

UNIVERSIDAD POLITÉCNICA DE MADRID
Escuela Técnica Superior de Ingenieros de Minas y Energía



**Assessment of Pyrotechnic Industry:
Adaptation of Processes and Materials
to Sustainable Development**

DOCTORAL THESIS

Submitted for the degree of Doctor by:

David León Ruiz
MSc Mining Engineering

Madrid, 2025



UNIVERSIDAD POLITÉCNICA DE MADRID
Escuela Técnica Superior de Ingenieros de Minas y
Energía

**Doctoral Degree in Research, Modeling and Analysis of
Environmental Risk**

**Assessment of Pyrotechnic Industry:
Adaptation of Processes and Materials
to Sustainable Development**

DOCTORAL THESIS

Submitted for the degree of Doctor by:

David León Ruiz

MSc Mining Engineering

Under the supervision of:
Dr. Blanca Castells Somoza

Madrid, 2025

Title: Assessment of Pyrotechnic Industry: Adaptation of Processes and Materials to Sustainable Development

Author: David León Ruiz

Doctoral Programme: Research, Modeling and Analysis of Environmental Risk

Thesis Supervision:

Dr. Blanca Castells Somoza, Assistant Professor, Escuela Técnica Superior de Ingenieros de Minas y Energía, Universidad Politécnica de Madrid (Supervisor)

External Reviewers:

Thesis Defense Committee:

Thesis Defense Date:

This thesis has been partially supported by the Ministry for Ecological Transition and Demographic Challenge of Spain (Regulatory Agreement for the nominative subsidy contemplated in the general state budget law, of the Ministry for Ecological Transition and the Demographic Challenge, in favour of Laboratorio Oficial J. M. Madariaga–LOM of the Universidad Politécnica de Madrid).

Acknowledgement

In the first place, I would like to thank my supervisor Blanca Castells Somoza for her guidance, patience and continuous support during these years. Her expertise and supervision were essential for this research. Thank you for all your help. I will keep your friendship forever. I would also like to make a special mention to Javier García Torrent, for introducing me to the world of pyrotechnics and instilling in me this passion for the University.

I would like to thank Subdirección General de Minas del Ministerio para la Transición Ecológica y el Reto Demográfico (MITECO), Centro Tecnológico de Seguridad y Calidad en Industrias Energéticas y Minas (TECMINERGY) and Laboratorio Oficial J.M. de Madariaga for financial support and for letting me carry out the tests in their facilities, providing me with all kinds of resources, material and laboratory equipment. But above all, I would like to thank the magnificent people who make up the laboratory and with whom I have had the pleasure of working. I would like to thank Juan Casín, for his indispensable work as a contact with MITECO, Ángel Santamaría, for his help performing the tests and also José Luis Lorenzo, Sergio Domene and Sergio Barón, who were always ready to collaborate in any task.

I would like to thank my supervisor during my research stay, Dragoslava Stojiljković, and the people I have worked with there, Miloš Radojević, Nebojša Manić and Aleksandar Milivojević, for their help, guidance, and advice to my research, but even more for making me feel at home in Serbia.

Thanks to all the pyrotechnical associations and companies that have collaborated in the development of this thesis and the Escuela Técnica de Ingenieros de Minas y Energía, for being my second home during my whole university period and hopefully for many years more. I would like to thank all those with whom I have had the pleasure of working, David, Marcelo, María Jesus, Liliana, Yolanda, Cristina, Fernando, María, Miguel, Laureano, Lucía and Luije, as well as all my colleagues in the department. I would like to make a special mention to Isabel, who has been with me since even before I started this adventure.

I would also like to thank the external reviewers, Maria de las Nieves Fernandez Añez (Western Norway University of Applied Sciences) and Jorge Martin Molina Escobar (Universidad Nacional de Colombia), for their willingness to review the thesis and their disinterested comments, which have undoubtedly improved the

document presented. Thanks to them, the thesis is eligible for International Mention.

To my family, for celebrating all my successes as if they were their own. Especially my parents, Julián and María Oliva, for the values you have passed on to me, for your support over so many years and for being an example of perseverance and motivation. You are undoubtedly responsible for getting me this far. Thanks to my brother, Alberto, to have given me incredible moments and taught me the meaning of the word courage.

Finally, I would like to give special thanks to Andra, for all her affection in the good times, but above all for her unconditional support and advice in the regular ones. You are an example for me.

Abstract

Pyrotechnics as a sign of celebration have been a common practice in many countries for thousands of years, being valued for their ability to create unique visual and sound effects. In addition, its use is associated with other areas such as maritime or land signalling, military operations, fishing, etc. In recent years, the pyrotechnics sector has faced several social challenges, which it needs to address in order to continue to coexist with the rest of society. These challenges should drive the sector towards a more sustainable model, in line with the Sustainable Development Goals (SDGs) contained in the 2030 Agenda.

Criticism of the sector focuses on the atmospheric emissions released during its use and the noise impact generated in urban environments, affecting certain groups, especially domestic animals. This study proposes an exhaustive evaluation of all the processes involved in the pyrotechnic and fireworks sector, analysing in depth the most relevant and current aspects, with the aim of proposing tools to the sector for its defence and on which to work on a more sustainable product model.

The results indicate that pyrotechnics generate comparable and even less harmful noise and environmental impacts than other established emitters in society. Moreover, different alternative compositions such as nitrogen-rich compounds (nitrocellulose) or the addition of inert materials were evaluated and their environmental benefits and technical feasibility were assessed. The evaluation of these compositions indicates a reduction in emissions of gases that directly influence the greenhouse effect, such as CO₂, and other pollutants. In addition, tests carried out with inert materials demonstrate their possible implementation in compositions intended for the bursting effect, reducing not only the sensitivity to ignition and the risk of explosions, but also the sound impact produced. In contrast, compositions such as nitrocellulose require further testing, evaluating different properties such as nitrogen content, in order to verify their implementation as a propellant in aerial articles.

This sustainability-focused approach can improve public perception of the sector, reduce its environmental footprint and improve safety without compromising the quality of performances.

Resumen

La pirotecnia como signo de celebración es una práctica común en multitud de países desde hace miles de años, siendo valorada por su capacidad para crear espectáculos visuales y sonoros únicos. Además, su uso se encuentra asociado a otros ámbitos como la señalización marítima o terrestre, operaciones militares, pesca, etc. Durante los últimos años, el sector pirotécnico se enfrenta a diversas dificultades sociales, las cuales necesita afrontar para continuar coexistiendo con el resto de la sociedad. Estos desafíos deben impulsar al sector hacia un modelo más sostenible, en línea con los Objetivos de Desarrollo Sostenible (ODS) contenidos en la Agenda 2030.

Las críticas al sector se focalizan en las emisiones atmosféricas liberadas durante su uso y en el impacto sonoro que se genera en ambientes urbanos, afectando a ciertos colectivos, especialmente a animales domésticos. Este estudio plantea una evaluación exhaustiva de todos los procesos que engloban al sector pirotécnico y a los fuegos artificiales, analizando en profundidad los aspectos más relevantes y de actualidad, con el objetivo de proponer herramientas al sector para su defensa y sobre las que trabajar en un modelo de producto más sostenible.

Los resultados indican que la pirotecnia genera unos impactos sonoros y medioambientales comparables e incluso menos perjudiciales que otros emisores afianzados en la sociedad. Además, se valoraron diferentes composiciones alternativas como compuestos ricos en nitrógeno (nitrocelulosa) o la adición de inertes y se evaluaron sus beneficios medioambientales y su viabilidad técnica. La evaluación de dichas composiciones indica una reducción en las emisiones de gases que influyen directamente al efecto invernadero, como el CO₂, y otros contaminantes. Además, los ensayos realizados con materiales inertes demuestran su posible implementación en composiciones destinadas al efecto de estallido, reduciendo además de la sensibilidad a la ignición y el riesgo de explosiones, el impacto sonoro producido. En cambio, composiciones como la nitrocelulosa requieren ser sometidas a una mayor cantidad de ensayos, evaluando diferentes propiedades como su contenido en nitrógeno, para poder verificar su implementación como propulsor en artículos aéreos.

Este enfoque centrado en la sostenibilidad puede mejorar la percepción pública del sector, reducir su huella ambiental y mejorar la seguridad sin comprometer la calidad de los espectáculos.

List of publications

León, D., Castells, B., Amez, I., Casín, J., & García-Torrent, J. (2023). Experimental Quantification of Fire Damage Inside Pyrotechnic Stores. *Applied Sciences*, 13(10), 6181. <https://doi.org/10.3390/app13106181>

León, D., Amez, I., Radojević, M., Manić, N., Stojiljković, D., Milivojević, A., ... & Castells, B. (2024). Emissions and Fire Risk Assessment of Nitrocellulose as a Sustainable Alternative in Pyrotechnic Compositions. *Fire*, 7(8), 265. <https://doi.org/10.3390/fire7080265>

León, D., Amez, I., Paredes, R., Pantelakis, D. & Castells, B. Sustainable Alternatives to Reduce Emissions and Sound Pressure Level of Flash Powder. [Pending to be published]

Table of Contents

<i>Acknowledgement</i>	<i>iii</i>
<i>Abstract</i>	<i>v</i>
<i>Resumen</i>	<i>vi</i>
<i>List of publications</i>	<i>vii</i>
<i>List of Figures</i>	<i>xi</i>
<i>List of Tables</i>	<i>xv</i>
1. Introduction	1
1.1. Adaptation to sustainable development	1
1.1.1. Agenda 2030	1
1.2. Pyrotechnic industry	3
1.2.1. Chemistry of pyrotechnics	3
1.2.2. Current situation in the pyrotechnic sector	7
1.2.3. Current legislation	9
1.2.4. Challenges	13
1.2.5. Alternatives to the sector	15
1.3. Environmental impact	16
1.3.1. Atmospheric impact	16
1.3.2. Sustainability	21
1.4. Sound impact	22
1.4.1. Animal welfare	22
1.4.2. Animal ear	23
1.4.3. Sound effects of pyrotechnics	25
1.4.4. Current situation	27
1.5. Industrial safety	27
2. Background	31
3. Objectives of the research	33
4. Materials and methods	35
4.1. Pyrotechnic sector operations	35
4.1.1. Materials and manufacturing process analysis	35
4.1.2. Life Cycle Analysis of pyrotechnic products	38
4.2. Assessment of atmospheric emissions	44
4.2.1. Theoretical analysis of national and international pyrotechnic shows	44
4.2.2. Emissions produced by socially accepted emitters	49
4.3. Analysis of the effect of sound on animal welfare	52
4.3.1. Sound attenuation. Articles for sale to the public	52
4.3.2. Influence of climatic conditions	58

4.3.3.	Sound attenuation. Professional fireworks shows	59
4.3.4.	Sound comparison with everyday emitters	66
4.4.	Alternative compositions	68
4.4.1.	Theoretical emissions comparison between nitrocellulose and traditional powder.....	68
4.4.2.	Experimental emissions test with nitrocellulose and inert materials	69
4.4.3.	Sound pressure level tests of flash powder alternatives.....	74
4.4.4.	Explosion pressure analysis with nitrocellulose and inert materials.....	75
4.4.5.	Thermogravimetric Analysis (TGA) and Mass Spectrometry (MS) comparison between nitrocellulose and black powder	76
4.4.6.	Comparative risk analysis between nitrocellulose and black powder	77
5.	Results and discussion	79
5.1.	Environmental impact of pyrotechnic products	79
5.1.1.	Results of the Life Cycle Assessment	79
5.1.2.	Global interpretation.....	87
5.2.	Theoretical emissions	88
5.2.1.	Fireworks professional shows.....	88
5.2.2.	Comparison with everyday atmospheric emitters	91
5.3.	Sound spectrum of pyrotechnic articles	94
5.3.1.	Theoretical and practical results of sound attenuation	94
5.3.2.	Influence of climatic factors	107
5.3.3.	Comparison with everyday sound emitters.....	109
5.4.	Sustainability and technical feasibility of alternative compositions.....	113
5.4.1.	Evaluation of propellant and perchlorate substitutes	113
5.4.2.	Evaluation of burst powder substitutes	123
5.4.3.	Fire risk assessment	130
6.	Conclusions	135
7.	Future research lines	139
	References	141
	Annex A: Operations and processes of the pyrotechnic sector.	161
	Annex B: Sound test specifications.	167
	Annex C: LCA detailed results.	171
	Annex D: Sound tests detailed results.....	179

List of Figures

Figure 1.1. Basic principle of combustion reactions.....	4
Figure 1.2. Pyrotechnic sector in Spain [23].....	7
Figure 1.3. World map of pyrotechnic material trade in 2019 [25].....	9
Figure 1.4. Decomposition clock of materials used in pyrotechnics.....	14
Figure 1.5. Main pollutants in the pyrotechnic sector in Spain in 2021. a) Atmospheric emissions. b) Direct emissions to water. c) Indirect emissions to water [52].	16
Figure 1.6. Hourly average PM _{2.5} concentrations ($\mu\text{g}/\text{m}^3$) averaged between monitoring locations during Independence Day and control days [55].	17
Figure 1.7. Daily concentrations of the main pyrotechnic pollutants in Girona (Spain) [61].	18
Figure 1.8. a) Fountain. b) Table bomb. c) Mine. [80].	20
Figure 1.9. Five Domains Model [93].	23
Figure 1.10. Sound level attenuation with distance.....	25
4.1. Operations and processes in the life of pyrotechnic devices.	35
Figure 4.2. Simplified flow diagram of the Life-cycle model.	39
Figure 4.3. Flash banger design.....	40
Figure 4.4. Pyrotechnic shell design.....	41
Figure 4.5. Location of firing point PD1 and the corresponding measuring points used in the experimental study. Aerial photo from Google Maps.	55
Figure 4.6. Location of firing point PD2 and the corresponding measuring point used in the experimental study. Aerial photo from Google Maps	56
Figure 4.7. Photographs from the measurement points. Top left: 50 m. Top right: 100 m. Bottom left: 200 m. Bottom right: 50 m inside the building.	57
Figure 4.8. Verification of the sound level meter by sound calibrator.	61
Figure 4.9. Relationship between frequency weightings A and C [155].....	62
Figure 4.10. Firing point and measuring equipment location at Ajalvir fireworks show.	63
Figure 4.11. Photographs of the locations of the measuring equipment at the fireworks show in Ajalvir. Left: sound level meter. Right: dosimeter 3.	64
Figure 4.12. Firing point and measuring equipment location at the Mascletà.	65

Figure 4.13. Photographs of the locations of the measuring equipment at the Mascletà. Top: Dosimeter 1. Bottom: Sound level meter.	66
Figure 4.14. Emerson XStreamIR mobile tower gas analyser.	70
Figure 4.15. Sound pressure level test setup.	74
Figure 4.16. Design of explosion pressure analysis tests.	75
Figure 4.17. NETZSCH QMS403DAëolos® quadrupole mass spectrometer coupled to the NETZSCH STA449F5 Jupiter® [160], [161].	77
Figure 4.18. Diagram of the sub-processes assessed in the HAZOP risk analysis.	78
Figure 5.1. Network diagram of the LCA for flash banger (FB).	82
Figure 5.2. Network diagram of the LCA for pyrotechnic shells. a) Cardboard shell (CPS). b) Plastic shell (PPS).	85
Figure 5.3. Carbon footprint of common products and activities [168].	87
Figure 5.4. Comparison of CO ₂ emissions released in different scenarios.	93
Figure 5.5. Experimental results of sound attenuation for articles to the general public.	97
Figure 5.6. Distance between the bursting point of the aerial article and the receiver.	98
Figure 5.7. Sound spectrum recorded during the fireworks display in Ajalvir.	101
Figure 5.8. Sound spectrum recorded during the fireworks display of La Mascletà.	103
Figure 5.9. Comparison between experimental and theoretical sound pressure level of battery of shot tubes category F3.	104
Figure 5.10. Comparison between experimental and theoretical sound pressure level of flash banger category F3.	105
Figure 5.11. CO concentration (ppm) measured in Fountains comparison.	117
Figure 5.12. CO ₂ concentration (% vol.) measured in Fountains comparison.	117
Figure 5.13. Thermogravimetric curves for nitrocellulose (using argon atmosphere) and black powder (using helium atmosphere). a) TG and DTG curves. b) DTA curves.	119
Figure 5.14. a) Mass spectrometry results for amu 12, 14, 16, 17, 28, 44; b) Mass spectrometry results for amu 26, 27, 30, 32 and 46.	121
Figure 5.15. CO and CO ₂ emissions for flash powder alternatives.	124
Figure 5.16. Sound pressure level generated by flash powder alternatives.	126
Figure 5.17. Explosion pressure curve generated by a banger under study.	127

Figure 5.18. a) Distribution of risk on the causes analysed. b) risk distribution according to the sub-process studied.....	134
Figure A.1. Detailed flow diagram of Flash Banger (FB) functional unit.	163
Figure A.2. Detailed flow diagram of Pyrotechnic Shells functional units.	164

List of Tables

Table 1.1. Main oxidising agents in pyrotechnics [18], [19].	5
Table 1.2. Responsible elements for colour in pyrotechnic reactions.	6
Table 1.3. Air quality levels [33], [34].	13
Table 1.4. Audible spectrum of different species [102], [103], [104], [105].	24
Table 4.1. Pyrotechnic reactions that take place inside the articles [18], [19].	38
Table 4.2. Functional units for LCA.	41
Table 4.3. Quantities of material per functional unit.	42
Table 4.4. Transport distances of raw materials.	43
Table 4.5. Theoretical emissions released by functional units.	44
Table 4.6. Estimated distribution of the pyrotechnics devices used during the festivities of Villaviciosa de Odón.	45
Table 4.7. NEC per shell studied at the show in Villaviciosa de Odón.	46
Table 4.8. NEC per comet studied at the show in Villaviciosa de Odón.	46
Table 4.9. NEC per roman candle studied at the show in Villaviciosa de Odón.	47
Table 4.10. NEC per mine studied at the show in Villaviciosa de Odón.	47
Table 4.11. Detailed studied design of the Macy's Independence Day show.	49
Table 4.12. Emission limits according to standard EURO 6 for private cars [146].	50
Table 4.13. Average carbon dioxide (CO ₂) emissions in commercial aircraft depending on the route distance [150].	51
Table 4.14. Samples tested for experimental analysis of sound attenuation.	53
Table 4.15. Equipment for sound attenuation tests. Articles for sale to the public.	54
Table 4.16. Equipment for sound attenuation tests.	58
Table 4.17. Tested samples for the analysis of climatic influence on sound attenuation.	59
Table 4.18. Equipment for sound attenuation tests. Ajalvir fireworks show.	60
Table 4.19. Equipment for sound attenuation tests. La Mascletá.	60
Table 4.20. Flash bangers tested in comparison to usual emitters.	67
Table 4.21. Fountains samples for the emissions tests.	71

Table 4.22. Composition of flash powder alternatives tested.....	72
Table 4.23. Flash bangers used as containers.	73
Table 4.24. NNEC compositions for the tests.....	73
Table 4.25. Definition of nodes for the HAZOP analysis.	78
Table 5.1. LCA results for the main impact categories.	80
Table 5.2. Emissions released during La Pólvora of Villaviciosa de Odón (Spain).	89
Table 5.3. Emissions released during Macy’s Fireworks show (United States).	89
Table 5.4. CO and CO ₂ emissions released by daily vehicle traffic on the M-30 ring road. ...	91
Table 5.5. CO ₂ emissions released by different commercial flights.....	92
Table 5.6. Comparison of experimental sound attenuation in ground and aerial devices. ...	99
Table 5.7. Maximum sound level recorded at the professional show in Ajalvir.....	99
Table 5.8. Maximum sound level recorded at the professional show of La Mascletá.	102
Table 5.9. Comparison between real and theoretical attenuation in Ajalvir’s show.	106
Table 5.10. Comparison between real and theoretical attenuation in La Mascletá show. .	107
Table 5.11. Influence of climatic conditions on Fountains.....	108
Table 5.12. Maximum sound values recorded in the comparison of everyday emitters and pyrotechnic articles.	109
Table 5.13. Frequency range generated by everyday emitters and pyrotechnic articles....	111
Table 5.14. Theoretical emissions comparative between nitrocellulose and potassium perchlorate Fountains.	113
Table 5.15. Theoretical emissions comparative between nitrocellulose and black powder Table bombs/Mines.	114
Table 5.16. Theoretical emissions comparison of nitrocellulose and black powder as propellants in a professional show assuming 9,732 kg of NEC.	114
Table 5.17. CO and CO ₂ concentrations measured in the comparison of F1 Fountains	116
Table 5.18. CO and CO ₂ concentrations for each gram of sample.	118
Table 5.19. Maximum explosion pressure registered (kPa).	128
Table 5.20. Detailed risk analysis by HAZOP methodology results.....	130
Table A.1. Hazard Divisions of Class 1 of ADR hazardous materials and articles [137].	162
Table A.2. Pyrotechnical reactions for the production of visual colour effects [18], [19]. ..	165

1. Introduction

1.1. Adaptation to sustainable development

Sustainable development refers to the relationship between achieving human development goals while not affecting the natural systems such as resources and ecosystems on which society and economy depend, i.e. the possibility of meeting present needs without influencing the possibility of meeting future needs [1].

