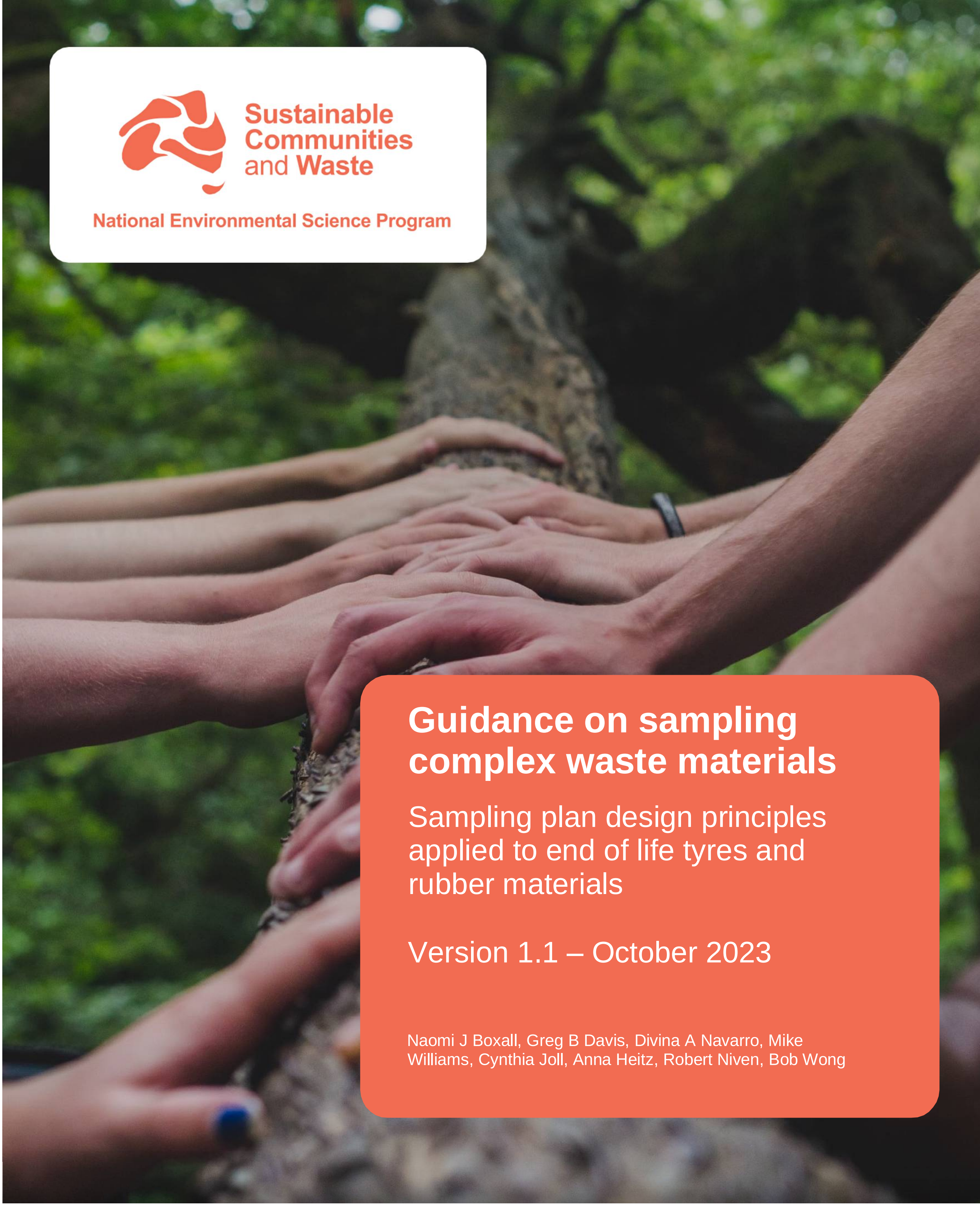
Sustainable Communities and Waste

National Environmental Science Program



Guidance on sampling complex waste materials

Sampling plan design principles applied to end of life tyres and rubber materials

Version 1.1 – October 2023

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Citation

Boxall NJ, Davis GB, Navarro DA, Williams M, Joll C, Heitz A, Niven R, Wong B. 2023. Sampling guidance for complex waste materials: Sampling plan design principles applied to end of life tyres and rubber materials. Version 1.1 – October 2023. Prepared for the Australian Government Department of Climate Change, Energy, the Environment and Water, 25 pp. DOI: https://doi.org/10.25919/8cha-qw40

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Important disclaimer

Acknowledgements and affiliations:

The guidance development was funded by the National Environmental Science Program Sustainable Communities and Waste Hub. We appreciate the feedback on prior drafts by Glen Walker and Sarah Stone (Australian Government Department of Climate Change, Energy, the Environment and Water).

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Document ID: IP3004

Executive Summary

This document outlines principles of sampling plan design for complex waste materials, demonstrating the application of these principles for the development of robust and relevant waste sampling plans.

The objective of designing robust and relevant waste sampling plans is to ensure that data generated from characterisation is high-quality and can be used with confidence by decision makers when assessing the presence and risk of chemicals identified in wastes and waste derived materials.

Through a review of relevant general waste sampling, contaminated sites and specific sampling guidance, a 5-point, iterative sampling plan design framework has been proposed, with the view of providing transferrable sample plan design advice across multiple complex waste streams and waste derived materials. The principles and framework are applied to the sampling of end of life (EOL) tyres and rubber materials.

This document is designed as an iterative guidance document that will be modified and updated as the research advances. As such it is denoted Version 1.0.

Glossary of Terms

Term	Definition
Chemicals of concern	Chemicals that can have long-term adverse effects on humans or ecosystems
Chemical exposure	Concentration or amount of a particular agent that reaches a target organism, system, or (sub)population in a specific frequency for a defined duration.
Chemical hazard	Inherent property of an agent or situation having the potential to cause adverse effects when an organism, system, or (sub)population is exposed to that agent
Chemical risk	The probability of an adverse effect in an organism, system, or (sub)population caused under specified circumstances by exposure to an agent.
Circular economy	An economic system based on the reuse and regeneration of materials or products, especially as a means of continuing production in a sustainable or environmentally friendly way.
Hazardous waste	Waste prescribed by the *Hazardous Waste (Regulation of Exports and Imports) Act* 1989, which has any of the characteristics mentioned in Annex III to the Basel Convention, including: explosive; flammable liquids/solids; poisonous; toxic; ecotoxic; infectious substances.

