. (2021) conducted a targeted search of the keyword 'economic' in all identified publications. The researchers found only 139 papers out of 6,539 publications (2%) mentioning this keyword. Screening of these publications revealed most publications did not provide any economic analysis or comparisons with conventional methods to support their claims that the proposed nanomaterials' application is economically viable (Davarazar et al., 2021). Similarly, Kamali et al. (2019), who performed a review of publications that addressed initial investments, operational and maintenance costs of nanomaterials' application in industrial wastewater treatment, found substantial gaps in knowledge. Operational costs were addressed more often than other cost issues. In several studies, costs of nanomaterial synthesis, costs of application of nanomaterials in comparison to conventional chemicals used in wastewater treatment, energy consumption issues (in case of photocatalysis) were discussed (Kamali et al., 2019). However, the scarcity of studies does not allow to make any conclusions on the effectiveness and efficiency of the application of particular nanomaterials in specific wastewater treatment processes.

Annex 6. Answers to Specific Questions not Covered in the Conclusions

In this Annex, we provide answers to specific questions raised in the Technical Specifications of the study that were not covered in the conclusions.

Question	Answer
Does the presence of nanomaterials in waste streams of materials hinder or bring detrimental impacts on recycling from technical and regulatory perspectives? (e.g., due to specific hazards, or leading to classify certain waste streams as more hazardous)?	impacts of nanomaterials. It also could be attributed to the absence of studies on the recycling of waste containing

Table 27: Answers to specific questions not covered by the conclusions

Question	Answer
What are the main nanomaterial- containing recyclate streams and how do nanomaterials behave in the circular economy?	The research does not provide any information on the availability of nanomaterials in recyclate streams. The experts made assumptions about the potential presence of nanomaterials in the recycled products. These assumptions were based on the presence of nanomaterials in products that are processed in recycling facilities. The fate of nanomaterials in recycling facilities is unknown because of the lack of studies in this field.
What issues arise from the incorporation of abatement system residues containing nanomaterials in residue-based secondary products?	The literature review did not identify studies that would discuss the presence of nanomaterials in secondary products based on abatement system residues. The experts mentioned the application of slags and bottom ash for construction and flu ash for backfilling, and agricultural use of sludge. They also commented that the application of such residues is strictly monitored and limited due to the presence of hazardous materials (not in nanoform).
Is there evidence that the use of nanomaterials could lead to a reduction in other waste streams (e.g., the substitution of harmful materials problematic in waste treatment by nanomaterial- containing materials)?	No studies and examples from experts were identified.
Deepen the understanding of the fate of MNMs in waste treatment processes, particularly in the following areas: where scientific findings are currently contradictory (anaerobic denitrification processes of wastewater treatment, flue gas treatment of incinerators), where there is an insufficient number of studies available (recycling facilities, landfills).	The impact of nanoparticles on nitrogen removal is discussed in section 4.5. The laboratory experiments have shown an adverse impact of silicon dioxide and aluminium oxide on nitrification and denitrification, with some inhibitory effects of titanium oxide on nitrifying and denitrifying bacteria. However, the studies were performed on the laboratory scale. The literature review did not identify any studies focusing on the fate of nanomaterials in recycling. The sections 4.4 and 4.8 discusses the fate of nanomaterials in landfills. However, most studies have been conducted in laboratory settings under conditions that were too far from realistic to make any sound conclusion.
Investigate the impact of the agricultural application of sludge containing MNMs.	 Three reasons do not allow provide a sound answer to this question: a) The available estimations of the environmental concentrations for some groups of nanomaterials show that they pose no risks for the environment and human health (see details in section 4.8). b) The toxicological studies provide substantial information about the mechanisms of nanomaterials' toxicity. However, most toxicity experiments were performed in laboratories and used high doses of nanomaterials for studying the effects. These studies did not produce any quantitative measures that could be useful for evaluating the risks of nanomaterials in the environment. c) Techniques for measuring nanomaterials in the environment do not allow to distinguish between the manufactured and natural nanomaterials present in the environment.

Question	Answer
Assess the effectiveness of sub- standard waste treatment technologies (e.g., incinerators with inadequate flue gas treatment, clay liners in older landfills or uncontrolled landfills).	We identified only one study addressing the fate of titanium dioxide in the uncontrolled landfill of construction and demolition waste in Brazil (see section 4.4). Otherwise, information on the effectiveness of waste treatment facilities (especially, in the context of nanomaterials) in Europe is scarce and mostly based on estimations.
Assess the effectiveness of real scale operations such as actual plants or pilot plants incorporating all stages of waste treatment processes and using actual waste products.	Research on the behaviour and fate of nanomaterials in real waste management facilities is scarce. Only two studies evaluated nanoemissions from waste incineration plants and made conclusions about the efficiency of cleaning installations (see section 4.8 for details). The scarcity of studies does not allow to make any generalised conclusions about different waste treatment facilities and all waste treatment operations.

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