Many government authorities are committed to create a more sustainable future through various agreements and strategies that will foster industry transformation. 2030 Agenda for Sustainable Development stands out among the most important policy frameworks [2], [3]. This action plan, endorsed by the UN and accepted by its member states during the Summit in New York in September 2015, details 17 Sustainable Development Goals (SDGs) and 169 targets, covering social, economic and environmental areas. On the other hand, the European Green Pact also pursues an ambitious goal: to achieve climate neutrality in Europe by 2050, focusing on essential aspects such as clean energy, sustainable mobility, energy efficiency and waste management [4].

1.1.1. Agenda 2030

The 2030 Agenda, whose plan is to achieve the SDGs by 2030 under the slogan ‘Leave no one behind’, can be understood as the evolution of the Millennium Development Goals (MDGs) elaborated in the year 2000, with a vision of sustainability and a much broader scope, complementing the 8 goals that the MDGs included [5]. The 2030 Agenda implies a common commitment, but each country sets out specific challenges to work on in its own Action Plan, which is subject to a Voluntary National Review.

The growing recognition of the need to minimize environmental impact across all industries extends to the pyrotechnic sector as well [6], [7]. The adoption of sustainable policies by pyrotechnic companies aimed at aligning pyrotechnics and SDGs can have multiple benefits. Firstly, this would allow companies to identify opportunities for innovation and growth, and reduce the risk of negative impacts on the environment, society and the economy. For example, the implementation of these policies, can help reduce the environmental impact of pyrotechnics by imising

emissions and their carbon footprint [8], [9]. In addition, the adoption of sustainable practices can help to improve safety in the manufacture, storage and transport of products [10], [11].

Alignment with the SDGs would therefore allow companies to enhance reputation and branding, as pyrotechnic companies can demonstrate their commitment to sustainability and social responsibility. This increases customer loyalty and attracts new customers and talent looking to support responsible companies, and can open up new market opportunities, innovation and growth for companies in the sector.

Among the SDGs contained in the 2030 Agenda, the ones that are most directly related to the pyrotechnics sector are the following:

SDG 7 - Affordable and clean energy



The pyrotechnics industry is a sector that is advancing at the same pace as the rest of society and as a result, processes are becoming increasingly mechanised. The sector needs to implement or improve energy efficiency, investing in research and development to create more sustainable products, and adopt as far as possible the use of renewable energies, since, according to UN data, energy production accounts for approximately 60% of greenhouse gas emissions [12]. In the same way, implementing automation systems in processes and promoting sustainable practices in the supply chain can optimise the resources employed [13].

SDG 9 - Industry, innovation, infrastructure



In recent years, the pyrotechnics industry has been evolving, modernising its processes and infrastructures and continuing to innovate in its work. This evolution must be oriented in a sustainable way, both in the processes and in the final products. In this way, making products with a low environmental impact by manufacturing them from biodegradable or easily recyclable materials can be an important step forward.

SDG 13 – Climate action



In recent years, climate change has been one of the biggest global problems, with record levels of carbon dioxide (CO₂) and other greenhouse gases in the atmosphere in 2019 [14]. Temperatures around the globe have risen, as have melting ice and sea levels, natural disasters are becoming more common, and several species of plants and animals have become extinct. Pyrotechnics, like the rest of society, must face this problem. The manufacture of more sustainable products, the use of renewable energies or promoting the recycling of the waste generated are some possible improvements [13].

SDG 15 – Life on land



Much of the biodiversity present in terrestrial ecosystems has been significantly affected in recent decades. Mainly due to climate change, the health of different species is worsening as new animal epidemics emerge [15]. Pyrotechnic industry must therefore address the above objective in order to try, in addition to reducing climate change, to avoid influencing the special animal and plant species present in the various ecosystems. Pyrotechnics should promote good practice guidelines, including aspects related to the protection of animals and species affected by fireworks displays.

1.2. Pyrotechnic industry

1.2.1. Chemistry of pyrotechnics

Fireworks are known as part of numerous cultural celebrations around the world. Pyrotechnics is defined as the technique for the preparation and handling of devices designed to produce combustion inside the device, resulting in reactions that trigger smoke, sparks, flames or controlled explosive reactions, depending on the type of composition used [16]. These chemical reactions that take place are oxidation-reduction (redox) reactions, where the reactants undergo changes in their oxidation states, i.e. there is a transfer of electrons between the reaction agents. These transfers produce light and heat (exothermic reactions) [17].

For this type of reaction to occur, four basic elements are necessary to form the fire tetrahedron as shown in Figure 1.1:

- Fuel: a flammable mixture that makes up the pyrotechnic article.
- Oxidising agent: a compound which is reduced (oxygen).
- Heat: activation energy of the fuel.
- Chain reaction: the process that allows the fuel-mixture reaction to progress.

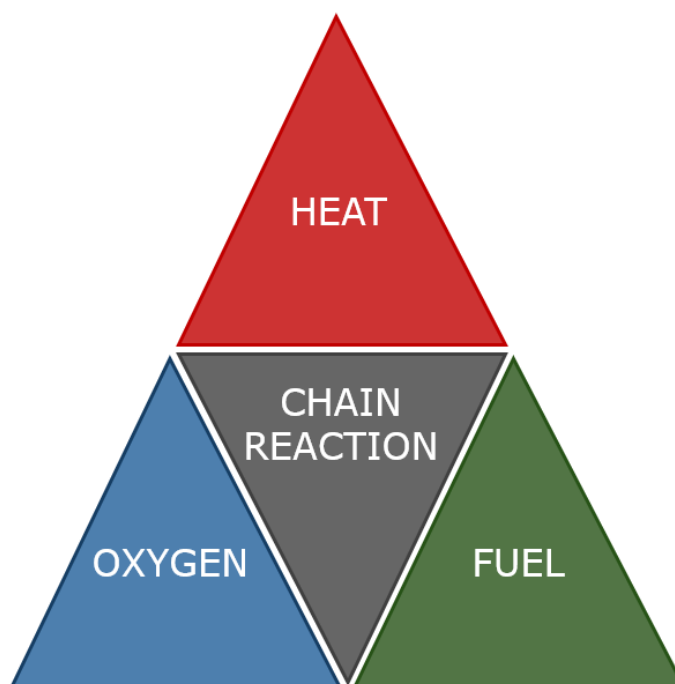


Figure 1.1. Basic principle of combustion reactions.

Base substances

The base substances that make up any pyrotechnic reaction are shown below:

- Oxidising agents, also called oxidisers, are the elements responsible for generating the oxygen necessary to produce the combustion reaction of the pyrotechnic mixture. They are basically metal salts consisting of anions with a metal cation. The main different types of oxidants that are known are shown in Table 1.1.

Table 1.1. Main oxidising agents in pyrotechnics [18], [19].

Oxidising agents	Nitrates	Chlorates	Perchlorates
Anions	NO_3^-	ClO_3^-	ClO_4^-
Decomposition reactions	$2\text{KNO}_3 (\text{s}) \rightarrow 2\text{KNO}_2 (\text{s}) + \text{O}_2 (\text{g})$	$2\text{KClO}_3 (\text{s}) \rightarrow 2\text{KCl} (\text{s}) + 3\text{O}_2 (\text{g})$	$\text{KClO}_4 (\text{s}) \rightarrow \text{KCl}_2 (\text{s}) + 2\text{O}_2 (\text{g})$
Observations	Give up only 1/3 of the oxygen content	Give up all the oxygen content in an explosive reaction	Contain more oxygen and give up all of it. Less likely to explode

- Reducing agents represent the fuel of combustion and react with the oxygen released by oxidisers to produce large quantities of gas at high temperature. Among the most common reducing agents used in pyrotechnics are sulphur and carbon which react with oxygen to form sulphur dioxide (SO_2) and carbon dioxide (CO_2).
- Ignition agents are the means of ignition of pyrotechnic articles which provide the heat and activation energy necessary for the reaction to start and thus achieve the desired effects with each type of firework.

In addition to these basic substances, other additives that modify the combustion characteristics are added to the pyrotechnic mixtures [19]. These are, for example, regulating substances, which can accelerate or slow down the speed of the reaction, depending on the type of element and its particle size, whereby confined mixtures experience an increase in the speed of the reaction due to an increase in pressure, which can trigger an explosion, or binding substances, which give the pyrotechnic composition a strong cohesion that consolidates the mixture, stability during storage and resistance to any type of solvent, including dextrin or Arabic gum.

Main pyrotechnic compositions

Black powder is one of the most commonly used pyrotechnic mixtures. It is made up of potassium nitrate (KNO_3), sulphur (S) and charcoal (C), with different percentages of each depending on the effect to be achieved [20]. This composition can be used as lift powder for aerial fireworks, opening charge in fireworks with subsequent sound or visual effects, ignition fuses, in spark-generating compositions or in compositions used to produce the characteristic sound effects of pyrotechnic shows such as whistles, buzzers, etc.

Flash powder, composed by potassium perchlorate and aluminium or magnesium ($\text{KClO}_4 + \text{Al/Mg}$), is responsible for producing the burst effect in pyrotechnic articles, reacting at a temperature of approximately 750°C [18].

On the other hand, colour-producing compositions are responsible for the most important effect of pyrotechnic articles. These compositions can produce coloured luminous photons thanks to the phenomenon of luminescence, which consists of the electrons of the metal cations producing the colour becoming charged and experiencing a state of excitation, due to the large amount of energy released in the combustion reaction. In this way, they rise to higher energy levels where they are very unstable and tend to return quickly to their fundamental energy level, the one they occupied before the excitation. In order to return to their fundamental state, they must emit the excess energy they have acquired, and it is in this emission that the excess energy is absorbed in the form of photons, which are responsible for the coloured light produced. Depending on the wavelength of the energy released, the colours produced will vary within the visible part of the spectrum, being closer to blue colours the more energetic the excitation of the electron and closer to red colours the less energetic it is [18], [21]. Table 1.2 shows the colours obtained depending on the salts used in the reaction.

Table 1.2. Responsible elements for colour in pyrotechnic reactions.

Colour	Chemical element
Yellow	Sodium salts ($\text{Na}_2\text{C}_2\text{O}_4$, $\text{NaNO}_3\dots$)
Red	Strontium salts (SrCO_3 , $\text{Sr}(\text{NO}_3)_2\dots$)
Blue	Copper salts or oxides (CuO , $\text{CuCl}\dots$)
Green	Barium salts (BaCl_2 , $\text{Ba}(\text{NO}_3)_2\dots$)
White	Aluminium and Magnesium salts (Al , Mg)
Gold	Iron (Fe)
Purple	Mixture of Strontium and Copper salts (SrCO_3 y $\text{CuCO}_3\dots$)
Orange	Calcium salts (CaCO_3 , $\text{CaCl}_2\dots$)
Silver	Titanium (Ti)

1.2.2. Current situation in the pyrotechnic sector

Pyrotechnic sector comprises a large number of workers and companies both nationally and internationally. It is a trade that can be defined as semi-automated and handcrafted, where practically all the tasks are carried out in a traditional way.

This industry is subject to significant risks due to the handling of potentially hazardous substances with a high explosive index, which is why basic recommendations on occupational risk prevention are perfectly defined in order to minimise accidents and their consequences.

Spanish sector

Fireworks are fundamental to many Spanish festivities. The sector is made up of large, medium-sized and small companies that carry out their activity in the fields of manufacturing, assembly and firing of pyrotechnic shows and the commercialisation of pyrotechnic articles. Many are small family businesses that have passed on this work and tradition from generation to generation [22].

According to the Spanish Pyrotechnics Association (Asociación Española de la Pirotecnia - AEPIRO), there are 125 manufacturing workshops, 100 fixed points of sale and around 500 temporary points of sale in Spain, due to the increase in demand during the festive season [23]. Figure 1.2 shows the distribution of these outlets.



Figure 1.2. Pyrotechnic sector in Spain [23].

As can be seen on the map, the presence on the eastern coast is more significant. It stands out in the Valencian Community with its well-known festival of Las Fallas.

These workshops and warehouses make up a total of more than 45 national pyrotechnic companies that carry out their activity in the fields of manufacture, assembly, firing of pyrotechnic shows and marketing of pyrotechnic articles. The companies in the sector employ more than 1,000 people permanently and directly, and 2,200 in the high season, reaching a turnover value in 2022 of approximately 115 million euros [24]. In addition, the indirect and induced employment impact of the sector amounts to some 50,000 jobs. Moreover, the presence of women in the pyrotechnics sector (36%) is significantly higher than in the Spanish industrial sector (24.6%) [24].

International sector

Pyrotechnics also represent an important industry in other countries, some of them mainly dedicated to manufacturing and exporting and others where fireworks are mostly imported from the former. According to the Observatory of Economic Complexity (OEC), pyrotechnic articles were traded in 2019 for a total of 1,370 M\$ [25]. Data from 2019 have been analysed because, since 2020, the COVID-19 pandemic generated significant alterations in several economic and social variables.

In the case of manufacturers and exporters, the main producer is China. This country has the largest pyrotechnics industry in the world, with an estimated 2,500 manufacturing workshops employing a multitude of workers. The difference that makes the Chinese product so competent is the low cost of labour, which results in a much cheaper product compared to its competitors. This makes it increase significantly in terms of exports, reaching 843 M\$ in 2019, or 62% of the total export of pyrotechnic articles.

Other major exporters of these pyrotechnic articles are France, Thailand and Spain, although the latter accounting for only 1.3% in 2019.

In terms of importing countries, USA tops the list by a wide margin. Fireworks are one of the main activities on United States Independence Day and are one of the reasons for the large quantities of imported pyrotechnics. According to OEC data, a total of \$368 million worth of pyrotechnics were imported into the United States in 2019, 95% of which originated from Chinese.

Following USA is Germany, with 141 M\$ of imported pyrotechnic material, and in third place in 2019 was the Netherlands with 46 M\$ of imported pyrotechnic material.

A world map showing the difference between exported and imported pyrotechnic material during 2019 according to data obtained from the Observatory of Economic Complexity (OEC) can be seen in Figure 1.3.

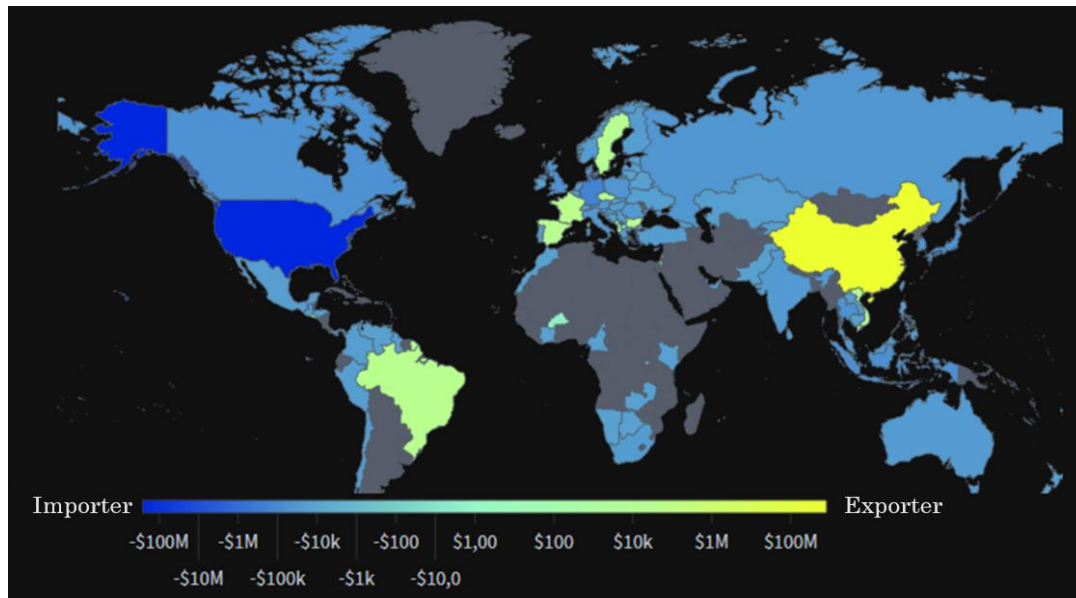


Figure 1.3. World map of pyrotechnic material trade in 2019 [25].

1.2.3. Current legislation

At the national level in Spain, the regulations governing the pyrotechnics sector are the Royal Decree (RD) 989/2015, of 30 October, approving the Regulation on pyrotechnic articles and cartridges [26]. The approval of the aforementioned regulation was an essential milestone as it exempted pyrotechnics and cartridges from the scope of application of RD 130/2017, of 24 February, which approved the regulation of explosives, separating both matters into two different regulations, whose justification is based on the fact that the technical requirements in the field of safety do not have the same degree of complexity and exigency.

In addition, the RD incorporates several European directives, being particularly relevant Directive 2013/29/EU of the European Parliament and of the Council of 12 June 2013 on the harmonization of the laws of the Member States relating to the placing on the market of pyrotechnic articles [27], which seeks, among other

things, to “ensure a high level of protection of human health and safety and the protection of consumers and professional end users”.

In addition, the different European regulations, drawn up by the Technical Committee CTN-UNE 22 Mining and explosives, and mandatory standards required to obtain the CE marking are as follows:

- EN 15947:2022. Pyrotechnic articles. Fireworks, Categories F1, F2 and F3: Fireworks falling within this division are those articles which are accessible to consumers without special knowledge. They are divided into 3 categories according to their hazardous nature:
 - Category F1: very low hazard fireworks with an almost negligible noise level intended for use in confined areas including residential buildings.
 - Category F2: fireworks of low hazard and low noise effect intended for use in outdoor confined areas.
 - Category F3: fireworks which are of medium hazard and have a sound level which is not harmful to human health and are intended for use in large outdoor areas.
- EN 16261:2012. Pyrotechnic articles. Fireworks, Categories F4: Fireworks falling into this category are highly dangerous fireworks intended for use by experts only, i.e. pyrotechnic articles for professional use and therefore not accessible to consumers.
- EN 16256:2012. Pyrotechnic articles. Theatrical pyrotechnic articles: This category includes fireworks whose use is intended for, and restricted to, theatres. They are subdivided into two categories according to their dangerousness and the users authorised to handle them:
 - Category T1: within this category are pyrotechnic articles intended for theatrical use which present a low hazard. Accessible to the general public.
 - Category T2: this category includes pyrotechnic articles intended for theatrical use which do not meet any of the construction or performance requirements of the regulations for category T1. They are accessible only to persons with specialist knowledge.

- EN 16263:2015. Pyrotechnic articles. Other pyrotechnic articles: This category includes those which are not covered by fireworks or theatrical articles, and which are not covered as ignition systems. These articles are subdivided into two categories according to their hazardousness:
 - Category P1: they meet the requirements applicable to this category.
 - Category P2: pyrotechnic articles which present a high hazard and which do not meet the construction and performance requirements of category P1. Their use is restricted to experts.
- EN 16265:2015. Pyrotechnic articles. Other pyrotechnic articles. Ignition devices: This category includes pyrotechnic articles used as ignition devices. Again, they can be divided into categories P1 or P2, as indicated above.

These European regulations establish, among other things, the maximum sound pressure level, the allowed compositions, the maximum Net Explosive Content (NEC) and the safety distances for each of the categories and articles mentioned.

From the current Spanish legislation on pyrotechnics, it can be extracted that human safety is a priority and that all areas and elements (manufacture and design, storage, transport, sale, use, etc.) are subject to important controls and restrictions to guarantee as much as possible the safety of people. However, at present, animal welfare is not directly covered by the regulations because, although it is true that some measures indirectly protect the animal sector, there is no specific, proper and well-designed regulatory framework at the national level.

There are different regulations worldwide that take into account the effect of noise produced by pyrotechnic articles on pets and livestock by establishing a distance where animals should be placed in a pyrotechnic show, the maximum noise level produced by an article for sale to the public or limitations on its use.

In Australia, the Northern Territory Government, the only part of Australia where the marketing and use of pyrotechnic articles is legal, uses as a measurement value for pyrotechnic articles LCF_{max} whose limit (measured with a sound level meter) is 115 dB [28].

Tasmania permits fireworks displays for the general public, under certain circumstances and by permit [29]: an application must be made at least 21 days before the intended display, and notice must be given to police and fire departments, site owners and managers, and any neighbours within a 1-km radius.

The permit carries restrictions on time, duration of use, quantity of fireworks, and supervision. It also ensures minimum distances from spectators and private buildings such as schools and churches.

One of the countries where most progress has been made in establishing requirements for the use of pyrotechnic articles and in establishing minimum safety distances so that pets and livestock suffer as little as possible from the use of these products is New Zealand.

In New Zealand the use of pyrotechnics is regulated by two standards, Health and Safety at Work (Hazardous Substances) Regulations 2017 (LI 2017/131) [30] and Code of practice for outdoor pyrotechnic displays HSNO COP 30 [31], which, in both regulations set a minimum 200 m safety distance for captive animals and livestock at fireworks displays.

In addition to New Zealand, another of the pioneering countries to include provisions in its regulations to ensure the safe use of fireworks and that such fireworks do not cause harm, distress or injury is Scotland. In 2022, the Fireworks and Pyrotechnic Articles (Scotland) Act 2022 [32] was published. This Act restricts the sale of certain fireworks and pyrotechnic articles to persons under 18 years of age, limits the supply and use of certain fireworks to specific periods of time, prohibits the possession of pyrotechnic articles in certain circumstances and for related purposes and provides power to local authorities to designate fireworks control areas where the use of fireworks is not permitted.