Abbreviations

Abbreviation	Definition
6PPD (-Q)	*N*-(1,3-dimethylbutyl)-*N*'-phenyl-*p*-phenylenediamine (-quinone)
ARA	Activity risk assessment
BPA	Bisphenol A
CAS RN	Chemical Abstracts Service Registry Number
CSIRO	Commonwealth Scientific and Industrial Research Organisation
DCCEEW	Australian Government Department of Climate Change, Energy, the Environment and Water
DPG	Diphenyl guanidine
EC	Electrical conductivity
EOL	End of life
HDPE	High density polyethylene
HMMM	Hexa(methoxymethyl)-melamine
HSE	Health, safety and environment
NATA	National Association of Testing Authorities
NESP	National Environmental Science Program
OTR	Off the road
PAH	Polyaromatic hydrocarbons
PFAS	per- and poly-fluoroalkyl substances
PP	Polypropylene
PPE	Personal protective equipment
QA/QC	Quality Assurance/Quality Control
RP	Research Plan
SCaW	Sustainable Communities and Waste
SMILES code	Simplified Molecular Input Line Entry System codes
TSA	Tyre Stewardship Australia
US EPA	United States Environmental Protection Agency

Contents

1. Background

The risks of chemicals (including currently undefined chemicals) in our waste streams need to be better defined. The gap in knowledge and data can inhibit our ability to safely move toward achieving national and state policy action targets to divert materials from landfill and accelerate their reuse. The presence of chemicals of concern can impact recyclability and the safe reuse of waste materials. As we move towards resource recovery and a circular economy, we must ensure material reuse is safe, and risks associated with persistent chemicals are minimised for human, environmental and social well-being.

There is an increasing international and national focus on achieving safe reuse options for waste materials [1, 2, 3]. Information and data generated through the sampling and characterisation of waste streams will be used to assess the fate and availability of chemicals as wastes are processed and reused as secondary materials in Australian and globally. Underpinning these priorities is ensuring that data are robust and representative of relevant waste streams, of demonstrably high quality. Representative sample collection for reliable analysis relies on the well-designed sampling of heterogeneous wastes and the subsequent handling of waste samples before analysis.

This document outlines guidance on robust and representative sampling for end of life (EOL) tyres as a waste stream example, with the view of developing transferrable guidelines for sampling other complex waste and waste-derived materials. This sampling guidance aims to enable the identification, characterisation, and quantification of the risks of chemicals contained in waste-derived and secondary materials to human and environmental health. EOL tyres are a current national priority waste stream [1, 4, 5].

Like most wastes, EOL tyre waste streams are composed of highly heterogeneous materials. EOL tyres have multiple components (e.g., rubber, plastics, steel, and other materials); hence, generating valid and relevant data that provides confidence related to the risk assessments for safe waste reuse is a challenge. In addition, EOL tyres have been demonstrated to contain known chemicals of concern (e.g., heavy metals, bisphenol A (BPA), N-(1,3-dimethyl butyl)-N'-phenyl-p-phenylenediamine (6PPD) and its oxidised product 6PPD-quinone (6PPD-Q)), shown to impact human and ecosystem health [6, 7].

The fate of chemicals during reprocessing and reuse of waste-derived materials needs to be better characterised. The design of robust and statistically relevant sampling campaigns is critical for generating high-quality analytical data related to the composition of these wastes. The need for appropriate and robust data severely limits risk-based decisions regarding the safe recovery and reuse of resources obtained from these wastes. Guidance that enables robust sampling and the generation of high-quality chemical characterisation data will underpin decision-making related to the safe reuse of waste.

It should be noted that the guidance developed here is expect it to be updated iteratively as sampling and analysis of waste streams are undertaken, with a particular focus here on data related to EOL tyres. We expect the general framework that underpins this sampling guidance to be applied to other wastes in a manner that considers information and data relevant to those materials and chemicals that may be present.

Using EOL tyres as a test case, this guidance has been developed as a template to design representative and robust sampling plans for other complex and emerging waste streams and secondary materials destined for reuse in the circular economy.

2. Principles of sampling plan design for complex waste materials

Through a review of relevant general waste sampling, contaminated sites and specific EOL tyre sampling guidance [8-16], a 5-point, iterative sampling plan design framework has been proposed, with the view of providing transferrable sample plan design advice across multiple complex waste streams and waste derived materials. The sampling plan design framework is illustrated in Figure 1, and described briefly here.

In this document, the application of this sampling plan design framework is demonstrated using EOL tyre and rubber materials as the target waste material for sampling.

1. Develop/update a conceptual understanding of the waste stream

A conceptual understanding of the target waste stream and processes involved in waste handling and recycling is a critical step in sampling plan design, which includes defining the purpose of the sampling campaign and understanding how and why the data generated from collected samples will be used, who the data users will be and how the data generated will achieve the purpose of the sampling plan.

2. Design your sampling plan

A preliminary sampling plan for waste or waste derived materials can be developed by combining the established conceptual understanding of the waste material, a review of existing or acceptable guidelines and standards related to sampling of similar or like materials, where available, or an understanding of gaps in knowledge, and an assessment (using available literature and information) or judgement (when literature and information is limited) of the likely types of chemicals present in the waste.

In future iterations of sampling plans that go beyond initial characterisation of waste materials, a sampling plan must consider the application of statistics to design appropriate sampling strategies that can generate information with quantitative insights related to the materials being sampled.

3. Implement the sampling plan

Following the designed sampling methodology, samples can be collected and appropriately stored prior to analysis. At the same time, metadata related to the sampling event should also be recorded.

4. Characterisation of samples

Samples should be characterised by accredited analytical laboratories, considering instruction guidelines related to consistent data reporting for efficient data analysis and review.

5. Review data and revise sampling plan

After samples have been characterised, the data generated should be analysed, interpreted, and reported as required. The sampling plan can be iteratively modified based on this review process to ensure that sampling is undertaken in a manner that supports the goal of the sampling plan.