Legislation, along with other types of regulations, becomes a crucial element in managing the conflict between pyrotechnic noise and animal welfare.

On the other hand, pyrotechnic activity can contribute to the emission of air pollutants that can affect air quality. The World Health Organisation (WHO) updated its Global Air Quality Guidelines in September 2021, setting new levels for a number of pollutants with the aim of protecting public health. These values provide global guidance on thresholds and limits for key air pollutants that pose health risks. For its part, the European Union has established a legislative framework to ensure cleaner air and protect the health of its citizens. Directive (EU) 2024/2881 of 23 October 2024 updates ambient air quality standards, aligning them more closely with WHO guidelines. Table 1.3 indicates the air quality levels set by both standards.

Table 1.3. Air quality levels [33], [34].

Standard	Pollutant	Established levels
WHO	PM2.5	Annual: 5 $\mu\text{g}/\text{m}^3$
		Daily: 15 $\mu\text{g}/\text{m}^3$
	PM10	Annual: 15 $\mu\text{g}/\text{m}^3$
		Daily: 45 $\mu\text{g}/\text{m}^3$
	NO ₂	Annual: 10 $\mu\text{g}/\text{m}^3$
		Daily: 25 $\mu\text{g}/\text{m}^3$
EU	SO ₂	Daily: 40 $\mu\text{g}/\text{m}^3$
	CO	Daily: 4 mg/m^3
	PM2.5	Annual: 10 $\mu\text{g}/\text{m}^3$
		Daily: 25 $\mu\text{g}/\text{m}^3$
	PM10	Annual: 20 $\mu\text{g}/\text{m}^3$
		Daily: 45 $\mu\text{g}/\text{m}^3$
	NO ₂	Annual: 20 $\mu\text{g}/\text{m}^3$
		Daily: 200 $\mu\text{g}/\text{m}^3$
	SO ₂	Annual: 20 $\mu\text{g}/\text{m}^3$
		Daily: 50 $\mu\text{g}/\text{m}^3$
		Hourly: 350 $\mu\text{g}/\text{m}^3$
	CO	Daily: 4 mg/m^3

1.2.4. Challenges

In recent years, the pyrotechnics industry has been experiencing great social difficulties and is faced with the need to adapt in order to continue to coexist alongside the rest of society.

Several difficulties come from the critics of society due to the environmental pollution produced by pyrotechnic devices, as part of the products generated in the combustion reactions inside the devices are emissions that may produce environmental pollution [35]. The main combustion products are mainly composed by sulphur dioxide (SO₂), carbon dioxide (CO₂), carbon monoxide (CO), metallic particles suspended in the atmosphere and solid particles such as soot [36], [37]. Besides contributing to the climate change by releasing greenhouse gases (GHG) emissions, most of the particles suspended in the smoke produced by pyrotechnic devices are fine particulate matter PM2.5, which are inhalable suspended particles whose size is lower than 2.5 micrometres and could affect humans [38], [39], [40], [41]. Moreover, there is evidence that the ClO₄⁻ ion may affect the thyroid gland,

as it makes iodide absorption difficult and may trigger hypothyroidism [42], [43], [44]. In addition, groundwater contamination via the soil from rainfall, related to the production, handling and use of perchlorate, harms micro-organisms and aquatic fauna [45], [46], [47].

The solid waste from the containers that include the pyrotechnic mixtures are usually made of plastic materials and in some cases metals, such as aluminium, although as pyrotechnics develop, they are being replaced by paper and paper derivatives such as cardboard, due to the high decomposition time of the former [48], as shown Figure 1.4.

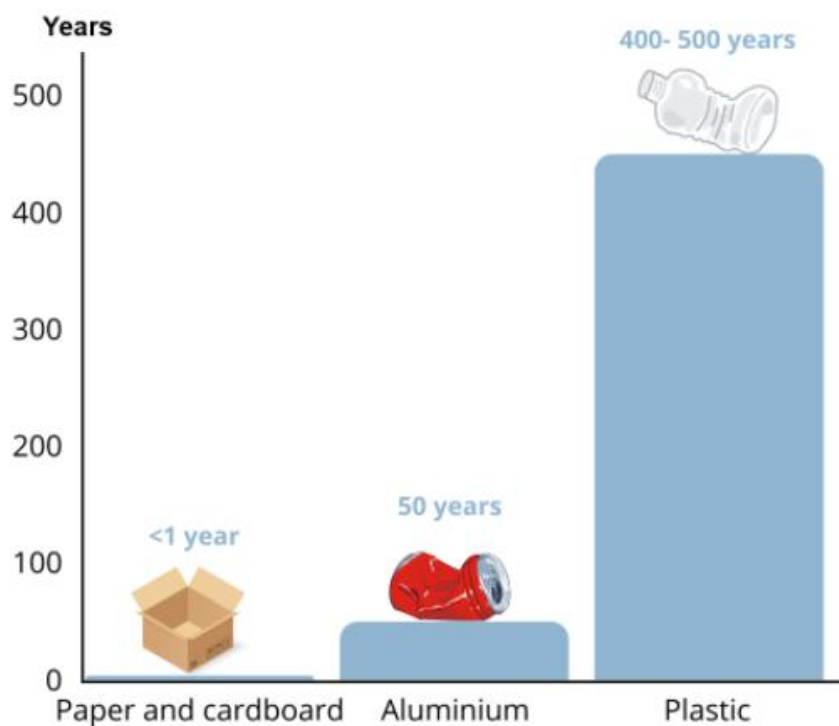


Figure 1.4. Decomposition clock of materials used in pyrotechnics.

The number of pets in urban areas has increased exponentially in recent years. One of the social concerns associated with this comes from the effect of pyrotechnic noise on these animals, due to their close exposure, as fireworks displays are often also set off in the urban areas where they live. These anthropogenic sounds sometimes negatively affect animal welfare, producing stress, fear, anxiety, phobia, hearing damage and/or altering important behaviours, according to evidence reported by animal carers and professional animal associations [49]. However, the lack of studies does not help to identify the specific reason or the real effect. Moreover, people with ASD (Autism Spectrum Disorder) are one of the

groups most affected by pyrotechnics and their sound effects, as this disease causes hypersensitivity to sounds in those who suffer from it and, therefore, the sound produced by fireworks, added to the lack of knowledge of these on their part, provoke anxiety and terror attacks in these people.

Every day, society is more aware of the risks of these shows and the pyrotechnics sector must address these concerns of society, seeking the coexistence of all the actors involved.

1.2.5. Alternatives to the sector

Due to a certain international concern for replacing or modifying fireworks with other types of more sustainable devices, alternatives have emerged and are gaining importance in different shows. The main alternatives currently being employed range from the use of compressed air as a propellant for small items, as in confetti party poppers, to light and sound shows with drones or laser lights.

Drones flying coordinated in the air, create light shows and movement accompanied by music to liven up the show. This new alternative to fireworks is a technique that is increasing its importance on a large scale in recent years, since Intel created the first show of this type simultaneously flying 100 drones in 2015, to expand this number in different shows reaching 2,000 drones flying in a coordinated manner on Intel's 50th anniversary.

Laser light shows have also become more and more important as restrictions on pyrotechnics have become more stringent. These shows consist of projecting silhouettes and sets of lights onto some surface or into the dark sky. In the 2017 Chinese New Year, more than 400 cities in China banned the use of fireworks for the general public, which in most cases was replaced by these new light and sound techniques [50].

However, with these alternatives, the variety of effects and characteristic noises that fireworks provide is lost, since there are currently no technologies that can match the effects achieved by fireworks such as the sound and the light [23], [51]. In addition, fireworks are worldwide known elements that provide great fame to certain festivities, some of which are better known even for the pyrotechnics than for the festivity itself.

1.3. Environmental impact

1.3.1. Atmospheric impact

Pyrotechnics, like all other sectors, is working to reduce its environmental impact. This commitment is represented in different studies which investigate fewer polluting compositions [6], [35]. Pyrotechnics, present in a multitude of festivities, has a long tradition and great worldwide recognition. It is a sector known for the quality and artistry in the manufacture of fireworks and other pyrotechnic products [18]. However, the manufacture and use of pyrotechnic products can generate significant environmental impacts due to the generation of air pollutants, including GHG emissions, and waste resulting from the use of non-renewable materials.

The Spanish Ministry for Ecological Transition and the Demographic Challenge has a State Registry of Emissions and Pollutant Sources (PRTR) that provides data on emissions to air and water from this activity. The data obtained for the pyrotechnical sector are shown in Figure 1.5.

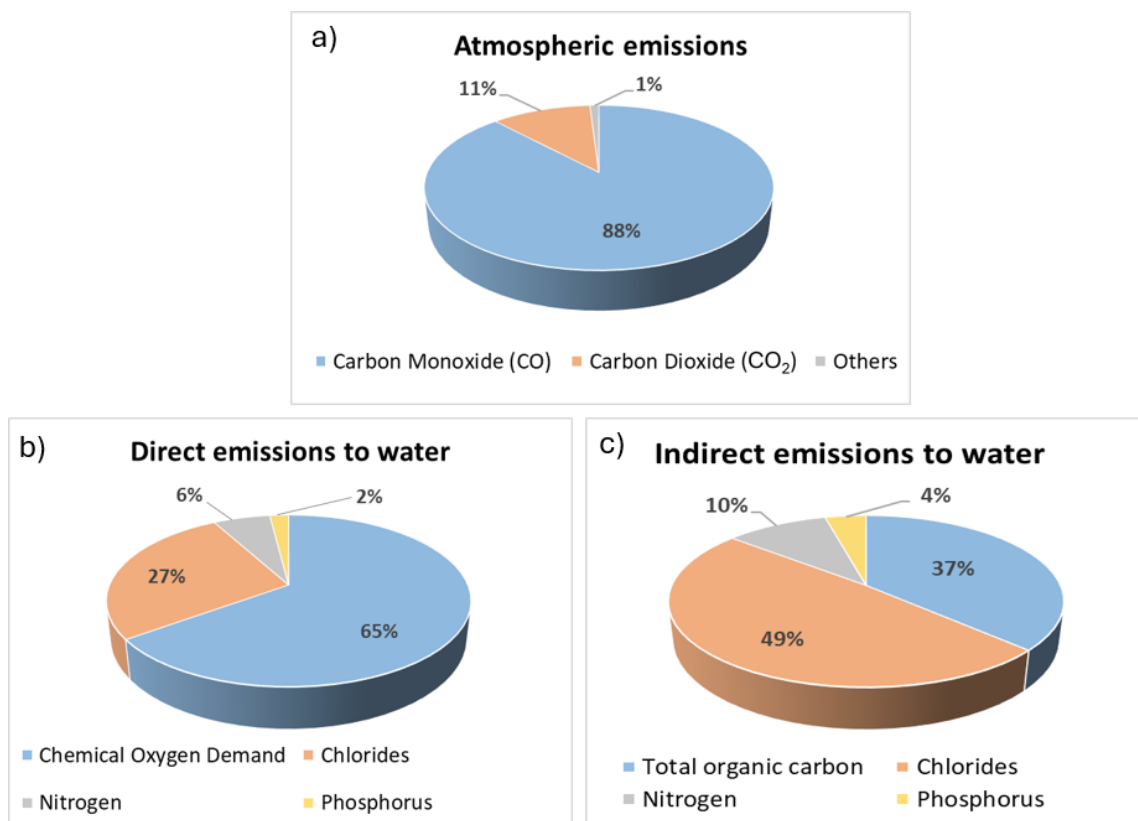


Figure 1.5. Main pollutants in the pyrotechnic sector in Spain in 2021. a) Atmospheric emissions. b) Direct emissions to water. c) Indirect emissions to water [52].

In recent years, several studies have focused on comparing the levels of particulate matter in the air during world celebrations known for their fireworks displays, in order to assess the actual emissions produced by these shows [53], [54]. Seidel and Birnbaum, studied the influence of the released fireworks during Independence Day in United States of America, analysing PM_{2.5} values in 315 different monitoring locations. They observed that although the average value of these monitoring stations during Independence Day only reached half of the NAAQS (National Ambient Air Quality Standards), there was a noticeable increase mainly in midnight, as can be seen in Figure 1.6.

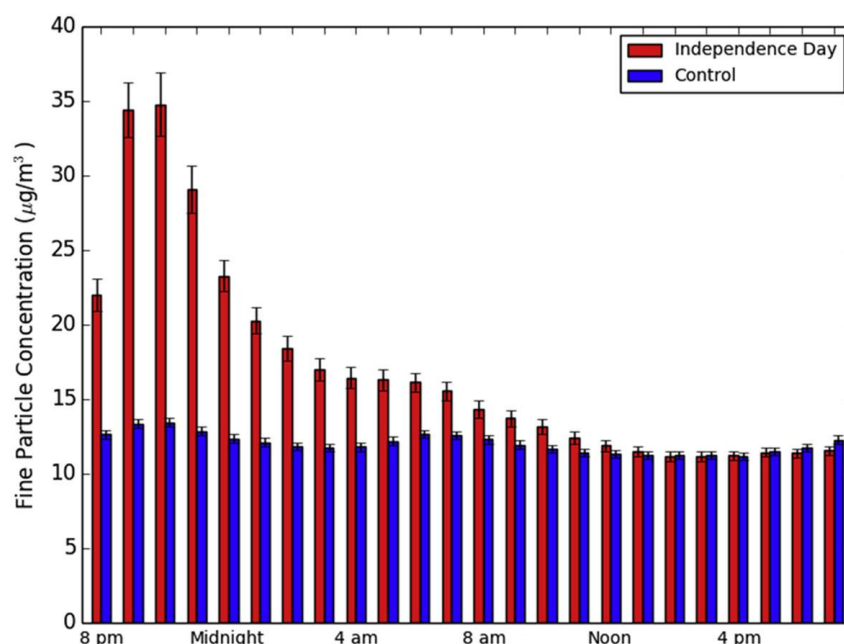


Figure 1.6. Hourly average PM_{2.5} concentrations (µg/m³) averaged between monitoring locations during Independence Day and control days [55].

When focusing on a monitoring station in Ogden (Weber County), which is located close to the place where fireworks public exhibitions took place, it was found an average concentration on Independence Day of PM_{2.5} of 61 µg/m³, value that exceeds the National Ambient Air Quality Standard for PM_{2.5} 24-hour set at 35 µg/m³ [55]. Other measurements during, and after a 4th of July fireworks display in downtown Minneapolis, Minnesota were carried out using a mix of low-cost sensors (CO and CO₂). The results showed that the concentration of CO increased 32% while that of CO₂ increased 17% overnight [56].

In China, during Chinese New Year, Tang et al. [57] studied Potentially Toxic Metal (PTM) pollution levels and Pb isotope signatures in pyrotechnic ash and road

dust samples from eight cities. The study showed that pyrotechnic events contributed 70.1%, 50.4%, 36.6% and 35.5% of the Sr, Cu, Cr and Pb values to these road dust, respectively. In addition, tests about the influence of fireworks on CO₂ emissions were carried out by Huang et al. It was observed during the Spring Festival (or Chinese New Year) that the CO₂ mixing ratio was higher than the annual average value as well as CO, PM₁₀ and PM_{2.5} [58]. Hickey et al. have also studied the toxicity of particulate matter emitted during the use of fireworks. Toxic metals, such as Pb, were found at extremely high levels [59].

In Spain, the Fallas Festival of Valencia, is one of the world largest pyrotechnic shows. Moreno et al., focused their research on the PM₁₀ (inhalable suspended particles whose size is between 10 and 2.5 micrometres) levels in a station located 1 km to the northeast of the centre of the pyrotechnic show [60]. They found that metallic elements together with potassium are the main products generated by firework release and, therefore, the ones that increased the most: Sb (x52), Sr (x37), Pb (x22), K (x12). According to Moreno et al. [60], the same phenomena was recorded in two different locations of Girona (Spain) during the Bonfires of Saint John pyrotechnic shows, as they recorded PM_{2.5} level data and can be seen in Figure 1.7.

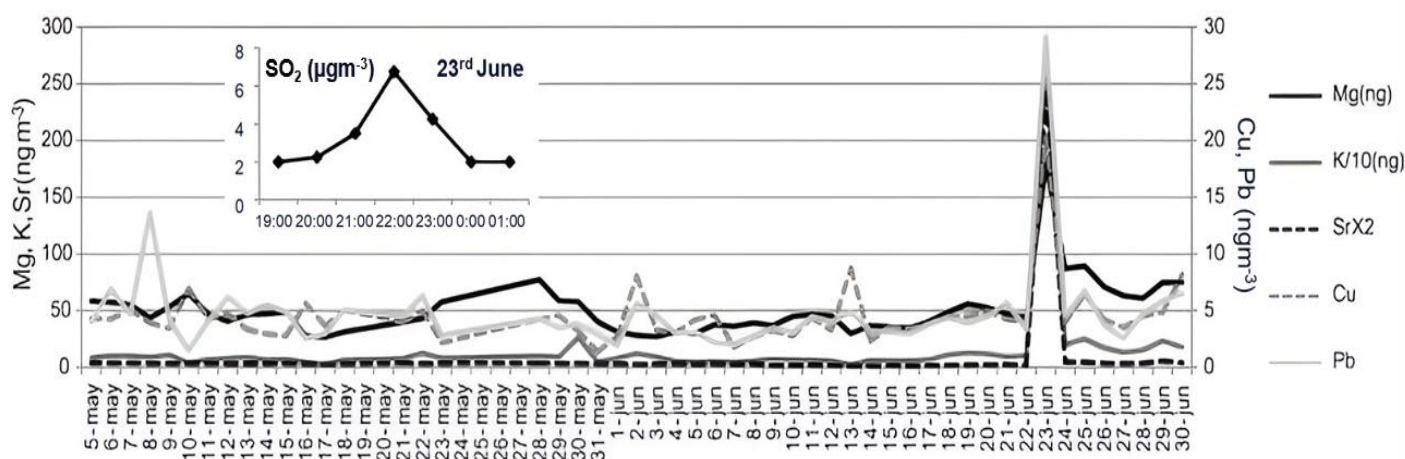


Figure 1.7. Daily concentrations of the main pyrotechnic pollutants in Girona (Spain) [61].

Air quality measurements in Vadodara (India) during the festival of Diwali for the consecutive years 2009, 2010 and 2011, indicate that during the festival day, the average levels of SO₂ and NO_x increased 23 and 3 times, respectively, compared to a regular day [62].

While SO_2 and NO_x contribute to the formation of acid rain and smog, CO_2 is a potent greenhouse gas that contributes to climate change by trapping heat in the atmosphere and, together with methane (CH_4), they are the most abundant greenhouse gases, contributing between 80-85% of the greenhouse gas emissions [63]. However, CO does not contribute directly to the greenhouse effect [64], but favours the appearance of gases that do contribute directly to it [65]. CO's half-life in the atmosphere is about three months [66], allowing it to slowly oxidise to produce CO_2 and contribute to the formation of tropospheric ozone [67], [68].

However, fireworks displays contribute a relatively small fraction of greenhouse gas emissions compared to sectors like transport or energy production. Otto cycle and diesel internal combustion engines, or aviation engines (especially turbofan or fanjet engines, which are the latest aviation engines generation) are based, as pyrotechnics, in the combustion reaction. Fuels might change, but the chemical principles of the reactions do not, which is a gas production and particle emissions released to the atmosphere as products of the required combustion chemical reactions to their function. The same fact can be applied to smoking or emissions produced by heating systems. The difference between all these emitters and pyrotechnic devices lies in the frequency of their use. While pyrotechnic shows take place in singular occasions, the other mentioned emitters are used every day in a constant way. In the European Union, fireworks emitted around 6,500 metric tons of CO_2 equivalent in 2012, a fraction of the total emissions which exceeded 4 billion metric tons that year [69]. However, their regular use can lead to ongoing air pollution and contribute to climate change. Despite their small contribution, efforts to reduce emissions from fireworks displays are important [70].

Some manufacturers are exploring alternative materials like nitrogen-rich compounds and perchlorate-free compositions to produce less pollution due to there is evidence that ClO_4^- ion may affect the thyroid gland, as it makes iodide absorption difficult and may trigger hypothyroidism [42], [43], [44]. In addition, groundwater contamination via soil from rainfall, related to the production, handling and use of perchlorate, harms micro-organisms and aquatic fauna [45]. According to Wilkin et al., measurements before a fireworks display recorded perchlorate concentrations in the surface water of a lake between 0.005 and 0.081 $\mu\text{g/L}$ [71]. After the show, these concentrations reached values ranging from 24 to 1,028 times the mean reference value. This highlights the need for sustainability measures in all sectors, including the use of environmentally friendly pyrotechnic materials.

Nitrogen-rich compounds, more precisely components such as nitrocellulose, can be considered as a possible solution to the generated emissions during pyrotechnic shows. These nitrogen-rich compounds, known as smokeless powder or white powder, obtain their energy from the high standard enthalpy of formation, which predominates over the energy released in the oxidation of carbon, from which energy is obtained in the case black powder [35]. These results in combustion products are less harmful to the environment, mainly due to the reduction in solid products which occurs when the compositions do not burn completely (soot) and, therefore, producing effects with more clarity due to less smoke [72], [73], [74], [75]. Because of these characteristics, nitrogen-rich compounds have replaced black powder in various solid rockets such as ammunition [76]. Still, the environmental advantages are tempered by challenges associated with nitrocellulose, as the production process of nitrocellulose involves the use of nitric acid and other nitrogen compounds [77], [78], which present environmental implications, raising concerns about pollution.

In addition, nitrocellulose is currently used in the pyrotechnic industry as a substitute for perchlorate in category F1 fountains for indoor use and as elevation powder for table bombs and mines [79]. According to EN 15947:2022, fountains produce the emissions of sparks and flames with aural effect other than report or without aural effect. Table bomb's principal effect is the report with ejection of streamers, confetti and/or novelties and mines provide an ejection of the content in a single burst producing a widely dispersed visual and/or aural effect in the air. Figure 1.8 shows photographs of these products.



Figure 1.8. a) Fountain. b) Table bomb. c) Mine. [80].

The content of nitrogen is an essential parameter in nitrocellulose pyrotechnic devices, as it directly influences their performance and safety. With a nitrogen content below 12.6%, nitrocellulose is more stable and less explosive [81], making it suitable for pyrotechnic applications such as fireworks, providing rapid combustion and vibrant colours without compromising safety [72]. Several studies have analysed different types of compositions used as perchlorate-free oxidant. Anhydrous 5-aminotetrazole [82] and periodate salts [83] have been studied as pyrotechnic oxidizers in mixtures with barium (to produce green colour) and strontium (to produce red colour), but these studies are not very detailed, as they only simulate a hypothetical situation.

Several studies have tested the thermal stability of nitrocellulose associated with ammunition [84], [85] and others have analysed its specific application in fireworks as a propellant, binder or perchlorate-free compound [6], [86], [87], [88], without taking into account the environmental impact of both compounds. Therefore, while nitrocellulose presents potential benefits for reducing some of the most important environmental impacts during pyrotechnic events, a comprehensive assessment of its use as a substitute needs to be carried out in order to determine if the environmental challenges are properly addressed and correct performance of the devices is achieved. Furthermore, the substitution of flash powder with nitrocellulose may require adjustments to achieve the same operating and safety conditions.

1.3.2. Sustainability

The Life Cycle Assessment (LCA) methodology has emerged as an essential tool for sustainable development by measuring the environmental impact of products and services throughout their life cycle. The European Commission has been implementing different life cycle policies for two decades [89], steadily increasing its applications and establishing itself as a fundamental pillar of European sustainable policies.

Every day, more and more research on LCA is revealing important information on sustainability assessing the environmental impact of a product, process or service during all the stages of its life. However, no such analysis has been carried out on pyrotechnic products and there are no circular economy indicators to quantify the impacts of the supply chain of market products. Previous studies have analysed the explosives sector which, although they do not use the same compositions as

fireworks, can provide useful information due to a similar working principle. Ferreira et al. [90] examine the production of a civil explosive and compare five different compositions based on ammonium nitrate, water, mineral oil, polycarboxylate and a sensitizing agent considered as extruded polystyrene (XPS). The results showed that the highest environmental impact comes from the production of ammonium nitrate, i.e. the raw material phase, and that the addition of sodium nitrate leads to a reduction of these impacts ranging from 7% to 14% [90]. Costa et al. [91] provide preliminary results on LCA of Royal Demolition Explosive (1,3,5-trinitroperhydro-1,3,5-triazine – RDX) production in a military explosives unit. The study concluded that hexamine nitration is the most relevant process for the environmental impact categories under study (acidification, ecotoxicity, eutrophication, global warming, human health...), but stresses the need to develop the study with more specific information on stages such as transport, highlighting the lack of data [91].

Although these previous studies can provide some information to extrapolate to the pyrotechnics sector, it is necessary to go deeper into this industry to obtain important data on its sustainability indicators.

1.4. Sound impact

1.4.1. Animal welfare

Animal welfare is a concept that in recent years is becoming a social concern and standardized both in specific fields (veterinary medicine, livestock or research) and in society in general. Animal welfare includes three interrelated elements: the proper functioning of the organism, the emotional state of the animal and the possibility of expressing some normal behaviours specific to each species [92]. The Five Domains Model of Mellor et al., shown in Figure 1.9, has been one of the most widely used to understand the concept and the way in which both external and internal elements of the animal are interrelated.

There is sufficient evidence to demonstrate that some sounds, many of them anthropogenic, have the potential to negatively affect the welfare of animals through various pathways such as hearing damage, psychological stress, impairment of proper communication or modifying their behaviour, among others. Depending on the characteristics of the sound being received and the

particularities of the animal exposed to it, the impact of these welfare effects can vary dramatically, from increasing the stress response (with or without long-term consequences) to simply not generating any negative effects at all.

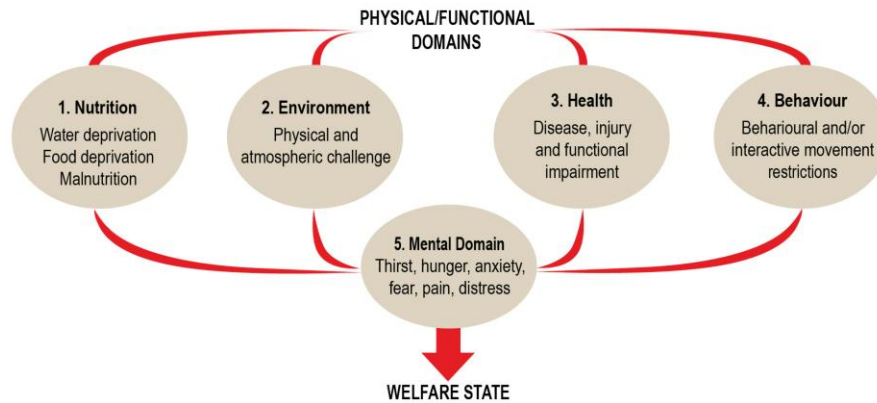


Figure 1.9. Five Domains Model [93].

According to studies, sound intensity is considered the most determining factor in the relationship between sound and animal welfare [68], [94], although the frequency spectrum audible to each animal will also determine whether or not an animal perceives a sound [95], [96]. Intermittency, predictability, repeatability and the ease of detecting a sound are also considered crucial factors.

In addition to the factors inherent in the sound, there are external conditions that also influence sound transmission and the sound intensity perceived by a receiver. A greater distance between the sound source and the animal reduces the likelihood that a sound will affect its well-being [97], [98]. The presence of natural or artificial barriers can modify certain sounds, attenuating or amplifying them depending on their design [99], [100]. Finally, the medium of sound wave transmission has a significant influence on the reception of sound [101], but in the case of pyrotechnic devices, the transmission medium is always air.

1.4.2. Animal ear

Individual and species factors are crucial in understanding how the sound level produced by pyrotechnics variably affects animals. Each species is different in its auditory characteristics and its perception and tolerance to sound [95]. This means that the same spectrum, type and level of sound that is very problematic for one species may be less problematic for another. Similarly, individual characteristics such as genetics (including breed), animal behaviour, physiological and health

status, age and especially past experiences are also very important and must be taken into account when studying and understanding the relationship between noise (pyrotechnic or otherwise) and animal welfare [96]. It is especially important to know and take into consideration the hearing abilities and sensitivities of the different species, which are highlighted in Table 1.4 below.

Table 1.4. Audible spectrum of different species [102], [103], [104], [105].

Species	Scientific name	Audible spectrum (Hz)
Horse	<i>Equus caballus</i>	55-33,500
Canary	<i>Serinus canaria</i>	250-8,000
Pig	<i>Sus scrofa</i>	55-40,000
Rabbit	<i>Oryctolagus cuniculus</i>	96-49,000
Bottlenose dolphin	<i>Tursiops truncatus</i>	150-150,000
African elephant	<i>Loxodonta sp</i>	16-12,000
Hen	<i>Gallus gallus</i>	125-2,000
Cat	<i>Felis catus</i>	45-64,000
Human	<i>Homo sapiens sapiens</i>	64-23,000
Sheep	<i>Ovis aries</i>	125-40,000
Dog	<i>Canis lupus</i>	67-45,000
Cow	<i>Bos taurus</i>	23-35,000

The vast majority of non-human mammals can hear a wide range of high-frequency sounds that are not audible to humans. That is, they have much higher upper limits, in many cases double the upper limit of human hearing [106]. In the case of birds, amphibians and fish, by contrast, the upper limits are generally well below those of most mammals, including humans [107].

The most adverse problem that could be triggered by a very high sound pressure level in animals are mainly hearing damage of varying severity [95]. The consequences of auditory overstimulation can be highly variable and may or may not be irreversible depending on the structures affected and the damage generated. The soft tissues of the inner ear are vulnerable to noise so that auditory stimulations of sufficient duration and intensity may generate a cell death that results in hearing loss that can be permanent if the connections of the auditory sensory cells are damaged, ultimately irreversibly affecting the hearing function. This is especially important in mammals, since they generally do not have the capacity to regenerate these auditory cells [108], [109].

Another type of problem, which also affects animal welfare, and which can also arise due to the exposure of animals to an intense sound pressure level, is the appearance of phobias, stress, fear or anxiety.

Due to the number of evidence reported by animal caregivers and professional associations (especially veterinary), and by the number of articles investigating this aspect, it seems that the major way in which an intense sound pressure level affects welfare is the appearance of negative affective states associated with stress response, fear, anxiety and/or phobia. Stress, fear and their derivatives are problems of well-being in themselves, but in turn, they can cause or aggravate other problems [49], [110].

1.4.3. Sound effects of pyrotechnics

Sound effects produced by pyrotechnics have certain particularities, both in the characteristics of the sound emitted and in the way it appears. These characteristics can be summarized as intense sound level, brief, intermittent and variable in number of repetitions, variable in type and frequency, unpredictable, with a variable origin in many cases difficult to determine for the animals, infrequent in long periods of time and frequent in short periods and of non-homogeneous appearance.

As a point sound source, a pyrotechnic device emits acoustic energy in all directions with equal intensity [111]. When a point sound source emits in the open air, there is only a direct field, since the waves propagate freely without connecting any obstacle. In this case, the sound pressure level decreases as we move away in the proportion shown in Figure 1.10. As the distance doubles, the sound pressure level decreases by 6 dB [112].

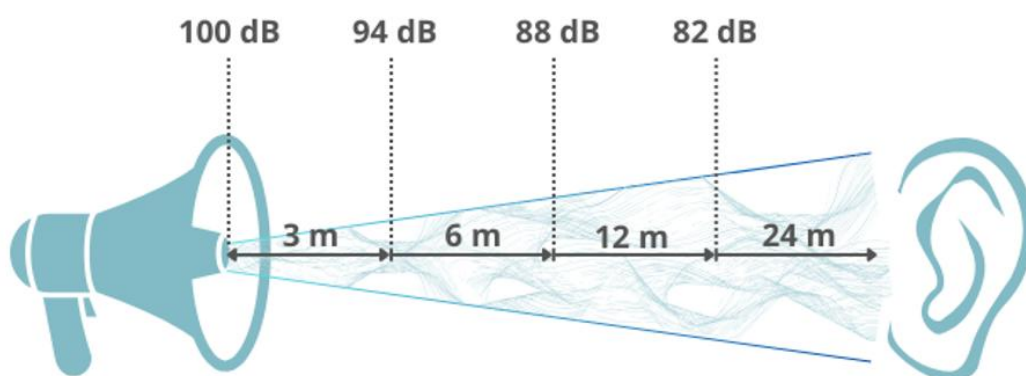


Figure 1.10. Sound level attenuation with distance.

The sound scale has logarithmic characteristics. This is the reason for the previous occurrence of attenuation and for the fact that, if there are two or more point sound sources influencing the point, the total intensity is not calculated as the sum of them. In the presence of two non-coherent sources, i.e. generating two independent signals, the total sound pressure will be calculated according to Eq. (1) [113]:

$$L_{total} = 10 \log_{10}(10^{L_1/10} + 10^{L_2/10}) \quad (1)$$

Where:

L_{total} is the sound pressure level generated by two different sources.

L_1 is the sound pressure level of source 1.

L_2 is the sound pressure level of source 2.

Measurement of sound parameters

The sound spectrum emitted by pyrotechnic devices, as established in the standards that regulate it, is measured by means of a sound level meter. The pyrotechnic regulations for the certification of pyrotechnic devices establish the A-weighted Impulsive time scale (LAI_{max}) as the sound measurement scale. The Impulsive time scale uses a reduced time constant that evaluates the influence of short duration sounds, while the A-weighting is the standard weighting of audible frequencies designed to reflect the noise response of the human ear. In order to recognise sound levels measured under the scale described above, the unit of measurement is indicated as dB(AI). No fireworks should produce a maximum impulse sound level greater than 120 dB(AI) or equivalent, at their respective safety distances depending on their category.

In the affection of high sound levels in animals, the lack of control of these unpredictable, intermittent and difficult to contextualize characteristics of pyrotechnic sound effects, are as important as the intensity produced when generating welfare problems [93], [114]. Moreover, these situations are aggravated by the fact that, in many cases, animals are also unable to develop natural behaviours that allow them to control their exposure to the stimuli (fleeing, moving away, hiding or confronting the source), as is the case of most pets exposed to pyrotechnic noise in their homes.

1.4.4. Current situation

Numerous studies have confirmed the existence of an impact on animal welfare due to the firing of pyrotechnic devices. According to Lindstedt, 30% of horses tested in Finland and 55% of those tested in Sweden showed fear of pyrotechnic sound effects during New Year's Eve. Horses located in rural areas showed 6 times less risk than those in urban environments [115].

According to Blackwell et al. in a survey of a large number of dog owners, fear of the sound effects produced by pyrotechnics was described as the most common cause of fear response in dogs [49]. The same was the conclusion obtained by Hakanen et al. in their survey [116]. According to Carrieri-Rocha et al. 90.6% of dogs living near a soccer stadium where fireworks were set off on match days showed an increase in fear and anxiety associated behaviours on match days [117].

According to the RSPCA (Royal Society for the Prevention of Cruelty to Animals) in its 2019 report, limiting the maximum sound pressure level of pyrotechnic products to 90 dB(AI) at the safety distance would be a particularly relevant measure that could lead to significant improvements in animal welfare [118]. This level is based on usual maximum noise levels tolerated by living organisms.

However, most of these investigations are based on surveys or observations, with no justification of the actual cause of welfare effects or their effect on the animal. Although European pyrotechnical regulations do not independently address animals, it seems likely that some of the regulations on the use and design of pyrotechnic products, established to protect the hearing health of humans, have worked to prevent, in many contexts, injury to animals.

Because of that, it is necessary to address these concerns by proposing alternative device designs that not only maintain the performance standards of pyrotechnic articles but also significantly reduce emissions and noise levels.

1.5. Industrial safety

Although fireworks are seen by society as a form of entertainment and celebration and do not present any risk or problem if they are properly used, respecting the firing sites, the necessary safety standards, etc., they can cause much more danger than most people think when they are not used responsibly. They can cause burns, injuries, acoustic problems and even death.

In order to have a complete view of pyrotechnics safety implications, some of the most important accidents suffered by the pyrotechnical sector are the following:

In 2000, in Guangdong (China), 75 people died and 160 injured in a fireworks factory. In 2016, there was a fireworks depot explosion in Paravur (India) where 111 people died and several were injured [119].

Similar accidents have occurred in Spain. In 2018, in Tui (Pontevedra), 2 people died and 37 were injured by an explosion in a warehouse of pyrotechnic articles. The same year in Olocau (Valencia), a worker died by the explosion of a pyrotechnics stand and in the well-known María Angustias pyrotechnics in Guadix (Granada), 3 people died and 2 others were injured by the explosion of the manufacturing workshop [120].

This reflects the reality of the danger of handling pyrotechnic articles and therefore makes the existence of a certain regulation, which controls both the festivities and all the processes involved in the life cycle of pyrotechnic articles, really necessary.

The widespread use of flash powder, one of the main components in pyrotechnic devices, has been identified as a significant contributor to these challenges, which leads to the need to explore sustainable alternatives. Flash powder is primarily composed of potassium perchlorate and metallic compounds [18], and plays the main role in achieving the spectacular sound effects of pyrotechnic shows. The key factor of flash powder is the pressure it generates inside the container, which allows the release of a shock wave with sufficient energy to cause the explosion or opening of the pyrotechnic device [121]. If the overpressure achieved by the combustion of the explosive powder is not sufficient, the pyrotechnic device will not function properly. In the case of pyrotechnic shells, a very common element in shows, bursting flash powder is necessary to achieve a correct opening in the air and trigger the desired visual effect [122].

However, as previously pointed out, its association with environmental pollutants and high sound pressure levels requires innovative solutions for the continued viability of the pyrotechnic sector. In recent years, different alternatives have been studied. As mentioned before, several pyrotechnic devices include aluminium in its composition. In this context, Azhagurajan et al. [123] studied the use of boron instead of aluminium in flash powder. As aluminium is substituted for boron, it increases by 20% the impact energy and 32% the friction charge required to achieve ignition of the composition, reaching values of 6.44 J and 247.2 N, respectively. This indicates that the analysed mixture reduces the risk of an accident compared

to traditional flash powder by increasing the energy required for ignition [123]. On the other hand, Rajendran et al. studied the behaviour of flash powder by substituting part of the sulphur it sometimes contains with tamarind seed. The results obtained indicated a reduction in the sound pressure level, as well as a lower amount of SO₂ released into the atmosphere [124]. However, none of the studies analysed the explosion pressure, a fundamental factor in pyrotechnic shells.

As previously mentioned, nitrogen-rich compounds could be a solution as a substitute for flash powder because of its environmental advantages and its high explosive character. The most notable advantage lies in its potential to reduce environmental impact compared to traditional explosive compounds like flash powder, mainly because it removes metal compounds, and potentially lowering the overall environmental footprint of pyrotechnic shows. However, the storage of pyrotechnic material can pose a high risk of accidents if the necessary measures are not taken [11] and it also happens with nitrocellulose, due to its instability, as it presents a natural autocatalytic process that leads to the natural degradation of nitrocellulose [125].

Therefore, the need to find compositions that are less sensitive to ignition and reduce the risk of an accident, without compromising the characteristics of pyrotechnic devices is still present.

In other combustible dusts, the addition of inert materials is known. Amez et al., added as calcium carbonate, sodium bicarbonate and gypsum in order to see how the ignition properties were affected by these inter materials. Thanks to this, they were able to increase the Minimum Ignition Energy (MIE), decreasing the ignition sensitivity of the tested combustible dusts [126]. Castells et al., analysed the addition of recycled glass and sodium bicarbonate to different types of biomass. Different behaviours were observed depending on the different inert materials, showing that not only the amount of inert added is important, but also its physicochemical properties [127]. In both cases, sodium bicarbonate proved to be a very effective inert.

The addition of these compounds presents safety improvements for explosive dust, as it is an effective way to reduce the risk of explosion and sensitivity to ignition [128]. Furthermore, inert materials reduce the environmental emissions generated in the combustion of different fuel compounds [129], [130], therefore reducing the contribution to the environmental footprint.

2. Background

In 2017, pyrotechnics began to suffer its first restrictions worldwide and, because of that, Laboratorio Oficial J. M. de Madariaga (LOM) of the Universidad Politécnica de Madrid, raised a plan to overcome the challenges that might lead to these restrictions. That was called “Defensa de la industria pirotécnica”.

Firstly, work was carried out on a study of the environmental impact of pyrotechnics and in September 2019 Bachelor’s Degree Final Project entitled “Analysis of Emissions Produced by Pyrotechnic Devices” (Análisis de las Emisiones Producidas por los Artificios Pirotécnicos) [131], carried out by David León and directed by Javier García Torrent, was presented.

Following this line of research, in 2019 the LOM organized the International Symposium on Innovation in Pyrotechnics in Pinto (Madrid), with the aim of attracting and bringing together the various pyrotechnics entrepreneurs in order to address the challenges that the industry was facing. The Symposium included in the program a presentation entitled “Análisis de Emisiones en Artículos Pirotécnicos” [132], whose objective was to analyse in detail different pyrotechnic processes to obtain real and contrasted data that provide insights to mitigate the emissions produced by the pyrotechnic industry.

In 2020, thanks to the Regulatory Agreement of the nominative subsidy contemplated in the general state budget law, from the MITECO, in favour of the LOM, the “Study of environmental emissions from fireworks displays” (Estudio de las emisiones ambientales de espectáculos pirotécnicos) is included among its actions.

That same year, the action “Study of the effect of pyrotechnic noise on animals” (Estudio del efecto del ruido pirotécnico en animales domésticos) was also included, as it was known that one of the main social rejections of fireworks shows was discomfort in pets. In fact, already in 2019, when the Symposium was held, quite a lot of rejection was observed by some sectors of the Pinto City Council, expressing the problems that noise causes not only in animals, but also in people belonging to the Autism Spectrum Disorder. For this reason, LOM collaborated with an association of parents of children with development deficits, who enthusiastically participated in the fireworks show of the Symposium.