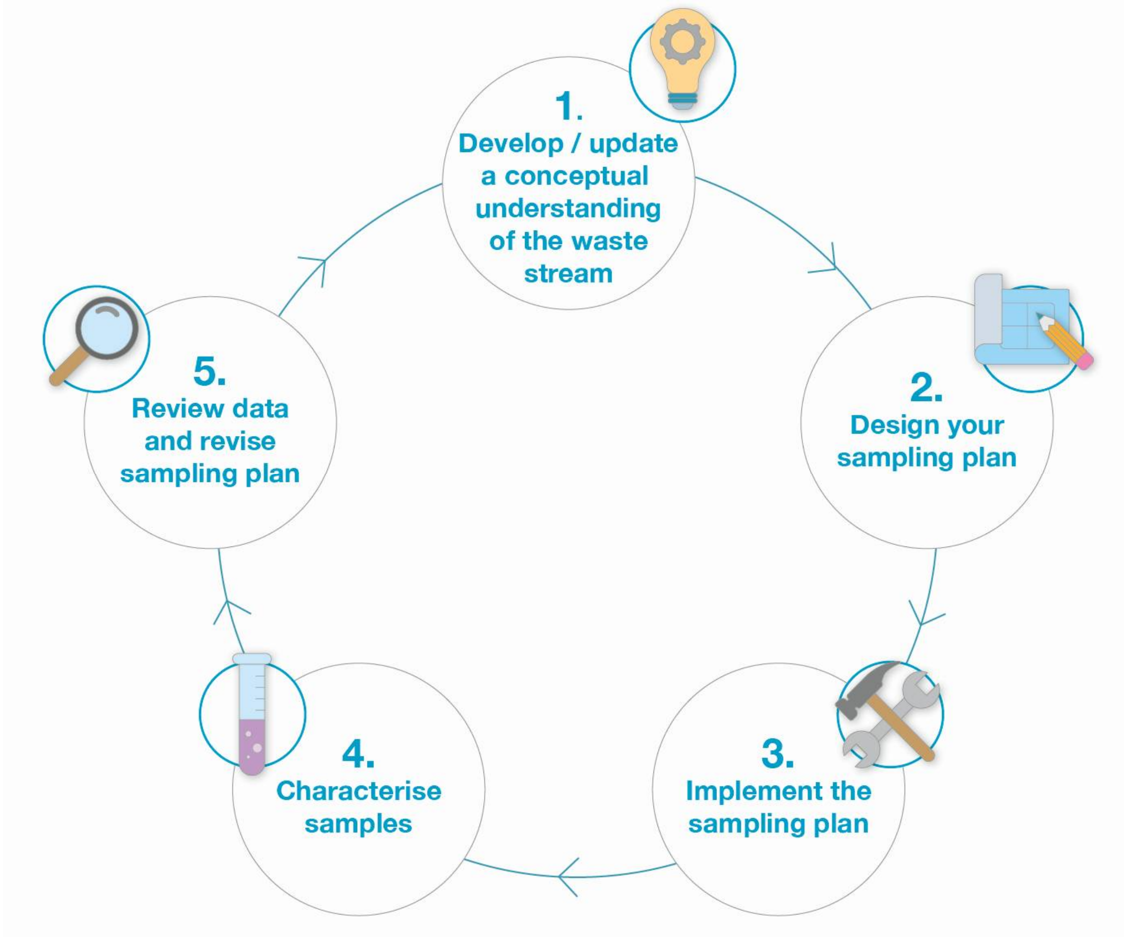

Figure 1 Principles of sampling plan design for complex waste materials.

3. Applying the principles of sampling plan design

3.1 Developing a conceptual understanding of the waste stream

3.1.1 Generic considerations

A conceptual understanding of the target waste stream and processes involved in waste handling and recycling is a critical step in sampling plan design. A conceptual understanding of the target material would include defining the purpose of the planned sampling event and how data generated from the characterisation of samples would achieve the purpose of the sampling plan.

As a guide, criteria for development of a conceptual understanding of the waste stream would include (but are not limited to):

- The purpose of the sampling plan and consideration of how analytical data may be used in the future;
- The source of the waste, including a basic understanding of process feedstocks;
- The form of the waste (i.e., solid, liquid, gas, and general condition of waste entering processes);
- How the process is engineered (e.g., is the feedstock sorted, shredded, crumbed, washed, treated);
- How the product is stored prior to and after processing (e.g., stockpiles stored indoors/outdoors, temperature, protection from the elements);
- Any other relevant handling procedures that may impact the composition or quality of samples; and,
- Any other relevant information pertaining to the process that has been captured by the waste management facilities related to the waste or products.

This conceptual understanding can include information related to the source of waste, how waste is collected and stored (e.g., temperature, presence/absence of water, if there are stockpiles), the end case scenarios of recovered materials and other information related to the management of wastes. Where possible, it would be beneficial to undertake a visual inspection of the site where sampling is planned to occur and gain an understanding of waste stream handling and processing.

3.1.2 EOL tyres as an example of developing a conceptual understanding

Using the guiding criteria outlined above, a conceptual understanding for EOL tyres and crumb rubber product can be determined. A summary of the application of the guiding criteria for generating a conceptual understanding for sampling EOL tyres and crumb rubber is provided in Table 1.

Here we briefly summarise information that would be relevant to developing a conceptual understanding of EOL tyres.

Table 1 Application of guiding criteria for the generation of a conceptual understanding for the sampling of EOL tyres and crumb rubber.

Guiding criteria	Consideration for the sampling of EOL tyres
Purpose of sampling plan	Initially, to generate high quality information related to the composition of tyre crumb and to build evidence based decision making for chemical prioritisation in these materials.
Source of waste	Feedstock composition (e.g., road tyres, truck tyres, origin of wastes).
Form of waste	Whole tyres, baled tyres, general condition notes (e.g., age, dirt, obvious degradation/wear).
Process and engineering considerations	How is the feedstock stored, handled, shredded, crumbed, treated, or washed? What temperature is the process? Are chemicals added in at any stage of the process? Is water added? What wastes are produced.
Storage of product before and after processing	How is the product stored? Are stockpiles stored indoors/outdoors? What is the temperature of storage? Are the products protected from the weather?
Other relevant handling procedures that may impact the composition or quality of samples	Determined through interview with the facility.
Any other relevant information captured by waste management facilities	Tonnages, process kinetics, issues with feedstocks, other relevant metadata.

Motivation and context

EOL tyres are a problematic waste stream in Australia with 478 kilo tonnes (kt) generated in 2020-21 [17]. In 2017-18, EOL tyres represented the third largest category of hazardous waste in Australia (6 %) [18]. Historically, whole EOL tyres have been stockpiled, sometimes posing a fire threat, or have been exported as a waste management solution.

EOL tyres are increasingly being recycled and reused in new materials. The Circular Economy Roadmap produced in 2020 [1] indicated that the major reuse markets for EOL tyres in Australia for the next 2 years were crumb rubber in spray seals (20 kt/year), and crumb and shreds incorporated into binders, adhesives, and glues (18 kt/y) and in soft-fall, playground, turf, and asphalt applications. The use of shredded and crumbed rubber as tyre derived fuel and as lightweight aggregate for use as fill was also predicted to increase in the next 10 years. There is an increasing concern arising that the behaviour and risk of contaminants within these reprocessed materials is not fully understood. The United States Environment Protection Agency (US EPA), for example, have invested in the characterisation of tyre crumb rubber to address potential exposure to chemicals present in these materials since it is widely used in synthetic field turf [14]. No such assessment has been conducted in Australia, and the risk related to chemicals of concern present in recovered rubber materials in secondary applications under relevant environmental conditions is unknown.

A goal of initial sampling might be to target EOL tyre crumb and shred materials for chemical characterisation and to determine total leachable components. The aim would be to generate high-quality data that can provide an evidence base for decision makers to assess any risks associated with the reuse of these materials. Using the iterative sample plan design principles described in this document, we expect to consider how the chemicals identified in EOL tyre fractions might relate to whole tyres in stockpiles, which could trigger further risk assessment of the storage and reuse of whole tyres in civil engineering or silage applications.

3.1.3 Understanding material workflows and market pathways for recovered EOL tyre materials

An indicative material workflow for EOL tyres is summarised in Figure 2. Although stockpiling and reuse of whole tyres occurs, we are focussing on the material flow related to recycling and recovery of EOL tyre materials for reuse in new materials. Shredded and crumbed tyres also have known reuse pathways in Australia and represent a significant proportion of the established market for recovered EOL tyre materials. As such, these materials provide an opportunity to understand risks associated with current reuse pathways of secondary materials generated from tyres.

Recycling leads to engineered size reduction of EOL tyres that are commonly shredded (approximately 50-150 mm diameter) or crumbed (<1 mm diameter). A schematic of a general size reduction pathway for EOL tyres to fine grained material (after Al-Fakih et al [19]) is depicted in Figure 3A, and the range of particle sizes indicative of crumbs to granules, are shown in Figure 3B. As dominant market pathways for recycled rubber products and size reduction may impact the availability of chemicals from waste materials, it is of interest to undertake representative sampling of both shredded and crumbed EOL tyres.

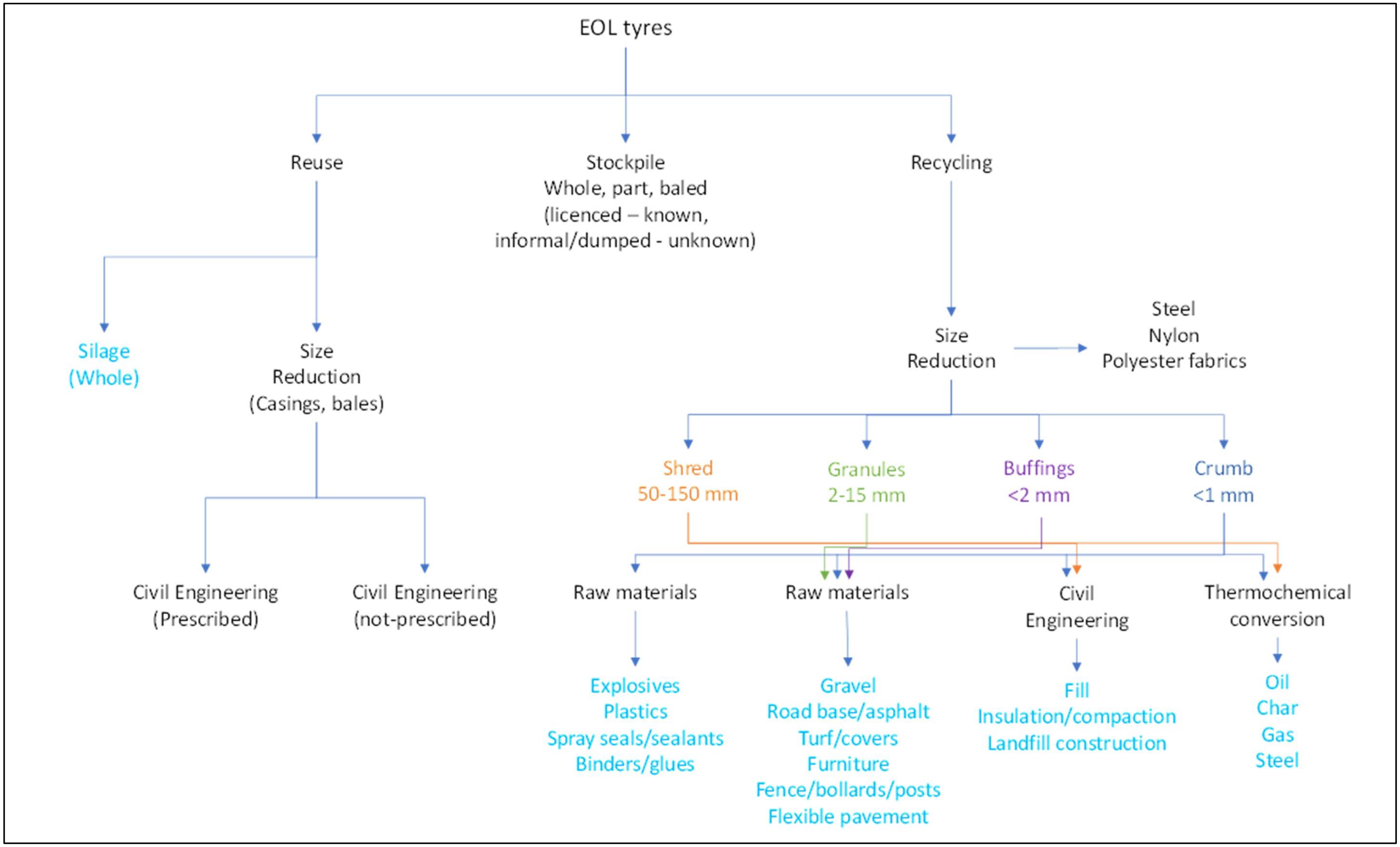

Figure 2 Indicative material handling flow sheet for EOL tyres. For the purposes of this conceptual understanding of EOL tyres, we are focussing on material flows related to the recycling path, including size reduced fractions that are intended for use as raw materials in manufacturing and construction or thermal conversion.

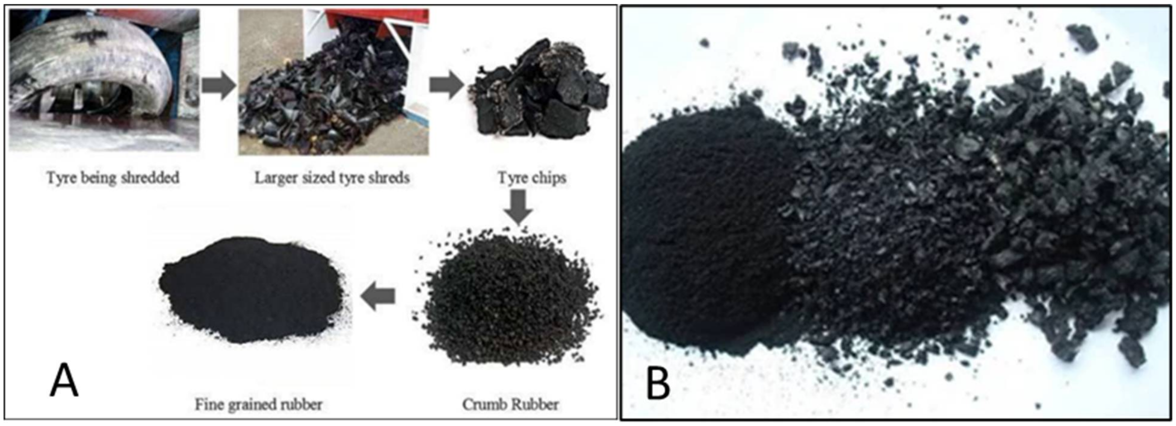

Figure 3 Process chain for shredding and crumbing EOL tyres (A), and indicative change in particle size when processing EOL tyres as crumb or granules (B).