In September 2021, the Master's Thesis entitled “Adapting Pyrotechnic Industry Processes to Global Sustainable Development Goals” (Adaptación de los Procesos de la Industria Pirotécnica a los Objetivos Globales de Desarrollo Sostenible) [133] was presented, carried out by David León and directed by Javier García Torrent, which received in 2023 the LOM-TECMINERGY award for the best Master's Thesis of the Promotion 2021-2022 on safety and quality in energy industries and mines. The theme of the work was the application of the 2030 Agenda to the pyrotechnical sector, which was continuously present in all kinds of events, initiatives, development programs, etc.

Seeing the growing interest of the State Administration, MITECO and companies in the sector in the Sustainable Development Goals, the LOM organized in April 2023 the Symposium on Sustainable Pyrotechnics [134], which included presentations on the work being developed for the Ministry in the context of the defence of the pyrotechnics industry. Presentations were given on “Sound pressure levels generated by the use of Fireworks” (Ángel Santamaría), “Impact of the sound of fireworks on animals” and “Aligning the pyrotechnic sector with Sustainable Development Goals” (David León) and “Proposal for a Strategic Plan for the pyrotechnic industry” (Juan Pous).

Many of these papers presented the current state of development of the work, including data that appear in this thesis. The presentation of Juan Pous, derived from his Bachelor's Degree Final Project “Strategic Plan Model for Companies in the Spanish Pyrotechnic Sector” (Modelo de Plan Estratégico para las Empresas del Sector Pirotécnico Español) [135], received the LOM-TECMINERGY Award for the best Bachelor's Degree Final Project of the promotion 2022-2023. Moreover, Juan Pous developed the document Strategic Plan Model for Companies in the Spanish Pyrotechnic Sector [13], a key document for the industry.

All these studies and events have laid the basis for the present research, which aims to deepen the analysis of sustainability and the adaptation of the pyrotechnics sector to new environmental and social challenges.

3. Objectives of the research

The main objective of this research is to align the processes, materials and compositions of the pyrotechnics industry with the Sustainable Development Goals contained in the 2030 Agenda, in order to achieve a pyrotechnics industry that is in line with the sustainable industrial development towards which we are moving. The aim is to provide data and tools for the defence of the sector, in order to achieve an appropriate coexistence with the rest of society. Four main objectives have been worked on.

The first objective arises from the need to carry out an exhaustive analysis of all the factors involved in the pyrotechnics sector, in order to identify the points on which to focus, to know the most critical stages of their processes and to compare with other sources to determine the magnitude of the problems. Sustainability indicators are a key factor for the different sectors, providing valuable information on their environmental impact. In this regard, this objective focuses on developing a set of sustainability indicators applicable to the pyrotechnics industry, establishing a framework for future comparisons and continuous improvement.

One of the sector's difficulties comes from the social criticism of the environmental pollution produced by pyrotechnic devices since fireworks displays produce certain greenhouse gas (GHG) emissions, such as carbon dioxide (CO₂), as well as carbon monoxide (CO), sulphur dioxide (SO₂), perchlorate products, etc. Therefore, the second objective focuses on the detailed analysis of the products emitted by pyrotechnic devices and the search for substitute compositions that reduce pollutant emissions, carrying out comparative studies between conventional pyrotechnic compositions and possible alternative compounds.

Moreover, due to the increase of domestic animals in urban areas, another difficulty faced by the pyrotechnics sector has arisen. There is evidence that shows, in certain cases, that animal welfare is affected when they are exposed to the sound effects produced by pyrotechnics. The need to study the real reasons and consequences of this affectation is essential to find viable solutions, so the third objective focuses on its analysis, as well as the search for possible safety and prevention measures to be taken by the sector. This objective is addressed in order to develop recommendations or alternative designs that mitigate their impact on animals and sensitive populations.

Finally, given the highly explosive character of pyrotechnic compositions and the industrial risk involved, which led to severe accidents in the past, the last of the objectives arises, which consists of analysing the thermal properties of the different compositions and searching for substitutes that, in addition to achieving environmental and sound benefits, reduce the risk present in the storage and transport of pyrotechnic devices. To address this objective, performance tests and risk analysis are carried out in order to propose safer compositions and handling practices.

4. Materials and methods

4.1. Pyrotechnic sector operations

4.1.1. Materials and manufacturing process analysis

Although in pyrotechnics we find a multitude of different articles, which may present specific processes in their manufacture, the general structure of processes shown in Figure 4.1 can be considered.



4.1. Operations and processes in the life of pyrotechnic devices.

This overall structure covers all stages and processes in the pyrotechnics sector, from the acquisition of raw materials stage to the waste recovery and recycling stage after the use. Detailed analysis of these stages can provide relevant information on the most critical processes and materials in the sector, which can be optimised.

Raw materials

The processes developed in the pyrotechnic sector, like most operations in other sectors, require a series of raw materials used as the basis for the manufacture of pyrotechnic elements, which must also be accompanied by other inert materials characteristic of these fireworks.

The raw materials are chemical compounds that are used in pyrotechnics for the elaboration of the different compositions. However, pyrotechnic articles are not only manufactured with these raw materials used to make the mixtures that generate the different effects but also require other types of materials that represent an essential part of these articles. The main pyrotechnic compositions used in pyrotechnics are black powder, flash powder and compositions that produce colour effects. These compositions were described in chapter 1.2.1 Chemistry of pyrotechnics. To manufacture these pyrotechnic mixtures, it is necessary to acquire different chemical compounds such as potassium nitrate (KNO_3), sulphur (S), charcoal (C), potassium perchlorate (KClO_4), aluminium (Al), magnesium (Mg), colour-producing salts such as strontium carbonate (SrCO_3) or barium

carbonate (BaCO_3), etc. In addition, other secondary compounds are used that perform important compaction functions, such as dextrin or Arabic/Acroids gum.

There are a multitude of materials that accompany the pyrotechnic mixtures in fireworks, from the most recognisable ones such as composition containers, containers, internal caps or plugs, fuse cover... to those that appear to a lesser extent and are more difficult to visualize, such as the elements that secure the closures (staples or threads), internal dividing elements (grids), etc [18]. The most common materials for these elements are cardboard, plastic, cotton, gypsum and clay.

Fireworks manufacturing

The first process to achieve a pyrotechnic device is the elaboration of the compositions it contains. The components of this mixture are sieved to obtain a homogeneous particle size and eliminate possible impurities, before being subjected to mixing. This mixing is carried out in different ways depending on the component and the manufacturer who performs the operation, as it can be done either manually or mechanically [136]. If the process is mechanised, the pyrotechnic compositions are combined in a mixer. In order to increase safety during the mixing of pyrotechnic compositions, binary mixtures (those consisting of two components which do not produce an explosive mixture with each other) are sometimes worked on first before being mixed to produce the target ternary mixture (explosive mixture).

Once the pyrotechnic compositions are in the ideal conditions of shape and humidity, the fireworks are assembled. This assembly process includes container filling, pressing and closing operations. When these processes are carried out on a large scale, they are usually mechanised. The mixture is fed into the container, frequently using a mechanised hopper that adds the necessary proportions. Once the container is filled, the pressing process depends on the intended effect. Pyrotechnic articles intended for bursting effects do not require pressing, whereas for propulsion or illumination effects, a hydraulic press is used to provide the necessary compression of the composition. Finally, the article is sealed with the caps, usually manually.

Distribution

Once manufactured, the transport of these items is of vital importance. This transport, as it contains hazardous materials, must comply with the standards set out in the European Agreement concerning the International Carriage of

Dangerous Goods by Road (ADR 21) [137]. This international agreement establishes key safety aspects, such as maximum quantities of NEC, type of transport vehicles, packaging and emergency procedures.

The articles may be taken directly to the places of pyrotechnic shows, to accredited points of sale to the general public, to the sale of accredited professionals for the firing of F4, T2 and P2 articles or to other pyrotechnic workshops for use [138]. To avoid accidents, hazardous materials are defined by risk divisions, which can be found in Table A.1 of Annex A.

Assembly and use

As previously pointed out, there are pyrotechnic devices both for domestic and professional use. The products available to the general public must be handled with safety precautions and in accordance with the instructions specified by the manufacturer on the labelling, in order to avoid accidents. The volume of articles in categories for use by the general public is very high and makes it difficult to control due to the freedom of location and timetables.

On the other hand, articles intended for professionals, as they have a higher risk, are subject to great limitations and the shows that use them must in any case be authorised in advance. The most common pyrotechnic show is the fireworks display, which consists of a large number of aerial products that represent in the air a multitude of effects, figures, colours and sounds and are usually fired on the occasion of local festivities. These shows are always fired by professionals.

After having organized the show in a theoretical way, hours before the firing, the pyrotechnic articles and the necessary material for its assembly are received at the firing site. When setting up the show, as well as during the firing, safety must be the main objective. Once the pyrotechnic articles that are going to participate in the show have been secured, they are connected. All the articles will be initiated by means of electric igniters, connected to the connection boxes that are initiated by means of a firing table [139].

The end product of fireworks displays is an impressive visual and sound panorama that accompanies a multitude of festivities. Such effects can also be achieved with articles of general public use, although on a smaller scale.

On the other hand, certain emissions are generated from the combustion of pyrotechnic compositions. According to the main pyrotechnic compositions, the reactions that occur are shown in Table 4.1.

Table 4.1. Pyrotechnic reactions that take place inside the articles [18], [19].

Compositions	Pyrotechnic reactions
Lift powder	$4 KNO_3 + 7 C + S \rightarrow 3 CO_2 + 3 CO + 2 N_2 + K_2CO_3 + K_2S$
Sound effects powder	$10 KNO_3 + 8 C + 3 S \rightarrow 6 CO_2 + 5 N_2 + 2 K_2CO_3 + 2 K_2SO_4$
Black powder for burst	$2 KNO_3 + 3 C + S \rightarrow K_2S + 3 CO_2 + N_2$
Flash powder	$KClO_4 + 4 Mg \rightarrow KCl + 4 MgO + \text{heat}$
Colour effects powder	$4 KClO_4 + (C_6H_{10}O_5)_n + 4 Mg \rightarrow 4 KCl + 5 H_2O + 6 CO_2$
 Salt dissociation	$+ 4 MgO + \text{heat}$
	<i>For nitrates:</i>
	$2 (AC)(NO_3)_x \rightarrow 2 (AC)O + X N_2 + X O_2$
	<i>For carbonates:</i>
	$(AC)CO_3 \rightarrow (AC)O + CO_2$
	<i>where AC can be defined as the element that produces the colour and X is the required value for stoichiometry.</i>

End of life

Once the pyrotechnic show is finished or the individual article has been fired by the general user, as well as during the production processes, waste is generated that can be disposed of, reused or recycled. The waste generated during the pyrotechnical sector processes can be divided into two large groups: waste from materials that have not been involved in the pyrotechnical process and declassified waste. The latter are all those containing certain pyrotechnic material and, in Spain, are governed according to Complementary Technical Instruction number 12, of RD 989/2015, of October 30, which approves the Regulation of pyrotechnic articles and cartridges [26].

4.1.2. Life Cycle Analysis of pyrotechnic products

Once the operations carried out in the sector are known in detail, LCA was used as a methodology to study the potential environmental impacts of a product or

service. It is regulated by international environmental management standards ISO 14040:2006 (Environmental management—life cycle assessment, principles and framework) and ISO 14044:2006 (Environmental management—life cycle assessment, requirements and guidelines) [140], [141]. These standards define the steps to be followed in order to carry out a life cycle correctly. The use of LCA can provide key data to the pyrotechnic sector on its environmental impact and help identify opportunities for improvement in terms of sustainability.

Life-Cycle model

Life-cycle analysis was performed using SimaPro (Version 9.5) software, which allowed the assessment of the environmental impacts of products or processes in the value chain. The methodology used was the Product Environmental Footprint (PEF). This method studied 16 impact categories, Climate Change (Global Warming Potential - GWP) among them.

The analysis assessed an unfavourable case of manufacture in a hypothetical pyrotechnic factory in the vicinity of Valencia (Spain), specifically in the municipality of Loriguilla, and its subsequent use in a pyrotechnic show in Valencia's Town Hall Square during the Fallas festival. The model followed a cradle-to-gate LCA and encompassed the following processes: acquisition of materials, transport, manufacturing, distribution, use and end life. The simplified flow diagram of the model is shown in Figure 4.2.

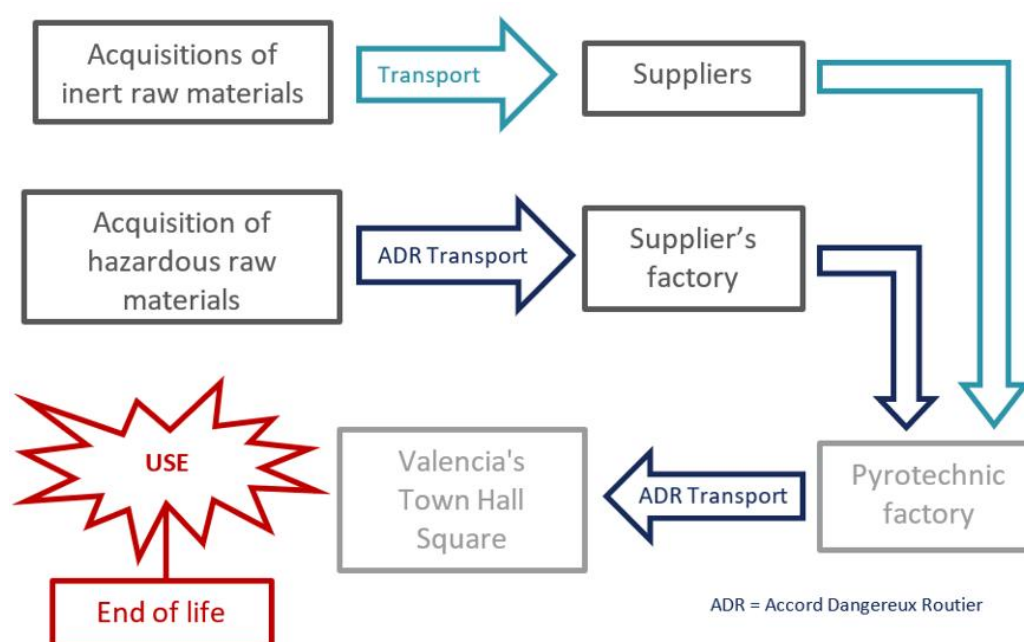


Figure 4.2. Simplified flow diagram of the Life-cycle model.

Two types of fireworks were analysed. One is the Flash Banger (FB) and the other was the pyrotechnic shell. A flash banger is a pyrotechnic article widely used by the general public. Specifically, in Spain they are a significant cultural component as they accompany and enrich many traditional festivities, such as the Fallas in Valencia. There are flash bangers of different categories of general use (F2 and F3) depending on their NEC and, therefore, the associated risk, but in any case all flash bangers have a similar design, which is shown in Figure 4.3.

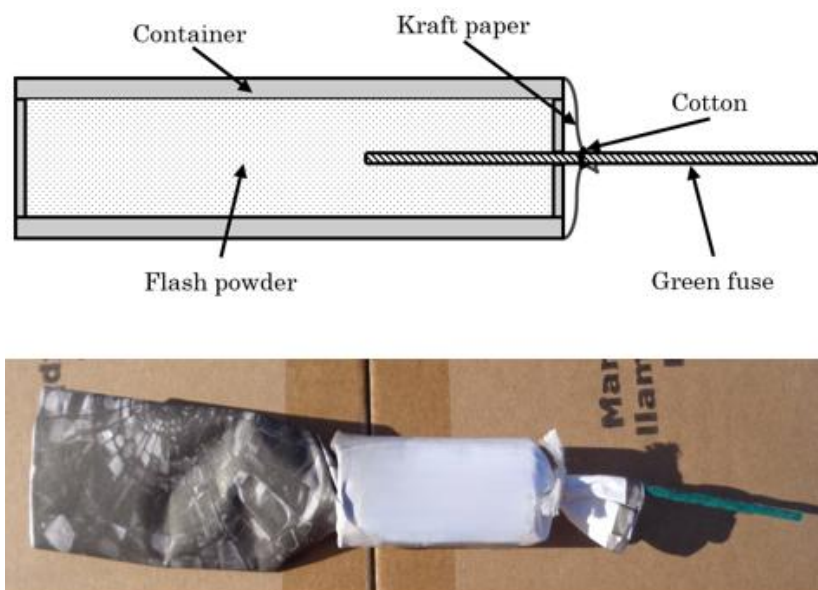


Figure 4.3. Flash banger design.

As can be seen, these articles consist mainly of a non-metallic container, usually made of cardboard, which contains the flash powder (KClO_4 + metal) intended to produce the bursting sound effect. This container tube is finally wrapped in kraft paper.

On the other hand, pyrotechnic shells are the main pyrotechnic articles in professional fireworks shows. This F4 category article (for professional use only) creates a visual and/or sound effect when it reaches a certain height, thanks to the black powder used as a lift powder, where the explosion occurs. Although there are different types of pyrotechnic shells, Figure 4.4 shows a common scheme of this article.

The material that makes up the pyrotechnic shell container can be of different types, although plastic and cardboard predominate. A comparison between a cardboard (Cardboard Pyrotechnic Shell - CPS) and a plastic (Plastic Pyrotechnic Shell - PPS) case was conducted. This analysis was noteworthy because the choice

of packaging could significantly influence the product's environmental impact [142].

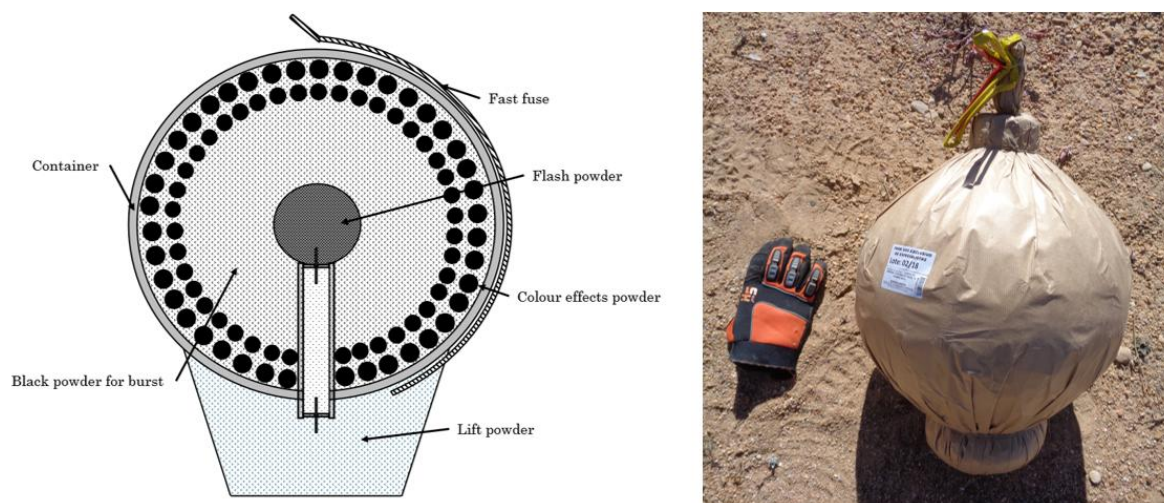


Figure 4.4. Pyrotechnic shell design.

The functional units were defined as shown in Table 4.2. The breakdown of the functional units was shown in Table 4.3. They were chosen based on the recommendations of the standards, analysing the following aspects by the Environmental Footprint methodology: their function, their measurement, their quality level and their lifetime. Detailed flow diagrams for each functional unit can be found in Figure A.1 and A.2 in Annex A.

Table 4.2. Functional units for LCA.

Reference	Analysed product	Functional unit
FB	Flash Banger	A flash banger of 5.15 g
CPS	Cardboard Pyrotechnic Shell	A pyrotechnic cardboard shell of 1,358.15 g
PPS	Plastic Pyrotechnic Shell	A pyrotechnic plastic shell of 1,435.45 g

Life-Cycle Inventory (LCI)

The main system inventory data were developed with the support of industry experts and various manufacturers, although some assumptions were made. Due to this, life cycle analysis was carried out without information from all actors in the value chain of the products under consideration. The secondary data was obtained from the EcoInvent database, version 3.8 [143].

The quantities of material required for the manufacture of the three functional units analysed, which can be seen in Table 4.3, were estimated by modelling standard products that can be found on the market. An important part of the FB is their green fuse as a means of ignition. This product is usually imported from China. Therefore, only its composition and its receipt directly at the factory were taken into account for the study. The analysed flash banger had an additional weight of 0.6 g for this green fuse (0.03 g of S, 0.18 g of C and 0.39 g of KNO₃).

Table 4.3. Quantities of material per functional unit.