3.1.4 Handling and storage of recovered EOL tyre materials before and after processing

Information related to the handling and storage of waste materials is likely to be dependent on the recycling contractors' preference and type of material to be sampled. Recovered EOL tyre materials may be handled, processed, and stored in various ways, including the use of conveyor belts, stockpiling of whole, baled or size reduced tyres, temporary storage, and mixing (**Figure 4**). In addition, it is important to also consider any wash steps or reagent addition, or specific conditions during processing that may impact the integrity of samples.

Figure 4 Images showing storage and handling of crumbed/shredded tyres, including (A) processed EOL tyre stockpiles, open to ambient environment; (B) bagged EOL tyre crumbs; (C) coarse shredded tyres, stored in a stockpile; (D and E) use of a conveyor to move material to a stockpile housed inside a processing facility.

Storage of these materials could be in a relatively protected ambient environment inside of a processing facility, or outside in the open air, exposed to rainfall and other conditions that would be pertinent to consider during the development of a conceptual understanding of waste materials. Consideration of site-specific handling and storage conditions of waste materials and a visual inspection of the site will likely indicate potential sampling locations along the waste management pathway. Images in **Figure 4** demonstrate some of the various storage and handling of crumbed/ shredded EOL tyres.

3.1.5 Other site- and material-based information relevant to a conceptual understanding for EOL tyres and rubber materials

The volume/mass of EOL tyres being handled at a facility targeted for sampling or its throughput might dictate the sampling intensity. High intensity sampling may be warranted if EOL tyre material at a facility has high volume throughput and high variability. *A priori* consideration of the variability of a stockpile or source of EOL tyres to be sampled might be problematic but may be assessed via records of received materials to a processing plant, or via visual inspection. Additionally, where time permits, low-cost analysis approaches (pH, Electrical Conductivity (EC), metals as per New South Wales Environmental Protection Authority (NSW EPA) [15]) could be used to screen for the degree of variability in material stockpiles to support visual inspection and other records obtained during the development of a conceptual understanding of EOL tyres and rubber materials.

3.2 Developing a sampling plan

3.2.1 Generic considerations

A preliminary sampling plan for waste or waste derived materials can be developed by combining the following instruments:

- The established conceptual understanding of the waste material (Section 3.1);
- A review of existing or acceptable guidelines and standards related to sampling of similar or like materials, where available, or an understanding of gaps in knowledge;
- Consideration of handling and health safety and environmental issues; and,
- An assessment (using available literature and information) or judgement (when literature and information is limited) of the likely types of chemicals present in the waste.

At this point, we have an established conceptual understanding of the targeted waste material and its handling (presented in Section 3.1), and this section describes the review of the relevant existing or acceptable guidelines and standards related to sampling of similar or like materials, where available. In addition, we present an indicative assessment (using available literature and information) or judgement (when literature and information is limited) of the likely types of chemicals present in the waste. Below we continue to use EOL tyres as an example.

3.2.2 Review of existing or acceptable guidelines and standards relevant for EOL tyres

This sampling guidance was prepared in consideration of relevant guidelines and principles related to the characterisation of wastes [8-12] and contaminated sites (water and land) [13], as well as specific guidance related to EOL tyres and rubber materials [14-16], where available. The literature relating to sampling of wastes has not been exhaustively reviewed.

General waste sampling guidance

It is recognised that waste materials are likely to be highly heterogeneous and sample collection will need to be as representative of the entire material as possible. Here, we outline some of the available guidance documents and distil some principles that might guide sampling, particularly for EOL tyres.

It is recognised that sampling of EOL tyres might occur or be necessary across a range of scales depending on the reuse scenario and how secondary rubber products are sourced and processed. There is a notable variation based on the source of materials (whether sourced from single tyres, to stockpiles of tyres), the particle size of materials produced (e.g., shredded, crumbed), and end use scenarios (e.g., reused in road materials, soft fall matting or as tyre derived fuels). It is also recognised that tyres may have a highly variable (and largely unknown) composition and concentration of chemicals and chemical mixtures present. For example, off the road (OTR) and urban passenger tyres have considerable compositional differences based on the standards of manufacture that are dictated by use [20]. Metadata associated with a sample such as the type or use of tyres, brand of tyres, country of manufacture, and shredding/crumbing processes would provide context to any sampling and subsequent chemical analysis.

Several overseas countries have guidance on sampling of wastes. The US EPA [9] provides practical guidance on approaching the sampling of wastes including waste piles, impoundments and enclosed waste in drums and tanks. This document also discusses equipment that is appropriate to use when sampling from various waste streams. Standardised guidance for waste sampling is also available, including liquid and solid wastes [11, 12]. Generally, there is considerably less guidance available for the sampling of solid waste in Australia.

The NSW EPA [15] recognises the heterogeneity of waste and cautions "Where practicable, safe, and appropriate, it is desirable to separate a mixture containing different classes of wastes before classifying them separately. For example, if waste tyres (special waste) are mixed with lead-acid batteries (hazardous waste), it would be desirable to separate the wastes so only the hazardous component is classified as hazardous waste." but says that "Selectively choosing sample results to classify waste introduces bias and violates fundamental statistical principles". In most cases, it would be unreasonable and impractical to separate individual wastes or waste components for analysis. Instead, designing a relevant sampling and analytical campaign that addresses the fundamental characteristics and variability of these materials is critical to ensure confidence in data characterisation and the subsequent decisions made regarding the residual risk of the reuse of waste derived materials.

Contaminated site assessment and characterisation

The design of a sampling and analytical plan for complex wastes such as EOL tyres is likely to be a balance between ensuring representativeness and the financial and/or logistical constraints of sampling and analysis that may bias a sampling event. Understanding and defining the goal of the sampling event and resolution of data required would be key considerations when developing an appropriate sampling plan, and other non-waste guidance materials should also be considered.