	Component	FB (g)	CPS (g)	PPS (g)
Inert material	Cotton	0.05	0.2	0.05
	Paper	1.2	83.7	8.7
	Cardboard	2.4	175.9	----
	Plastic bag	----	1.5	----
	Plastic	----	----	309.7
Hazardous material	Aluminium (Al)	0.26	5.285	5.29
	Magnesium (Mg)	----	152.51	152.51
	Sulphur (S)	0.03	57.0	59.47
	Charcoal (C)	0.18	86.11	89.88
	Barium Carbonate (BaCO ₃)	----	42.28	42.28
	Strontium Carbonate (SrCO ₃)	----	48.32	48.32
	Dextrin	----	26.75	26.86
	Potassium Dichromate (K ₂ Cr ₂ O ₇)	----	6.04	6.04
	Acroids Gum	----	32.50	32.61
	Arabic Gum	----	4.62	4.83
	Potassium Nitrate (KNO ₃)	0.39	325.13	338.61
	Potassium Perchlorate (KClO ₄)	0.64	310.31	310.31
	Total	5.15	1,358.15	1,435.45

The energy input made the difference between the manufacture of flash bangers and the pyrotechnic shells. In the former, there was no energy input flow. This was because the construction of this element in Spain is handcrafted, according to the manufacturers. In contrast, the shells tested consumed energy during the manufacture of the pyrotechnic stars that produced the colour effect. The powder coating of these fireballs was done using a dragee coating machine. The time it took to complete the process of manufacturing the pyrotechnic stars can vary

depending on its speed, the number and size of stars being manufactured simultaneously and the complexity of the design. No real data was available about the actual time of the coating in this sector, so for this analysis, an assumption was made of a working time of 4 hours to achieve 8 kg of product. The consumption of the shell according to the functional unit was 0.6 kWh.

Regarding distribution, since no data on capacity and type was available, neither from value chain actors nor from research, the intermediate data of the typical truck provided by the SimaPro software was chosen. These data represent a 24 tonne truck with emission standards corresponding to Euro 5. The information was grouped by type of supplier (hazardous material and cotton supplier (S1), paper supplier (S2), cardboard supplier (S3) and plastic supplier (S4)) for the first stage, as a finished article for distribution and by type of material and management for the end of life. Data and locations of common suppliers in the pyrotechnic sector and recycling plants that are usually used by pyrotechnic companies located in the Valencian Community were used and can be seen in Table 4.4.

Table 4.4. Transport distances of raw materials.

Material	Supplier to factory (km)	Factory to the firing point (km)	End of life (km)
Hazardous materials	60	40	
Cotton			23
Kraft paper	80		28
Cardboard	70		28
Plastic	30		23

During a fireworks display, the only outflows were considered to be emissions released into the atmosphere and waste management. Fireworks displays emit particles into the atmosphere in the form of smoke from the combustion reactions of the products. The pollutant compounds typically released into the atmosphere include carbon dioxide, carbon monoxide and suspended metal particles. The information used for the theoretical calculation of the emissions of the analysed products was based on the theoretical chemical reactions [18], which can give an idea of the emissions of the articles under study. These analysed pyrotechnic reactions are shown in detail in Table 4.1. The theoretical analysis of the emissions produced by the functional units under study, which were included in the LCA, is shown in Table 4.5.

Table 4.5. Theoretical emissions released by functional units.

Product	Emissions released (g)		
	FB	CPS	PPS
KCl	0.35	165.4	165.4
Al ₂ O ₃	0.63	3.17	3.17
CO ₂	---	318.19	331.29
CO	---	19.08	16.96
N ₂	---	43.34	45.41
K ₂ CO ₃	---	31.38	27.89
K ₂ S	---	145.55	156.49
MgO	---	90.36	90.36

After the explosion of a firework, theoretically, the only waste generated came from inert material. For the analysis, the ideal scenario was considered. It was taken into account that the waste to be treated consisted of all the inert material of each product. Therefore, after the use of the products in the Fallas of Valencia, the municipal waste management was responsible for collecting and transporting them to their final destination: paper, cotton, cardboard and plastic. The simulation envisaged that paper, cardboard and plastic were sent to a sorting facility and be prepared for recycling. Cotton, on the other hand, was taken to a landfill site.

4.2. Assessment of atmospheric emissions

4.2.1. Theoretical analysis of national and international pyrotechnic shows

Since atmospheric emissions were known to be one of the causes of environmental impact and one of the main causes of social criticism to which the pyrotechnic sector is subjected, a detailed theoretical analysis was carried out on the pollutant emissions generated by the combustion of pyrotechnic articles.

Villaviciosa de Odón

The festivities of Villaviciosa de Odón (a municipality belonging to the Community of Madrid) are well known nationally for the fireworks display known as “La Pólvora”. This professional pyrotechnic show is considered the largest and most

famous in the Community of Madrid and one of the most important in Spain, due to the large amount of fireworks that contains and the multitude of people who come to see its sound and visual effects.

The case study in the present research was the pyrotechnic show of 2018. According to the information of the city hall website, the show was composed by approximately 5,000 pyrotechnic devices that included more than 2,000 kg of pyrotechnic compositions that were released into the atmosphere during the show that lasted around 23 minutes. The show was composed by different devices that lead to different colours and effects. Among the generic devices that were found in the show, the main elements were shells, mines, comets or roman candles, which produced colour, whistle or flash effects. Each of the mixtures contains different components and different mass percentages [51].

Table 4.6 provides information regarding the estimated number of devices that composed the pyrotechnic show. As the exact information was not public, the number of devices was estimated based on different smaller shows whose devices amount and types were known, and the effects that were obtained during the festivity.

Table 4.6. Estimated distribution of the pyrotechnics devices used during the festivities of Villaviciosa de Odón.

Pyrotechnic device	Units	NEC ¹
Shells	2,000	1,600 kg
Roman candles	500	187.5 kg
Mines	1,500	150 kg
Comets	1,000	50 kg

The pyrotechnic shells were the fundamental pyrotechnic device of the fireworks display. These pyrotechnic shells, like the rest of the articles that were fired during the fireworks display, present a lift powder, since they were aerial fireworks and after reaching the appropriate height (between 150-200 m) the bursting powder, composed of black powder and flash powder, was in charge of producing the explosion of the container showing the spectator visual effects achieved with the coloured stars and sound effects achieved with the cartridge tubes [19].

¹ Excluding the pyrotechnic composition in the initial fuse or transmitting fuses, according to European Standard.

The amount of pyrotechnic material in the container depends on the calibre of the shells. Estimates made for the study, based on actual data, assumed that 100 mm shells had about 450 g of NEC and 150 mm shells about 1,150 g of NEC. Half of the shells belonged to each of the calibres. Although the amount of pyrotechnic material varied, the percentage of each element remained fixed, these pyrotechnic shells being composed of 17% lift powder, 55% pyrotechnic stars, 17% black powder for burst, 2% flash powder and 9% sound composition. This means that the amount of pyrotechnic matter of each of the compositions contained in the pyrotechnic casing was as shown in Table 4.7.

Table 4.7. NEC per shell studied at the show in Villaviciosa de Odón.

Composition	NEC per composition (g)	
	100 mm calibre shell	150 mm calibre shell
Lift powder	76.5	195.5
Colour effect powder	247.5	632.5
Black powder for burst	76.5	195.5
Flash powder	9	23
Black powder for sound effects	40.5	103.5
Total	450.0	1,150.0

Comets were another pyrotechnic device fired during fireworks displays. They have a single pyrotechnic unit inside the tube that is ejected in a directional manner. The comets analysed in the study had a calibre of 30 mm. Taking as a basis that the composition of a comet is usually 40% lift powder and 60% colour effect, assuming that the comets fired in Villaviciosa de Odón had an NEC of 50 grams, it would mean that each comet had an amount of NEC per composition shown in Table 4.8.

Table 4.8. NEC per comet studied at the show in Villaviciosa de Odón.

Composition	NEC per composition (g)
Lift powder	20
Colour effect powder	30
Total	50.0

Roman candles were a device very similar to comets, in fact, what differentiates them was that this one had several comet units inside the tube that came out in succession with a specific delay [144]. In the case study, half of the units were analysed with 5 shots and the other half with 10 shots. Since the composition was the same as that of the comets, the quantities per item are shown in Table 4.9.

Table 4.9. NEC per roman candle studied at the show in Villaviciosa de Odón.

Composition	NEC per composition (g)	
	5-shots roman candle	10-shots roman candle
Lift powder	100	200
Colour effect powder	150	300
Total	250.0	500.0

The last pyrotechnic unit of the show studied was the mines. They were characterized by having a lift powder inside the container that lifts the pyrotechnic units inside. This one, unlike the comets, had several pyrotechnic units that are expelled simultaneously and can generate at the same time colour, sound and/or opening effects.

Mines contained a larger amount of pyrotechnic units and had a larger calibre than comets and roman candles and in these shows it is usually around 50 mm. A total NEC of 100 g per article was assumed. Of the total pyrotechnic mixture of the article, 40% represented the colour composition of the pyrotechnic stars, 35% composition of the sound effects and 25% lift powder. This gave a unit NEC shown in Table 4.10.

Table 4.10. NEC per mine studied at the show in Villaviciosa de Odón.

Composition	NEC per composition (g)
Lift powder	25
Colour effect powder	40
Black powder for sound effects	35
Total	100.0

Once these data were known and knowing the characteristic reactions of each type of effect, which are shown in Table 4.1, the emissions produced when firing this

spectacle could be calculated. The emissions produced by colour effect powder depended on the compound used for each colour. Red colour came from strontium (Sr), green from barium (Ba), blue from copper (Cu), orange from calcium (Ca) and yellow from sodium (Na). For the case study, it was assumed that all the shells produced a multicolour effect, using the above colours in equal parts. Taking as compounds responsible for colour production strontium, barium and sodium nitrates ($\text{Sr}(\text{NO}_3)_2$, $\text{Ba}(\text{NO}_3)_2$ and NaNO_3) and copper and calcium carbonates (CuCO_3 and CaCO_3), the emissions produced due to the colour production of these substances were calculated. The composition used to create colour effects in pyrotechnics is one of the most complex mixtures, as it requires the occurrence of multiple simultaneous reactions. First, a reaction is triggered that generates the heat necessary for the salt to dissociate and release the substance responsible for producing the colour. The substance absorbs the energy and goes into an excited state, which raises the energy level of the electron. In this state, the electron becomes unstable and releases excess energy in the form of visible light. This phenomenon is known as luminescence. The formulation of the powder for colour effects included 55 % KClO_4 , 16 % dextrin, 9 % magnesium and 20 % of a colour producing salt. The specific reactions corresponding to each of the colour-producing compounds can be seen in Table A.2 of Annex A.

Macy's Independence Day show

Macy's Independence Day show in New York is one of the most important world-famous fireworks shows worldwide. Macy's Department Store organised, through Pyro Spectaculars by Souza (an American pyrotechnics and fireworks company) the nation's largest Independence Day celebration. Several barges firing simultaneously in waterways surrounding New York City are the source of this show. This show was first celebrated on Independence Day on the 4th of July 1976 and in 2022 celebrated its 46th edition, which is the case of study.

According to information provided by the show's organiser, 50 pyrotechnic experts were responsible for firing approximately 1,920 shells per minute for 25 minutes [145]. This represents a total of 48,000 shells fired from five barges across the East River. The exact compositions and quantities of the show were not public, but the same pyrotechnic show structure as in Villaviciosa de Odón show was followed. The same amount of explosive material of each of the compositions and the same percentages of participation in the total mass of the article as in the previous studied show were analysed. The detailed structure of the show and its compositions are defined in Table 4.11.

Table 4.11. Detailed studied design of the Macy's Independence Day show.

Pyrotechnic article		Shells		Mines	Comets	Roman candles	
Calibre (mm)		150	100	50	30	30	
Number of shots		--		--	--	5	10
Articles (units)		24,000	24,000	12,000	36,000	11,520	12,480
NEC (g) / ud.		1,150	450	100	50	250	500
Composition	Lift powder	17 %		25 %	40 %	40 %	
	Colour effects powder	55 %		40 %	60 %	60 %	
	Sound effects powder	9 %		35 %	--	--	
	Black powder for burst	17 %		--	--	--	
	Flash powder	2 %		--	--	--	
Total NEC (kg)		38,400		4,560	3,600	1,200	

The same assumptions were taken into account for the colour compositions, estimating that all items produced multicolour effects. In this way, knowing the characteristic reactions of each type of effect, which are shown in Table 4.1, it was possible to calculate the emissions produced by this show.

4.2.2. Emissions produced by socially accepted emitters

Pyrotechnics generate certain pollutant emissions into the atmosphere that can influence air quality. However, fireworks displays usually occur in specific circumstances, associated with once-a-year celebrations. In contrast, there are a multitude of pollutant emitters that produce considerable amounts of GHG and other pollutants constantly, every day of the year. Therefore, a theoretical analysis and comparison of the pollutant emissions released into the atmosphere by some of these major emitters is carried out. This comparison between everyday emitters and fireworks shows contextualises the environmental impact of pyrotechnics in relation to other sources of pollutant emissions, providing a more objective view of their actual contribution to air pollution.

Internal combustion engines that circulate inside the ring road of Madrid

The in force regulations, referring to all vehicles registered after September 1st, 2015, compel all vehicle manufacturers to comply with emission limits since the year 2021. This European regulation classifies different levels of emissions depending on the fuel of the vehicle (diesel or gasoline) and depending on the masses and use of the vehicles.

The study case focused on private cars that were used every day for passenger displacements through Madrid M-30 ring road. For this type of vehicle, the maximum acceptable emissions were the following shown in Table 4.12.

Table 4.12. Emission limits according to standard EURO 6 for private cars [146].

Type of fuel	CO ₂ (mg/km)	CO (mg/km)	NO _x (mg/km)
Diesel	95	500	80
Gasoline	95	1,000	60

In the years prior to its implementation, manufacturers were adapting to the Euro 6 regulations. The case study focused on the levels of 2018 in order to have a proper comparison with the pyrotechnic show of the case study.

The real CO₂ emissions were measured according to the WLTP (World-wide harmonized Light duty Testing Procedure) developed by the United Nations Economic Commission for Europe (UNECE). This procedure officially applied to all new cars sold in the European Union from September 2018. The WLTP replaced the old NEDC (New European Driving Cycle), which had been criticised for being too lenient and for not accurately reflecting actual driving conditions. This procedure offered more realistic data by taking into account more dynamic driving behaviour, higher speeds and longer test distances. The obtained results from WLTP in 2018, could be approximated through an average that was found to be greater than the values established for these CO₂ emissions in EURO 6 standard, being approximately 120 mg/km for diesel vehicles and 160 mg/km for gasoline vehicles [147].

Taking as real values of CO emissions, generated by internal combustion vehicles in 2018 the limits established by Euro 6 regulations, the emissions produced by the vehicles that circulate through the ring road M-30 could be calculated.

According to several studies, the average distance that a person travels daily in order to reach the workplace could be estimated at 11.8 km, which meant 23.6 km per day [148]. On the other hand, EMESA (M-30 Maintenance and Exploitation Company) estimated that, during 2019, approximately 500,000,000 vehicles circulated through M-30 ring road, which led to an average of 1,369,863 vehicles per day. Moreover, in Spain without taking into account vehicles with other engines, which are currently of little relevance, it could be estimated that 65% of the total vehicles used a diesel engine, while the 35% remaining corresponded to gasoline engines [149]. According to these values, a daily traffic of 890,411 diesel vehicles and 479,452 gasoline vehicles took place in the M-30 ring road.

Commercial aircrafts

Commercial aircrafts intended for passenger transport are means of transport that is increasingly widespread and used in society. This leads to more flights which, at the same time, leads to higher fuel consumption and, therefore, higher emissions into the atmosphere.

Aircraft use turbofan-type engines, the latest generation of aviation engines, which use jet kerosene fuel. Fuel consumption in aviation suffers great variation depending on the route, the load transported or the number of passengers. Therefore, the amount of emissions produced significantly varies. However, according to data from The International Council on Clean Transportation (ICCT) in 2018, emissions of CO₂ released from commercial aircrafts can be estimated, depending on the distance travelled on the route, in the values that can be seen in Table 4.13.

From this data it could be noticed that, the lower the route distance, the greater the emissions per kilometre, due to the additional fuel consumed required in the take off and landing.

Table 4.13. Average carbon dioxide (CO₂) emissions in commercial aircraft depending on the route distance [150].

Distance	Average CO ₂ emissions (g CO ₂ /passenger·km)
< 500 km	155
Between 500 and 1,500 km	110
Between 1,500 and 4,000 km	95
> 4,000 km	75

The present case study focused on the CO₂ emissions of a BOEING 737-700 aircraft, with a maximum load capacity of 149 passengers, intended for short and medium distance flights. The flights studied originated from Madrid-Barajas Adolfo Suárez Airport and Valencia Airport (286.1 km), Stansted Airport (London) (1,263.5 km) and Moscow-Sheremetyevo International Airport (3,439.9 km) were the considered destinations. In this way, carbon dioxide emissions could be calculated for different flights depending on their distance.

4.3. Analysis of the effect of sound on animal welfare

4.3.1. Sound attenuation. Articles for sale to the public

Different European veterinary associations suggest that limiting the maximum sound level of pyrotechnics to 90 dB(AI) at the safety distance would be a particularly relevant measure that could lead to significant improvements in the welfare of animals when are exposed to the sound effects [118]. This value is not obtained by testing, so a detailed analysis of the most important generic types of pyrotechnic article is proposed, in order to verify the basis for this value and to establish the distances needed to reach this sound pressure level as a function of sound attenuation under different circumstances.

In this first study, pyrotechnic articles for sale to the public (categories F1, F2 and F3) were analysed in a theoretical-practical way, since they have the highest volume of use within the total and present the greatest difficulty in controlling their use, due to the existing freedom in terms of firing locations, times, etc. Items belonging to these categories are those that are accessible to consumers without the need for special knowledge, only by meeting a minimum age that varies according to the category [151]. The higher the category, the more dangerous the item is.

Experimental analysis

The aim of the experimental study was to obtain real sound pressure level values for the same pyrotechnic article at different distances, in order to establish the real attenuation ratio of each article. In this way, data was obtained on the effect of various factors such as the surface on which the sound source was located, the wind, the air temperature, the presence of barriers or the sound absorption by the

ground in terrestrial articles, since the ground act as a solid obstacle, reflecting a fraction of the acoustic energy and absorbing the rest.

Materials

In order to carry out this study, pyrotechnic articles from the different categories for sale to the public were used again, as well as different products (fountain, banger, rocket...) that produced different effects. In this way, the aim was to achieve results that cover the entire pyrotechnic catalogue currently on the market. The different articles tested are shown in Table 4.14.

Table 4.14. Samples tested for experimental analysis of sound attenuation.

Category	Generic type	NEC (g) per unit
F1 (indoor use)	Hand-held sparkler	0.5
F1	Fountain	1.4
	Table bomb	1.2
	Ground spinner	0.4
	Throwdown	0.015
	Snap	0.015
	Crackling granules	2.9
F2	Flash banger	0.35
	Fountain #1	4.5
	Flash banger	0.1
	Battery of shot tubes	13.75
	Combination of fountains and shot tube	157.8
	Spinner	2.14
	Roman Candle	5.3
	Mini rocket #1	0.3
	Mini rocket #2	0.25
	Ground spinner	3.4
	Fountain #2	60.7
	Battery of fountains	26.8
	Combination of shot tubes and mines	494.0
F3	Flash banger	0.92
	Rocket	17.1
	Battery of shot tubes	469.7

Equipment

The tests were carried out at Laboratorio Oficial José María de Madariaga (LOM)'s facilities located in Cuenca, where it had an authorised laboratory for the testing of pyrotechnic products. This equipment (which also belongs to the laboratory) included a sound level meter to measure the sound pressure level emitted by the articles, a digital anemometer to measure wind speed and ambient temperature, and a laser distance meter and measuring tape used to measure the different distances at which the sound level meter could be placed. The equipment used was correctly calibrated, verified and in optimum condition for use at the time of the tests. Equipment models are shown in Table 4.15.

Table 4.15. Equipment for sound attenuation tests. Articles for sale to the public.

Equipment	Model
Sound level meter	2250-Ligth BRÜEL & KJAER
Laser distance meter	LEICA DISTO D8
Anemometer	SMART SENSOR AS806
Measuring tape	RS AMIDATA

Specifically, the sound level meter used in the tests was the Brüel & Kjaer portable analyser model 2250-L. This equipment complied with the IEC 61672-1 standard, as it belonged to class 1 and had an open field microphone type 4950. In addition, it was equipped with a ZC-0032 preamplifier.

Methodology

The tests were carried out in November under the following environmental conditions:

- Temperature: 4.3 °C
- Relative humidity: 70%
- Wind speed and direction: 2.125 m/s NE direction.

In order to obtain the noise attenuation of the different pyrotechnic articles tested, several samples of each of these were fired at different distances previously established.

With a distance meter and a measuring tape, a total of twelve measuring points were located at different distances from the firing points. These points from which

the sound pressure level was measured are located at 1 m, 8 m and 15 m (the first three of which coincides with the safety distances established in the standard for articles of categories F1, F2 and F3 respectively), 2 m, 5 m, 10 m, 25 m, 30 m, 50 m, 100 m and 200 m. The first eleven points measured in an open field without any type of obstacle, one at each of the distances indicated above, were referenced from the firing point called PD1 and are shown in Figure 4.5. The figure represents an aerial photograph taken from Google Maps in which, due to its age, the concrete firing surface, in accordance with the regulations, is not located. This concrete surface, with a radius of 15 metres, has been represented by yellow circles that make visual reference to the safety distances indicated in the regulations for the different categories of pyrotechnic articles.