The National Environmental Protection Measure (NEPM) for assessing site contamination has guidance on sampling soil, soil gas and groundwater [13]. Principles from the NEPM on sampling of soils and stockpiles (Schedule B2 of NEPM 2013 – "Guideline on Site Characterisation") have relevance to waste piles of crumbed or shredded EOL tyres due to the need to sample representatively despite variability [13].

In sampling contaminated soils, several sampling schemes might be adopted – regular grid sampling, judgemental or informed targeted sampling, stratified sampling, transect sampling, composite sampling, and random sampling [13]. Apart from judgemental sampling, the other categories are largely probability-based designs, which apply statistical sampling theory and may involve random selection of sampling locations. The principles are applicable to stockpiles of processed EOL tyres, and for waste materials that may have similar characteristics to soils and sediments. Developing an understanding of the site and the requirements for analysis underpin decisions related to sampling strategies.

For contaminated site assessment, two key steps in site assessment are:

(i) the establishment of a conceptual understanding; and,

(ii) the establishment of data quality objectives (DQOs) that indicate what kind of data is needed, and how it can be collected.

The applications of these steps to solid waste streams help with designing a sampling plan for EOL tyres by ensuring that the sampling plan and relevant analysis and characterisation of wastes are based on a clear understanding of the material being investigated (i.e., the conceptual understanding). In addition, these steps also trigger an assessment of the potential chemicals present in the material and routes for analysis, which would ensure that sampling is undertaken in a manner that maximises quality and confidence in decision making.

Facets of the DQO procedure outlined in the assessment of contaminated site guidance is reflected throughout this document. While the application of contaminated site assessment DQOs does not relate perfectly when considering waste materials, the theory behind the conceptualisation, optimisation and iterative design of sampling and analytical studies is indeed relevant and important for ensuring the data generated from waste characterisation sampling is representative and high quality.

Specific guidance for characterisation of EOL tyres and rubber materials

Sampling of EOL tyres and secondary materials will be an iterative process. An initial sampling guideline, such as proposed here, following standard/recommended protocols designed to obtain representative samples, as has been developed for biosolids for example [21], will yield analytical compositional data that is likely to lead to updates to the guidance and resampling strategies. This strategy is not unlike the assessment of contaminated site guidance, where initial data refines the next stage of sampling and targets for subsequent sampling. The sampling guideline would be adapted to site/waste specific conditions, and a range of assessments of the chemical data obtained.

When developing this document, specific documents and guidance material related to sampling and characterisation of EOL tyres were considered including:

- US EPA Tire Crumb Rubber Characterisation [14];
- NSW EPA Resource Recovery Order for Waste Tyres [15];
- Australian Standard 1141.3.1-2012 Methods for sampling and testing aggregates – sampling – aggregates [16]; and,
- Scientific literature related to the detection and characterisation of chemicals in tyre and rubber materials [for e.g., 6, 7, 22, 23].

3.2.3 Assessment of chemicals contained in EOL tyres and rubber materials

Using available literature and information, an assessment related to the likely chemicals and chemical mixtures, and their approximate concentration ranges present in EOL tyres can be summarised. Consideration should also be given to the unknown chemical components of waste materials during early screening. It may be relevant to consider non-target chemical analysis to understand composition of waste materials as a goal of initial sampling campaigns. There is the requirement to consider and identify relevant analytical suites based on regulatory requirements to ensure data generated from samples meets these requirements and is cost effective.

In addition, information related to sample handling to ensure sample integrity with respect to specific analytical pathways can also be identified. Management of samples (including holding times and in perpetuity storage) can be recommended, as well as control measures for health, safety, and environment related risk management.

Known chemicals in EOL tyre waste

Table 2 lists some of the chemicals that have previously been identified in EOL tyres and rubber materials via scientific literature [for e.g., 6, 7, 22, 23] and regulatory sources [for e.g., 14, 15]. Global research efforts and regulatory priorities are likely to add to or change analytical needs. Table 2 indicates that a mix of inorganic and organic compounds could be present in EOL tyres, which can then lead to the development of a preliminary analytical plan relevant for the sample matrix and chemicals present, including information related to the methods for analysis, sample containers to be used, sample handling and storage conditions and relevant health and safety requirements during sampling.

Table 2 Examples of chemicals reported for EOL tyres and rubber materials.

Types and classes of chemicals*	Reference
Polycyclic aromatic hydrocarbons (PAHs)	7
Phthalates	23
Benzotriazoles and benzothiazoles	7
Bisphenol A/S/F	23
6PPD (6PPD-quinone) N,N'-Diphenyl guanidine (DPG) Hexamethoxymethyl-melamine (HMMM)	6, 7, 23
Inorganics (e.g., Pb, Zn, Cr, Cd, Co)	23

*Includes chemicals covered in US EPA Tire Crumb Characterization report [14]

As an example, inorganic compounds in EOL tyres and rubber materials might be analysed using Inductively Coupled Plasma (ICP) spectroscopy, while organic compounds using Gas Chromatography and Liquid Chromatography (GC and LC), along with mass spectrometry (MS) platforms. These may require both standard and non-standard laboratory methods – with a preference for analysis to be undertaken at accredited laboratories (in Australia it might be NATA accredited). General characterisation (pH, EC, %carbon) could be routinely analysed by most commercial laboratories, but some method development may be required due to the sample matrix. Together, specifying this information and on gaining the resultant analytical data, will identify and inform any additional measures required to ensure the integrity of the samples and the effectiveness of the sampling strategy.

3.2.4 Health and safety considerations

Health, Safety and Environment (HSE) risk assessments should be undertaken *a priori* to sampling to avoid, mitigate and prevent key risks. Risks might be associated with handling sharp or powdered materials, the presence and operation of machinery, the use of sampling equipment, laboratory practices, driving to and from sampling premises, and disposal of residual materials. Many HSE risks will be linked to the facility where sampling might occur and as such alignment with that facility's HSE protocols and an activity risk assessment (ARA) is critical for any sampling activities. A HSE risk assessment will also identify the appropriate personal protective equipment (PPE) required during the sampling event.

3.2.5 Preliminary sampling plan for EOL tyres and rubber materials

EOL tyre materials may be highly heterogeneous and sample collection needs to be as representative of the entire material as possible. An interim sampling plan is likely to be updated based on obtained data, and, as such, moving to a high-quality sampling plan will be an iterative process.

A sampling strategy needs to be confirmed by visual inspection of the EOL tyre materials and the engineering approach to handling, shredding, crumbing and storage. A sampling strategy may need to be adjusted due to engineering, machinery use, material flows or stockpiling approaches during handling and repurposing of tyres materials that are to be sampled. It is likely that stockpiled materials would be the common target for sampling. This information will be generated through the development of a conceptual understanding of the material to be sampled (Section 3.1).