Figure 4.5. Location of firing point PD1 and the corresponding measuring points used in the experimental study. Aerial photo from Google Maps.

At a distance of 50 m from the firing point PD2, the last of the measurement points was located inside the central building of the installation, in order to simulate a possible real situation of the receiver inside a house. This measurement point was located in front of a window from which the firing point was visually observed, as it was considered to be the most critical point exposed to sound inside the room.

This window remained closed during the tests. A schematic of the location of the points is shown in Figure 4.6.



Figure 4.6. Location of firing point PD2 and the corresponding measuring point used in the experimental study. Aerial photo from Google Maps

Once the firing and measuring points were located, the sound level meter was placed on a tripod so that it was stable and at a height of 1 m above ground level, as indicated in the test methods of the pyrotechnic articles regulations.

Firstly, a sample of each of the articles was fired at the safety distance currently established by the EN 15947:2022 standard and, depending on the sound pressure level reached, the different distances at which the rest of the samples were tested were established. The number of samples tested for each item depended on the sound pressure level obtained, as the higher the noise intensity, the more samples were tested at increasingly greater distances, in order to obtain the most accurate attenuation ratio possible. Figure 4.7 shows photographs taken during the tests from different firing points.



Figure 4.7. Photographs from the measurement points. Top left: 50 m. Top right: 100 m. Bottom left: 200 m. Bottom right: 50 m inside the building.

Once the tests were completed, the Measurement Partner Suite BZ-5503 post-processing software was used to analyse the values obtained.

Theoretical analysis

This study was based on Sound Pressure Level (SPL) data obtained for each of the different pyrotechnic articles analysed in the experimental study at the corresponding safety distance, depending on the category of the article. These safety distances corresponded to 1 m for category F1, 8 m for category F2 and 15 m for category F3. The aim of this study is to compare the theoretical attenuation of pyrotechnic articles with their actual attenuation in order to confirm the correct use of the theoretical equation in the sound attenuation calculation.

Methodology

In order to calculate the new safety distance at which the desired sound pressure level value of 90 dB(AI) could be achieved, and the sound pressure level at any distance, the theoretical calculation method for safety/protection distances was used, as set out in Annex C of EN 16261-3:2012 [152] and shown in Eq. (2):

$$R_s = 10^{\left(\log_{10} R_m - \frac{L_s - L_m}{20} \frac{dB}{dB}\right)} \quad (2)$$

Where:

R_s is the minimum safety distance.

R_m is the measurement distance (varies according to category).

L_s is the sound pressure limit (90 dB(AI) in the case study).

L_m is the sound pressure level, measured at the measurement point.

4.3.2. Influence of climatic conditions

One of the factors that can affect the attenuation of the sound pressure level is the medium through which it propagates. According to Brüel & Kjaer an HBK company [153], there are a number of atmospheric and meteorological factors that influence the propagation of sound. The first of these is the wind, both its direction and speed. When the wind blows from the noise source towards the receiver, higher noise levels can be observed, and the higher the wind speed, the higher the results will be. Other factors affecting noise attenuation are temperature and humidity [153].

In this analysis, the experimental tests of chapter 4.3.1 were repeated, evaluating the sound attenuation at another time of the year, with opposite weather conditions, to analyse the actual influence of these factors. These tests were carried out in May, in spring. Table 4.16 shows the different weather conditions obtained in the two test periods.

Table 4.16. Equipment for sound attenuation tests.

Weather conditions	Tests in November	Tests in May
Temperature (°C)	4.3	15.5
Relative humidity (%)	70	35
Wind speed (m/s)	2.125	3.152
Wind direction	NE	NE

The measuring equipment used and the test methodology were repeated. For the samples tested, of the total of 23 different products tested in the first study, 21 were acquired. The remaining two families were replaced by others of the same

generic type, category, effect, as well as an NEC and a design as similar as possible. Table 4.17 shows the samples tested, indicating in blue the two items used as replacements.

Table 4.17. Tested samples for the analysis of climatic influence on sound attenuation.

Category	Generic type	NEC (g) per unit
F1 (indoor use)	Hand-held sparkler	0.5
F1	Fountain	1.4
	Table bomb	1.2
	Ground spinner	0.4
	Throwdown	0.015
	Snap	0.015
	Crackling granules	2.9
F2	Flash banger	0.35
	Fountain	4.5
	Flash banger	0.1
	Battery of shot tubes	44.55
	Combination of fountains and shot tube	157.8
	Spinner	2.14
	Roman Candle	5.3
	Mini rocket	0.3
	Mini rocket	0.25
	Ground spinner	3.4
	Fountain	60.7
	Battery of fountains	26.8
	Combination of shot tubes and mines	494.0
F3	Flash banger	0.98
	Rocket	17.1
	Battery of shot tubes	469.7

The F2 category battery of shot tubes was replaced by the same article, but with a higher number of shot tubes, so it had a higher NEC although they reached the same maximum SPL. The F3 category flash banger was replaced by another with the same design and very similar NEC.

4.3.3. Sound attenuation. Professional fireworks shows

These tests again seek to analyse sound attenuation in order to estimate the required distance where the spectator perceives a sound pressure level of

90 dB(AI), as established by the RSPCA. In this case, measurements were carried out in two fireworks displays, which took place in a occasional manner, controlled in place and time, were fired by professionals with prior notice to the relevant authorities and were regulated by existing safety regulations.

Equipment

Different measuring equipment was used, located at different distances from the firing zone and in different circumstances, with a direct view or with buildings as a barrier. The equipment used for noise measurement was the sound level meter described above and dosimeters. The equipment used can be seen in detail in Table 4.18 and Table 4.19, for each of the shows under study. These devices were in continuous measurement from moments before the start of the show until moments after the end of the show, in order to observe the sound pressure level curve during the show and the difference with the sound pressure level measured pre-show and post-show.

Table 4.18. Equipment for sound attenuation tests. Ajalvir fireworks show.

Equipment	Model	Abbrev.
Sound	2250-Ligth BRÜEL & KJAER	SON
Dosimeter	NoisePen PULSAR	DOS1
Dosimeter	NoisePen PULSAR	DOS2
Dosimeter	4445 BRÜEL & KJAER	DOS3

Table 4.19. Equipment for sound attenuation tests. La Mascletá.

Equipment	Model	Abbrev.
Sound	2250-Ligth BRÜEL & KJAER	SON
Dosimeter	NoisePen PULSAR	DOS1
Dosimeter	4445 BRÜEL & KJAER	DOS2
Dosimeter	NoisePen PULSAR	DOS3
Dosimeter	DC-112 CESVA	DOS4

The dosimeters were carried by members of the work team and placed on the upper torso, as close as possible to the ear. For its part, the sound level meter, as indicated in the test methods of the pyrotechnical regulations, was placed on a tripod so that

it was stable and at a height of 1 m above ground level. Prior to the start of the measurement with the sound level meter, the equipment was checked by means of a portable sound calibrator, as shown in Figure 4.8, which was calibrated, verified and in optimum condition for use. This 3M sound calibrator, model AC-300, belongs to the LOM and has an uncertainty of 0.33 dB.



Figure 4.8. Verification of the sound level meter by sound calibrator.

The sound level meter was a more complete equipment than the dosimeter, as it has the capacity to measure the sound pressure level in different programmable scales and weightings, which cover practically the entire sound spectrum. In addition to the Impulsive time scale, defined in chapter 1.4.3 Sound of effects of pyrotechnics, the Equivalent (L_{eq}) and Peak (L_{peak}) time scales are the most common. The former represents the average sound level for a given period, while the latter measures the peak value of the sound pressure using a smaller time constant than the Impulsive scale. In addition, the C-weighting approximately represents the response of the human ear when exposed to relatively high sound levels, and is therefore mainly used to evaluate peak values at high sound pressure levels.

For their part, as a general rule, dosimeters were equipment used to measure noise oriented towards human safety, so they recorded the two scales indicated in RD 286/2006, of 10 March, on the protection of the health and safety of workers against risks related to exposure to noise as a threshold for the human ear, which are LA_{eq} and LC_{peak} [154]. Therefore, it was necessary to transform the values measured by

the dosimeter on the LC_{peak} scale to the LAI_{max} scale, in order to be able to make comparisons with the values measured on the sound level meter, which provided this scale. Both the impulse and peak time weighting represent the maximum value of the sound in a given time, the only difference being the exposure time or time constant during which the measurement is taken [155].

This transformation took into account the frequency ratio and dB difference as a function of weighting as shown in Figure 4.9.

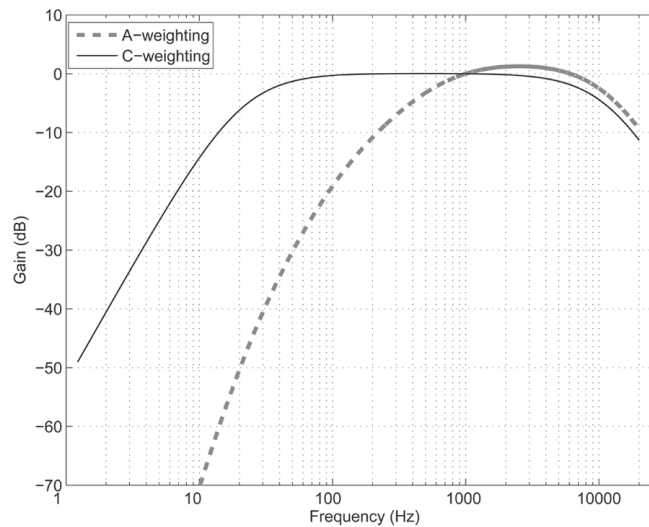


Figure 4.9. Relationship between frequency weightings A and C [155].

The sound level meter provided for the same instant the noise level measured in both LAI_{max} and LC_{peak} scale so that the difference of one versus the other could be calculated. This difference will be constant for the same noise as it moves in space, since the frequency will be the same (assuming the ideal case). It was assumed that the maximum noise measured at each of the devices during the measurement of the show was that emitted by the show itself. Therefore, knowing this difference between the two values measured in the sound level meter, the noise values on the LAI_{max} scale in the dosimeters could be estimated.

Ajalvir fireworks show

The first of the pyrotechnic shows analysed in this study was the fireworks display in Ajalvir, in February 2022, on the occasion of the patronal festival. The show had a total duration of approximately 12 minutes, during which shells, mines and banger shells were fired, creating a colourful and entertaining spectacle, observed

although it was a wide street and the noise came directly from the emitting source without any kind of direct obstacle. The second dosimeter was located at the edge of a parcel of land, at a distance of 295 m from the firing zone. In this case, there was an area of industrial buildings which prevented seeing the firing point but did not hinder the viewing of the show or the reception of the sound, as the fireworks were entirely aerial. The locations of the measuring equipment can be seen in Figure 4.11.



Figure 4.11. Photographs of the locations of the measuring equipment at the fireworks show in Ajalvir. Left: sound level meter. Right: dosimeter 3.

Both dosimeters 1 and 2 showed direct exposure to noise and in locations with few spectators, as was the case in the area of the sound level meter. On the other hand, for dosimeter 3, the location was the Plaza de la Villa de Ajalvir, located 562 m from the firing area. In this location, at the time of the show, there were crowds of people, as well as buildings of considerable height around the dosimeter, such as the church, which could be an obstacle to the noise.

Mascletá Plaza del Ayuntamiento de Valencia

The second professional show measurement was performed at one of the Mascletá held in the Plaza del Ayuntamiento in March 2022, during the celebration of the Las Fallas festival. The Mascletá of Valencia is one of the largest known pyrotechnic sound shows in the world and always follows a similar structure as shown in detail in Annex B.

The Mascletà on which the measurement was made, had a total duration of approximately 310 seconds, with an NEC of almost 150 kg from shells, batteries, flash bangers, etc. The maximum calibre of this Mascletà was 50 mm for aerial fireworks and 60 mm for ground fireworks.

In order to be able to make a comparison between the sound pressure level values obtained at different measurement locations, a total of four dosimeters and one sound level meter were used, as shown in Table 4.19. The distribution of the measuring equipment during the show is shown in Figure 4.12.

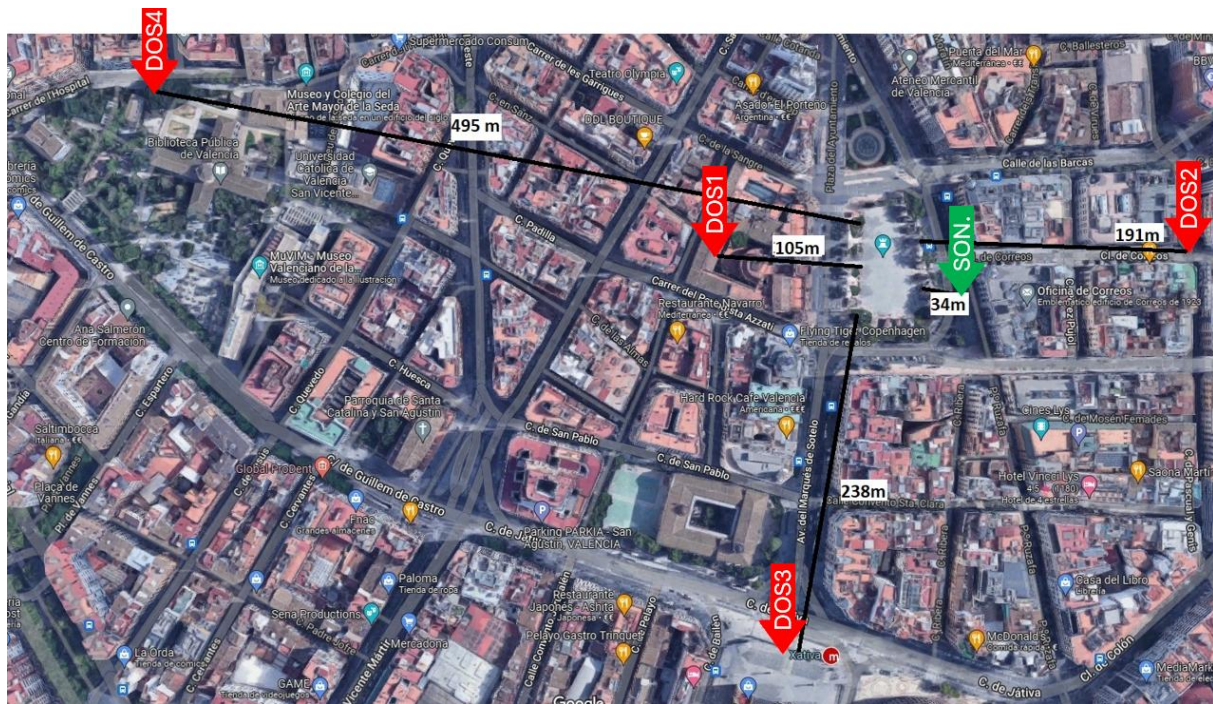


Figure 4.12. Firing point and measuring equipment location at the Mascletà.

As can be seen, the sound level meter (SON.) was located 34 m away from the show, just in front of the audience safety zone (safety distance established in accordance with the provisions of ITC 8 of RD 989/2015 [26]), so that the values obtained could be assimilated to the sound pressure levels obtained by spectators who approach the front line to watch the show. In this location, it was possible to watch the show directly, without any obstacles. The first dosimeter (DOS1) was located 105 m away. This equipment was placed on a table in a room inside the Town Hall, with no direct view of the square, which had the windows closed during the show, simulating a possible nearby house. The second dosimeter (DOS2) was located at a crossroads (Carrer de Correus with Carrer de Pascual y Genís) 191 m from the firing area. It had a direct view of the spectacle but was surrounded by tall

buildings in a somewhat narrow area. The third dosimeter (DOS3) was located at the gate of the Estación del Norte at 238m. This point also had a direct, although not complete, view and was located in a very large area in the front yard of the station, to know the influence of open spaces. Finally, the fourth dosimeter (DOS4) was located in the park of the Hospital de los Pobres Inocentes at 495 m distance. This point did not have a view of the show, being mainly terrestrial and surrounded by tall buildings in the direction of the show, simulating a spectator who was not directly looking at the show. At this point, there was practically no crowding, as at dosimeter 1, as it was inside the building. In contrast, at the other points, there was a large influx of spectators. Figure 4.13 shows the view of the show from different measurement points.



Figure 4.13. Photographs of the locations of the measuring equipment at the Mascletà.
Top: Dosimeter 1. Bottom: Sound level meter.

4.3.4. Sound comparison with everyday emitters

Since the value of 90 dB(AI) given in the RSPCA ‘Bang out of Order’ report [118] is based on experience and not on tests, the sound spectrum generated by different everyday emitters was analysed in order to verify the basis of this value. It was compared with the sound spectrum of several flash bangers, whose main objective is the production of a burst.

Measurements were made at different locations, exposed to different sound emitters and with a Brüel & Kjaer portable sound level meter model 2250-L. The specifications of the equipment are shown in chapter 4.3.1 Sound attenuation.

Articles for sale to the public. During the tests, the sound intensity (maximum SPL) on the LAI_{max} scale and the frequencies associated with the different emitters were recorded, in order to define differences between pyrotechnic articles and everyday sound emitters. Flash bangers tested are described in Table 4.20.

Table 4.20. Flash bangers tested in comparison to usual emitters.

Category	Flash banger	NEC (g) per unit
F2	#1	0.08
	#2	0.1
	#3	0.2
F3	#4	0.98
	#5	1.6

Five samples of each of the flash bangers were fired. The 2250-Ligth sound level meter was used, following the pyrotechnics test regulations and using the required safety distance depending on the category.

In addition, the sound intensity and frequency of different everyday emitters were recorded. First, a whistle (used to regulate traffic) and the horn of a vehicle were tested. For these specific sounds, two types of tests were carried out. The first one consisted of 5 measurements of a sporadic and punctual sound. The second consisted of 5 measurements of a sound emitted over a longer period of time. The sound level meter was placed 2 m away from the emitter, simulating a real situation.

The following two measurement points were located in urban areas. The first of the measurement locations was located at Calle Santa Engracia with the Glorieta de Cuatro Caminos subway in Madrid. This intersection was characterised by its high traffic and abundance of passers-by, although at the time of the tests, due to the time of day, the flow was not so high. The second location was in an interior space, specifically at Cuatro Caminos station on the platform of line 1. For these measurements, the sound level meter distance of 2 m was repeated.

At the last location analysed, a measurement of the dog's own barking was carried out. To carry out these measurements, a facility with several kennels was used, where a total of 8 dogs were kept, six of them medium-sized warren hound dogs and the other two larger Labradors. The sound level meter was placed at a distance of 8 m from the kennels, although to compare the values obtained with reality,

using Eq. (1), a correction was applied that provides the value corresponding to 0.5 m away.

Photographs detailing the different measurement locations can be found in Figure B.1 in Annex B.

4.4. Alternative compositions

In order to establish alternative compositions to conventional powder, reduce its environmental impact and address its social challenges, two possible substitutes were evaluated, nitrocellulose and the addition of inert materials.

4.4.1. Theoretical emissions comparison between nitrocellulose and traditional powder

Individual articles

According to EN 15947:2022-5, fountains and table bombs or mines without pyrotechnic objects inside are the only fireworks that can use nitrocellulose, always with a nitrogen content lower than 12.6% [79].

A theoretical emissions comparison was made between these types of fireworks, using both conventional black and perchlorate powder and nitrocellulose. This analysis is carried out to analyse the differences in pollutant emissions between these compositions and assess their potential environmental impact.

In the case of table bombs and mines, nitrocellulose was used as a lifting powder, thus acting as a substitute for black powder. The amount of nitrocellulose as propellant depends on the diameter of the container and the gross weight of the objects inside the devices. However, it can be estimated as 0.4% of the device's gross weight. Considering this estimation, for a 200 g gross weight table bomb/mine the nitrocellulose amount should be 0.8 g. The same amount of black powder was considered.

The reaction generated by the black lift powder is shown in Table 4.1. On the other hand, the nitrocellulose thermal decomposition reaction, based on its main products [156], [157], is defined in Eq. (3):



In the case of fountains, nitrocellulose is used as a substitute for the potassium perchlorate that accompanies the colour producing composition. According to the regulations, the maximum NEC for this type of fountain is 7.5 g, so taking this value as a reference and assuming 80% nitrocellulose (with a nitrogen content below 12.6%), this means that 6 g of this composition was used. On the other hand, the traditional powder reaction was an oxidizing/fuel reaction of potassium perchlorate (oxidizing) and dextrin (fuel). In this reaction, the percentages estimated were 58% for perchlorate (4.35 g) and 22% for dextrin (1.65 g). This reaction is detailed in Table 4.1.

Fireworks show

Previous research has studied the application of nitrocellulose as a propellant [72], [84], so the use of this composition in a professional pyrotechnic show, replacing black powder, is analysed.

The show analysed is the Macy's Independence Day show, knowing the background information detailed in chapter 4.2 Assessment of atmospheric emissions - Subsection 'Macy's Independence Day show'. Taking into account only the lift powder, which was composed of black powder, it was envisaged to replace 9,732 kg of black powder used as a propellant with nitrocellulose. Therefore, it was assumed that this total amount was replaced by nitrocellulose and the emissions were calculated theoretically, comparing the obtained results. A 1:1 substitution ratio was used, assuming that the same amount of nitrocellulose was sufficient to replace black powder and achieve the desired effects. This assumption allowed for a simpler direct comparison of their environmental impact.