The sample strategy employed for any waste material should be determined based on the goal of the sampling plan, the conceptual understanding of the material and site, and a review of accepted guidelines for the material, or a material that is similar.

3.2.6 Specific sampling considerations related to EOL tyres and rubber materials

The NSW EPA released The Recovered Tyres Order in 2014 that outlines the requirements that must be met by suppliers of recovered tyres for application to land for use in civil engineering structures and road making activities (using industry recognised standards such as the Building Code Australia) [15]. This order requires suppliers to submit a sampling plan, which includes a description of sample preparation and storage procedures for recovered tyres, as well as undertake sampling and testing of the recovered tyres in accordance with the submitted sampling plan and Australian Standard 1141.3.1-2012 Methods for sampling and testing aggregates – sampling – aggregates (or equivalent) [16].

1. Continuous processing

EOL tyre materials may be sampled from a continuous process from various locations throughout the site – that is, processing does not stop for the sampling to occur. This might lead to complexities in representative sampling. The frequency or periodicity of sampling or even once off batch sampling from a conveyor belt might need to be framed in the context of the rate of movement of the conveyor belt, and likely source variation of the EOL tyre materials. Khodier et al. [24] investigated the representative sampling of shredded waste from a conveyor system, by evaluating the theory of sampling against replicated experiments to determine sample variability. Where sampling of EOL tyres is to occur from a conveyor belt, such principles would need to be adopted, and perhaps pre-sampling to determine relative variability might need to be undertaken.

The NSW EPA Recovered Tyre Order [15] stipulates that characterisation of recovered tyres from continuous processes be completed by collecting 20 composite samples, taken from batch, truckload or stockpile that has not previously been sampled for characterisation purposes. The frequency of sampling specified is every 2 years. In addition to this characterisation, routine sampling of 5 composite samples per 4,000 tonnes (or part thereof) or every 6 months is required. The order does not stipulate how sampling must be completed from the site.

2. Non-continuous processing

Where samples are to be obtained from a non-continuous process, the NSW EPA Recovered Tyre Order [15] stipulates that one-off sampling of a batch, truckload or stockpile of recovered tyres can be completed by collecting 10 composite samples from every 4,000 tonnes (or part thereof) processed. The test results for each composite sample must be validated as compliant with the absolute maximum and maximum average concentration or other value listed in the order.

3. Stockpile sampling

For stockpiles, stockpiling may cause some segregation of grain sizes particularly on the exterior slopes as well as create some gradation in physicochemical properties from the surface inwards. Finer material may tend to accumulate at the toe of batters and coarser material towards the crest. Material may be distributed into different parts of a stockpile based on temperature or moisture content. Sampling might best avoid the outer surface of the stockpile and recover samples from >30 cm deep into the stockpile – this avoids surface effects caused by rainfall, incident ultraviolet (UV) exposure or other weathering or compositional changes that might be induced at the surface.

The NEPM [13] suggests for relatively uniform ‘soil’ stockpiles that the minimum number of samples be as in Table 3. This may have applicability to processed EOL tyre stockpiles – especially as an initial sampling strategy.

Table 3 Minimum number of samples recommended for initial assessment of stockpiles.

Stockpile volume (m^3)	No. of samples
<75	3
75 - <100	4
100 - <125	5
125 - <150	6
150 - <175	7
175 - <200	8

Sampling strategy

Based on the conceptual understanding (Section 3.1), and the review of available literature and information (Section 3.2), the following sampling strategies should be considered for EOL tyres and rubber materials:

A. Simple Random – many samples are taken, and total costs are high. Every possible point at the site has equal chance of being sampled. Simple random is used when variability is small, and field and analytical costs are low to detect peak concentrations.
B. Composite – multiple smaller samples are collected and combined. Subsamples are collected for additional analysis. Composite sampling is used when the average concentration and sampling of many samples for reduced cost is desired.
C. Stratified Random – The waste material is divided into two or more subsets. Each subset is sampled separately with one of the designs previously described. Stratified random sampling is used to improve the precision of design.

In the first instance of a study, the purpose of the sampling plan is likely to understand total, or average concentrations of chemicals that may be present in EOL tyre and rubber materials, so composite sampling may be most appropriate. However, upon review of the data generated from an initial sampling event, the proposed sampling strategy is likely to be modified to target specific analytes at sample frequencies that may be more representative of the materials being sampled from a specific site. This invokes the iterative nature of this sampling plan guidance, and the characterisation of complex waste materials.

Sample frequency

The NSW EPA [15] recommend composite sampling as it provides a valid approach especially where costs prohibit an extensive number of samples. However, where ‘mixing’ might be incomplete its use should be considered with caution because of the potential for individual high results to be masked by low results.

The NSW EPA [15] outlines a required frequency of:

- 20 composite samples every 2 years, plus 5 composite samples per 4,000 tonnes processed, or every 6 months; and

- 10 composite samples per 4,000 tonnes processed for a one-off sampling event, when validated with data limits provided in the order.

Given an initial sampling event for EOL tyres and rubber materials is likely exploratory in nature and no other sampling frequency guidance documents are available for EOL tyres or rubber materials, the sample frequency of 10 composite samples per 4,000 tonnes processed for a one-off sampling event would be sufficient to provide a baseline assessment of chemical contained in this waste. However, it should be noted that subsequent sampling events would be modified based on the data generated from the initial sampling event.

Sample handling and storage considerations

Ensuring the cleanliness, suitability and compatibility of the equipment used for sampling, and sample handling and storage is critical to enable the generation of high-quality data from any materials.

Based on the potential chemical composition and analytical methods identified for characterisation, specific sampling containers might be needed to ensure the integrity of the samples obtained. For EOL tyres and rubber materials, the general advice for sample containers is shown in Table 4. Where appropriate, seek direct advice from the analytical laboratory to ensure use of containers and container preparations are suitable prior to commencing a sampling campaign.

Table 4 General sample container advice relating to the sampling of EOL tyres and rubber materials to ensure the integrity of samples and the potential chemicals they contain.

Analytical method	Sample container material
Inorganic chemicals	Polypropylene (PP)
Organic analysis (except PFAS)	Glass (amber preferrable)
PFAS (and other fluorotelomers) analysis	High Density Polyethylene (HDPE)

Any equipment used will need to be decontaminated prior to sampling. In addition, re-cleaning of sampling equipment should occur between sampling events, especially if trace chemicals are being analysed in samples (e.g., per- and polyfluoroalkyl substances (PFAS)). During the design of the sampling plan, consider cross-contamination between samples and from sample handling, and identify measures to minimise chemical interference from machinery (e.g., heat, oil and grease, metal shavings), and during sampling operations. These measures may include, but are not limited to:

- Wearing the appropriate PPE;
- Changing gloves between samples; and,
- Rinsing sampling equipment between samples.

Considering transport and storage requirements for samples is also critical to ensure sample integrity. Some samples may be required to be chilled (4 °C) and shipped within a specific time for sample receipt and analysis. In addition, some samples may have a holding time limitation or are required to be archived in case further analysis is required. Seeking advice from the nominated analytical laboratory when designing the sample handling, storage and transport will define important parameters impacting sample integrity.

Quality control and assurance

Quality assurance and quality control (QA/QC) is a combination of processes designed to assure the quality of a sampling campaign and the data generated from collected samples. QA/QC processes are designed to ensure that the data collected from samples accords with sample theory, and that samples and the corresponding data are handled using appropriate procedures to minimise impacts to sample quality or composition and data integrity. To ensure the quality of samples and data generated from samples obtained from waste and waste derived materials, it is critical to follow QA/QC advice during a sampling campaign.

QA/QC procedures for sampling include defining the frequency and adequacy of trip, laboratory, and sample rinsate (wash) solutions from cleaning equipment that can be used as blanks. Blank samples are subjected to all aspects of sample collection, processing, transport, and laboratory handling and are used to trace sources of contamination that may be introduced into samples at any stage of sample handling. The reporting of blank samples, and other QA/QC samples is often variable, dependent on the data standards followed during sample plan design. Table 5 provides advice on field-based QA/QC samples that should be obtained and reported for sampling events. In addition to these, several laboratory QA/QC samples should also be planned and prepared to ensure the integrity of analytical methods during characterisation.

Table 5 QA/QC samples to be obtained in the field during a sampling event.

QC Sample Type	Definition	Purpose	Suggested frequency
Trip Blank	Analyte-free water prepared by the laboratory, then transported to the sample site and back to the laboratory with samples.	Ensures that samples are not contaminated during sampling and transport. Typically used for volatile compounds.	1 per sampling event, per waste type, per analyte type.
Field Blank	Analyte-free water poured into a container in the field and carried with field samples.	Assesses whether contamination may have occurred in the field.	1 per sampling event, per waste type
Rinsate or Equipment Blank	Analyte-free water collected after it has been poured over or through sampling equipment prior to the collection of samples.	Assesses whether the decontamination procedure of equipment between samples is adequate and no cross contamination has occurred.	1 per sampling event, per waste type

3.3 Implement the sampling plan

Following the designed sampling plan, samples can be collected and appropriately stored prior to analysis. Modifications to the sampling plan that occur during sampling and handling should be recorded for reporting purposes.

Identifying and gathering metadata associated with sampling EOL tyres and the engineering process and facility that is being undertaken to shred/crumb the tyres is important, as these may direct or alter the sampling strategy. In addition, linking metadata and unique sample identifiers is also critical to ensuring data generated from samples is traceable. Metadata should also include the location of samples obtained and photos associated with the sampling event [25].

A summary of metadata to be collected at the time of sampling is outlined in Table 6. Many other metadata can be collected, and there is no limit to the information that can be captured during a sampling event. The metadata collected may also change depending on the target waste materials being sampling.

Table 6 Metadata fields that should be captured during sampling campaigns for complex waste materials.

Metadata	Description
Sample name	A unique project specific sample name.
Sample collector	Name or initials of sample collector.
Sample type	Object type (individual sample, core, site). Material type (Solid, liquid; particle size). Sample features (sample description).
Sample condition	Commentary on age, condition or other aspects of the sample that may impact quality or composition.
Location information	Identifying where the samples were obtained, either on a map or using latitude/longitude or a location description. Note whether location is inside a building or outdoors.
Environment	Note general weather conditions (e.g., hot, cold, wet dry) and provide more details if sampling is done outside.
Replicates	A description of replicate frequencies.
Date of collection	The date samples were collected (including time).
Collection Method	A brief description of the collection method, including tools.
QA/QC	A brief description of sample QA/QC method.
Images	Any photographs or other images related to sampling.
Other notes	Any other information that is pertinent to the sampling campaign.
Project name	The name of the project for which the samples were obtained.

3.4 Characterisation of samples

Samples should be characterised by accredited (e.g., NATA accredited) analytical laboratories. To ensure data that is received from external sources is accessible and that QA/QC information can be validated, the analytical team will propose a minimum standard for reporting that can be included in requests for services from analytical laboratories. A minimum standard for reporting may include:

- Provision of raw data in accessible format (.csv or .xlsx) alongside .pdf reports;
- Provision of information related to methodology modification and implications to data quality; and,
- Provision of laboratory QA/QC methodology and outcomes.

The provision of data and information relevant to the data quality objectives and controls will enable efficient management and analysis of data, as well as provide information about the quality of the data generated from the samples obtained. Where possible, data should align with the principles outlined in the FAIR Guiding Principles for scientific data management stewardship [26], and the National Principles for Environmental Information [27].

3.5 Review data and revise the sampling plan

After samples have been characterised, the data generated should be analysed, interpreted, and reported as required. As a minimum, reporting should include (but is not limited to):

- A description of the conceptual understanding related to the waste materials and the site where sampling will be undertaken;
- The review of available literature and information relevant to the material targeted for sampling;
- The sampling plan;

- Methodology and modifications of methodology used for characterisation, including details of the analytical laboratories that carried out the analysis;
- Data interpretation, including QA/QC and inclusion of identifiers to chemicals analysed (e.g., Chemical Abstract Service Registration Number (CAS RN) and Simplified Molecular Input Line Entry System (SMILES) codes);
- An assessment against DQOs set when developing the sampling plan (Section 3.2); and,
- Identification of next steps and intention for iterative sampling plan design.

As this sampling plan guidance is designed to be an iterative process, the sampling plan should be reviewed upon consideration of the data, the QA/QC reporting, and any additional information that was garnered during the sampling campaign. Revisions and additional sampling events should also be based on comparison to literature and in consideration of relevant national and international waste sampling guidelines, and their development.

Critical evaluation should be undertaken to assess if DQOs have been met and hence if the sampling plan needs to be altered, or indeed if DQOs need to be modified.

Iterations of the sampling plan should consider whether sampling is representative and statistically meaningful and can address modified goals identified for consecutive sampling campaigns.

The view of employing this iterative sampling plan guidance is to ultimately build an assessment of risk for identified chemicals of concern.

4. Validation of the sample plan design framework

As at June 2023, this Version 1.0 sampling plan framework is not yet validated. As more intensive sampling of EOL tyres and other wastes is undertaken the framework is expected to become more robust, and indeed supported for more general use. In the meantime, it provides a pragmatic, and we believe logical approach for reliable sampling of such wastes.

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