The composition of the black powder used as lift powder is 78% potassium nitrate, 16% carbon and 6% sulphur, and its combustion reaction is shown in Table 4.1. The thermal decomposition reaction used for the analysis is shown in Eq. (3).

4.4.2. Experimental emissions test with nitrocellulose and inert materials

Equipment

These tests make it possible to compare the results obtained in the theoretical analysis and, therefore, to confirm the environmental impact assessment of each of the compositions. The emissions were recorded by an Emerson XStreamIR mobile tower gas analyser belonging to the LOM's gas detector laboratory, which

can be seen in Figure 4.14. The operation of this equipment was based on physicochemical parameters, as the sensors react to changes in the analysed gases and emit a signal which is interpreted with a measurement. Although the equipment was calibrated, the measurements were verified using a 300 ppm CO gas bottle and a 20% vol. CO₂ gas bottle.



Figure 4.14. Emerson XStreamIR mobile tower gas analyser.

The inlet flow of the gas analyser was connected to the single outlet of a hermetic reactor by means of a suction tube. This reactor had a volume of 10L. The samples evaluated in each test were placed inside the reactor. Once the sample was ignited through the ignition mean of the pyrotechnic article, the reactor shut down quickly before the device began to release gases. This ensures that, because the sample was in a hermetic container, the gases generated did not escape to the outside, but were confined in the reactor until the analyser pump was activated and drew them out through the suction tube. When the pump was activated, the gases released by the fountains were directed to the analyser, where the CO and CO₂ sensors recorded the concentrations of each gas in the inlet flow, expressed in ppm for CO and in %vol. for CO₂. The measure provided by the analyser was considered reliable when the measurement had reached a steady state.

The input flow to the analyser did not come exclusively from the gases emitted by the combustion of the fountains, as the tests were performed in an atmosphere of air trapped inside the reactor once it was closed. This made it possible to replicate

a situation similar to that of pyrotechnic articles when fired in an open space. It should be noted that, in addition to the gases generated by the combustion of the pyrotechnic composition, the reactor also collected the emissions produced by the ignition fuse. Although their impact was minor compared to the rest of the emissions, it was important to note that they can influence the results obtained.

Nitrocellulose and perchlorate compounds

An evaluation of environmental emissions by comparing nitrocellulose with perchlorate compounds, one of the most polluting compounds in pyrotechnics, was carried out by experimental tests measuring carbon monoxide and carbon dioxide.

As indicated in the theoretical analysis, F1 category fountains for indoor use are the only articles that can be found on the market with nitrocellulose or perchlorate compositions. Both compositions accompany those dedicated to producing the colour effects or sparks.

Five different F1 category fountains and one F2 category fountain, from different manufacturers and compositions, which can be seen in Table 4.21, were tested. Three of them were mainly composed of nitrocellulose, while the other three were based on potassium perchlorate compositions.

Table 4.21. Fountains samples for the emissions tests.

Samples	Type of article	Composition	Category	Ignition means	NEC (g)
A	Fountain	Nitrocellulose	F1	Sealing paper	2.2
B	Fountain	Nitrocellulose	F1	Sealing paper	4.1
C	Fountain	Nitrocellulose	F1	Sealing paper	4.1
D	Fountain	Perchlorate/metal	F1	Protruding fuse	1.4
E	Fountain	Perchlorate/metal	F1	Protruding fuse	6.1
F	Fountain	Perchlorate/metal	F2	Protruding fuse	4.5

Samples A and B came from the same manufacturer and contain the same composition, although different NEC, while sample C came from a different manufacturer. Nitrocellulose samples were characterised by the use of sealing paper as the ignition mean. Samples D, E and F represented different compositions from different manufacturers, based on perchlorate/metal, with which to compare the environmental impact of both compositions. The samples analysed were carefully selected, avoiding those with scratches, tears or signs that part of the composition may have been lost.

Tests were repeated twice for each sample in order to obtain reliable measures. Each test was carried out with one unit of each of the samples besides the tests on sample D, for which the test was carried out using two units to produce enough gas stream, thereby increasing the NEC to 2.8 g.

Flash powder alternatives

In order to analyse possible alternatives to traditional flash powder, the compositions presented in Table 4.22 are subjected to different tests.

Table 4.22. Composition of flash powder alternatives tested.

Abrevy.	Type	Composition
FP	Original Flash Powder	Perchlorate / metal
YN	Nitrocellulose	Yellow nitrocellulose
WN		White nitrocellulose
10B	Flash powder with inerts	10% Sodium Bicarbonate
20B		20% Sodium Bicarbonate
10G		10% Recycled Glass
20G		20% Recycled Glass

The original flash powder, consisting of 80% potassium perchlorate and 20% aluminium, was used as a reference. The two samples of nitrocellulose analysed came from different suppliers, with the one called white nitrocellulose being purer than the one called yellow nitrocellulose, which had a higher impurity content. Finally, two well-known inert materials such as sodium bicarbonate and glass powder were used to see their influence on the bursting and opening effects generated by the flash powder. Sodium bicarbonate (NaHCO_3) is one of the most studied and commercially available inert materials, while the use of recycled glass dust contributes to the circular economy. The particle size used for sodium bicarbonate was less than 300 μm , while glass powder was screened at 700 μm . These inert materials were added to the original flash powder composition in concentrations of 10% and 20% (w/w).

One of the main effects of flash powder is the burst and its use is widespread worldwide in pyrotechnic shells, where it achieves the opening of the article giving rise to its characteristic visual effects. Due to the technical complexity of the shells, in order to test the compositions described above, category F2 flash bangers were used as test samples. Three bangers, from different suppliers, with different NEC and similar designs, were used as containers for the compositions under study. For

this purpose, the bangers were previously emptied of their initial composition, removing one of their gypsum plugs and filled with the compositions to be analysed. The charge of the new banger was called New Net Explosive Content (NNEC). The plug removed at the beginning was rebuilt. Table 4.23 shows in detail the different flash bangers used in the tests and their initial NEC and Table 4.24 shows the NNEC of each of the flash bangers depending on the composition under study.

Table 4.23. Flash bangers used as containers.

Sample	Type of article	Composition	Category	NEC (g)
A	Banger	Perchlorate / metal	F2	0.08
B	Banger	Perchlorate / metal	F2	0.1
C	Banger	Perchlorate / metal	F2	0.2

Table 4.24. NNEC compositions for the tests.

Sample	NNEC (g)	Composition	Flash powder (g)	Nitrocellulose (g)	Inerts (g)
A	0.08	FP	0.08	---	---
		YN / WN	---	0.08	---
		10B / 10G	0.072	---	0.008
		20B / 20G	0.064	---	0.016
B	0.1	FP	0.1	---	---
		YN / WN	---	0.1	---
		10B / 10G	0.09	---	0.01
		20B / 20G	0.01	---	0.02
C	0.2	FP	0.2	---	---
		YN / WN	---	0.2	---
		10B / 10G	0.18	---	0.02
		20B / 20G	0.16	---	0.04

The first test consisted of an evaluation of the CO and CO₂ emissions of the different compositions, following the methodology described above. Two measurements were made for each composition and sample, each involving one banger. In this way, the aim was to represent reliable results.

4.4.3. Sound pressure level tests of flash powder alternatives

Although flash powder is sometimes used as a composition for the production of sound, in the case of pyrotechnic shells, the most important article in the pyrotechnic sector, this is not flash powder main use. Nevertheless, the sound levels reached during the firing of this type of article, as a result of opening it at the desired height, can be annoying in urban areas [158]. The different compositions shown in Table 4.22, used as alternatives of flash powder, were subjected to sound pressure level measurements.

The Brüel & Kjaer portable sound level meter model 2250-L was used for the tests. The specifications of the equipment are shown in chapter 4.3.1 Sound attenuation. Articles for sale to the public - Subsection 'Experimental analysis'. The measurements were carried out in accordance with the pyrotechnical standard EN 15947-4:2015, where the safety distance for category F2 articles was 8 m from the firing point to the spectator. The samples were fired on a concrete surface and the sound level meter was placed at a height of 1 m on a tripod so that it remained stable. The scale used for measuring sound levels in fireworks was the A-weighted scale, which focused on the maximum impulsive level, so these tests provided measurement values expressed in dB ($AI_{\max}$). A photograph taken during the tests can be seen in Figure 4.15.



Figure 4.15. Sound pressure level test setup.

To conduct these tests and ensure greater reliability, the tests were repeated 5 times. Therefore, 5 bangers were fired for each composition studied. Silicone was used in these tests to reconstruct the sealing plug of the container tube once it had been filled with the composition under study.

4.4.4. Explosion pressure analysis with nitrocellulose and inert materials

For new compositions to be considered suitable substitutes, it is not enough to reduce pollutant emissions and sound levels, but they must also ensure optimal performance of pyrotechnic devices.

One of the key factors of pyrotechnic shells is their internal overpressure, which is responsible for the opening of the article. Detailed measurements of the shock wave pressures generated by the explosions of each composition were therefore carried out. To capture this data, specialised pressure sensors were used, which were placed inside a fireproof enclosure, preventing gases from escaping to the outside. The sensor system, located in a test tank, allowed the pressures produced during firework detonations to be accurately recorded in a controlled environment. The data was collected for further analysis and to evaluate the effectiveness of the different compositions.

During these tests, two bangers of each of the compositions and samples were tested to obtain some representativeness. Unlike previous tests, it was necessary to remove the conventional fuse and use an electric igniter to detonate the banger, as the measurement system is programmed to be activated by an electrical signal. The design of the test equipment is shown in Figure 4.16.

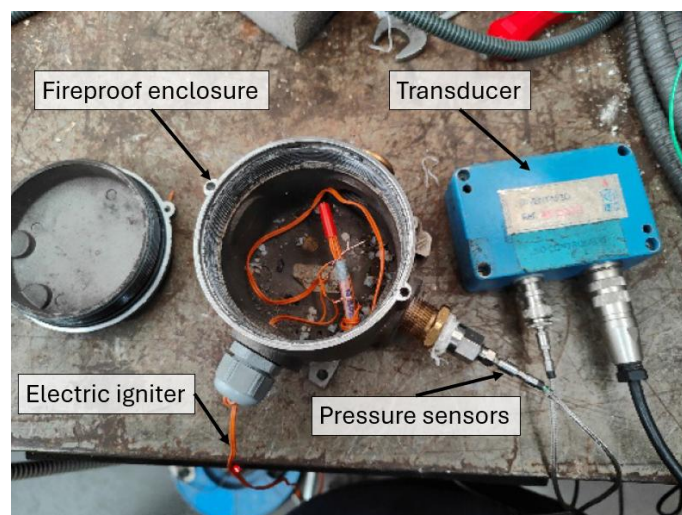


Figure 4.16. Design of explosion pressure analysis tests.

This electrical signal was sent from the computer and was responsible for igniting the banger. The recording program measured the first 500 ms after activation, thus

registering its shock wave. Due to the recording time limitations, these tests could not be performed with the fuse due to the delay of the fuse.

In addition, to simulate real-use conditions and to study the possibility of using these new formulations instead of flash powder, new gypsum plugs were made for the bangers that gave the samples a similar strength to the original.

4.4.5. Thermogravimetric Analysis (TGA) and Mass Spectrometry (MS) comparison between nitrocellulose and black powder

Knowing the high explosive character of nitrocellulose, it is necessary to evaluate its thermal properties when applied to pyrotechnics, in order to assess the thermal stability and decomposition behaviour and to compare them with traditional black powder, ensuring its safety and suitability for pyrotechnic applications. For this purpose, a thermogravimetric analysis (TGA) has been carried out.

For these tests, a NETZSCH STA 449F5 Jupiter® apparatus was used. This apparatus belonged to the Faculty of Engineering of the University of Belgrade. TGA records mass changes with time and temperature variation. The Derivative Thermogravimetry (DTG) allowed to define the thermal behaviour of the sample. This apparatus also allowed the determination of the Differential Thermal Analysis (DTA) which compares the temperature of the sample and the temperature of the empty reference crucible inside the furnace, calculating the difference. DTA is similar to Difference Scanning Calorimetry (DSC) and makes it possible to define the energetic effects (exothermic and endothermic peaks) of the sample degradation within the temperature range considered.

Additionally, mass spectrometry (MS) test was performed. MS identifies the products generated in the thermal degradation of the sample analysed, using the differences in the mass-to-charge ratio (m/z) of the ionised atoms or molecules. This allows the theoretical calculations to be verified by analysing the actual products obtained in the decomposition of nitrocellulose. Each molecule identified is composed of different fragments that are included in the respective molecule in different proportions. The intensity of each fragment and their ratios are available in the NIST database [159]. A NETZSCH QMS403D Aëolos® quadrupole mass spectrometer coupled to the NETZSCH STA 449F5 Jupiter® was available for this analysis, as can be seen in Figure 4.17. This apparatus, belonged to the Faculty of Engineering of the University of Belgrade. Coupling was accomplished using a 75

μm capillary made of quartz that was placed within a stainless steel transfer line, which was heated at 270 °C in order to prevent condensation of evolved gases.

The nitrocellulose sample was analysed twice to avoid possible deviations. The performed tests were non-isothermal, applying a constant heating rate of 10 K/min from 50 °C up to 600 °C. Nitrocellulose mass was set at $1.5 \text{ mg} \pm 0.5 \text{ mg}$, and the tests were performed using 50 mL/min argon flow as the carrier gas in order to produce an inert atmosphere. Regarding mass spectrometry, to detect all gases that were of interest for this research, atomic mass units (amu) within a range from 12 to 46 were scanned, where each of them was scanned for 0.2 s in a total of 177 bargraph cycles.



Figure 4.17. NETZSCH QMS403D Aëolos® quadrupole mass spectrometer coupled to the NETZSCH STA 449F5 Jupiter® [160], [161].

4.4.6. Comparative risk analysis between nitrocellulose and black powder

Once the thermal properties are known, the HAZOP (Hazard and Operability) methodology is used to carry out an analysis that considers nitrocellulose and black powder, providing significant data to help the transition to a more sustainable component in pyrotechnic devices. HAZOP risk analysis allows the identification of hazards and operational problems in industrial processes, in this case in the pyrotechnical sector. It evaluates how deviations from normal operating conditions can lead to safety hazards or problems in the operation of a system.

A HAZOP analysis was carried out focusing on the phases of transport from the factory to the warehouse and subsequent storage. The analysed process can be seen in Figure 4.18.



Figure 4.18. Diagram of the sub-processes assessed in the HAZOP risk analysis.

The first phase of the HAZOP analysis consisted of data collection, for which 21 pyrotechnic accidents in the pyrotechnics industry were analysed [11], [162], [163], [164]. The second phase looked for the nodes to be treated in the analysis, systematically locating them in the possible deviations of each parameter. Table 4.25 shows the nodes analysed in this study.

Table 4.25. Definition of nodes for the HAZOP analysis.

Subprocess	Node
Loading/unloading	Product handling by the operator
	Product
Transportation	Truck storage
	Operator's driving style
	Route
Transfer to storage	Product handling by the operator
	Product
	Packaging
	Fire protection system
Storage	Fire protection system
	Detectors
	Storage of material
	Product handling by the operator

Finally, the frequency and severity of each of the deviations analysed in the different nodes were evaluated. To conduct this analysis, a severity vs. frequency matrix were considered. Severity was evaluated as "low", "serious", "severe", "very severe" and "catastrophic". Frequency as "every week", "every month", "every year", "has happened" and "has never happened". Through this analysis of both compositions, the risks associated with their use in pyrotechnic devices could be identified.

5. Results and discussion

5.1. Environmental impact of pyrotechnic products

The materials and processes used in the manufacture and use of two of the main products in the pyrotechnic sector, the flash banger and the pyrotechnic shell, have been analysed in detail in order to obtain the environmental impact of these products.

5.1.1. Results of the Life Cycle Assessment

As mentioned in section 3, Life Cycle Assessment (LCA) is a fundamental tool for understanding the environmental impact of a product or service. Therefore, applying LCA to flash bangers and pyrotechnic shells (functional units are defined in chapter 4.1.2) will provide significant insights regarding the pyrotechnic industry environmental impact. The quantities and weights of each of the parts of the different items under study can be seen in Table 4.3. Taking this and the rest of the Life-Cycle Inventory (LCI) into account, the Life-Cycle Analysis was carried out. The different stages that have been studied and which encompass the entire process of procurement, production and use of fireworks are as follows: Acquisition and distribution of raw materials (1), Energy consumption (2), Transport to the show (3), Emissions (4) and End of life (5). The full results obtained through the PEF methodology used are included in Annex C, while Table 5.1 shows a summary of the results obtained for each of the functional units in the main impact categories under study.

Table 5.1. LCA results for the main impact categories.

Impact category	Units	Unit	Total	1	2	3	4	5
Climate Change	kg CO ₂ eq.	FB	0.0103	0.012	----	2.83x10 ⁻⁵	~ 0	-0.002
		CPS	4.65	4.29	0.18	0.0075	0.32	-0.15
		PPS	3.87	3.86	0.18	0.0071	0.33	-0.51
Particulate matter	Disease incidence	FB	6.62x10 ⁻¹⁰	9.8x10 ⁻¹⁰	----	2.13x10 ⁻¹²	~ 0	-3.2x10 ⁻¹⁰
		CPS	3.89x10 ⁻⁷	3.39x10 ⁻⁷	3.84x10 ⁻⁹	5.61x10 ⁻¹⁰	6.95x10 ⁻⁸	-2.33x10 ⁻⁸
		PPS	3.26x10 ⁻⁷	2.67x10 ⁻⁷	3.84x10 ⁻⁹	5.92x10 ⁻¹⁰	7.27x10 ⁻⁸	-1.86x10 ⁻⁸
Resource use, fossils	MJ	FB	0.18	0.32	----	0.0004	~ 0	-0.14
		CPS	65.4	71.1	4.49	0.11	~ 0	-10.3
		PPS	50.9	66.0	4.49	0.11	~ 0	-19.7
Resource use, minerals	kg Sb eq.	FB	1.71x10 ⁻⁷	4.29x10 ⁻⁷	----	1.27x10 ⁻¹²	~ 0	-2.59x10 ⁻⁷
		CPS	3.87x10 ⁻⁵	5.76x10 ⁻⁵	6.21x10 ⁻⁸	3.36x10 ⁻¹⁰	~ 0	-1.90x10 ⁻⁵
		PPS	4.17x10 ⁻⁶	2.34x10 ⁻²	6.21x10 ⁻⁸	3.55x10 ⁻¹⁰	~ 0	-1.93x10 ⁻⁵
Water use	m ³ world eq. deprived	FB	0.02	0.034	----	-6.49x10 ⁻⁸	~ 0	-0.014
		CPS	3.28	4.17	0.13	-1.71x10 ⁻⁵	~ 0	-1.02
		PPS	2.09	2.44	0.125	-1.81x10 ⁻⁵	~ 0	-0.48

Note: ---- means not applicable, because the flash banger manufacturing phase (stage 2) is considered hand-crafted.

Through these categories, an overview of the most relevant environmental effects for this type of products can be obtained:

- Climate Change (Global Warming Potential - GWP), which assesses the amount of GHG emitted during the entire life cycle of the product or process, expressed in kilograms of CO₂ equivalents.
- Particulate matter (PM), which assesses suspended particles that have serious effects on human health, especially in terms of respiratory and cardiovascular diseases. The unit of measurement used is Disease incidence, an indicator of the possible incidence of disease caused by these particles.
- Resource use, fossils (Abiotic Depletion Potential - ADP-fossil), which analyses the use of non-renewable resources that contribute to environmental degradation.
- Resource use, minerals (Abiotic Depletion Potential - ADP-minerals), which assesses the use of minerals whose extraction may have some environmental impact.
- Water use (Water Deprivation Potential - WDP), which looks at a key factor such as water use, especially in areas where water is a scarce resource. The unit of measurement used is m³ world eq. deprived, an indicator of the relative amount of water used based on the water scarcity of the region.

As can be seen, there are some common conclusions for the different functional units analysed. Looking at the results obtained for the different stages, it can be seen that the End-of-life stage (stage 5) results in negative impact values in all impact categories. This means that the end-of-life stage contributes to neutralising the environmental impacts generated in the previous stages. This repercussion on the total impact is due to the ideal scenario proposed in the LCA methodology for this stage, which assumes that the pyrotechnic compositions are completely burnt, with no unburnt residues remaining in the article's container, and that the inerts, treated as waste, are fully recovered and recycled after firing.

The main objective of the analysis is to assess the environmental impact corresponding to the category of climate change, due to the current context of research and sustainability. Furthermore, it is directly related to the further studies included in this project, assessing GHG emissions, especially CO₂. Therefore, the research is mainly focused on this category.

Flash banger (FB)

Looking at the analysis for each of the three units studied, important conclusions can be drawn. Starting with the flash banger, it can be seen that the stage of acquisition of raw materials and their distribution (1) is the one that contributes the most to the environmental impact. Specifically, for the climate change category, its influence on the total impact is 99% (without taking into account the end-of-life stage), with an impact of 0.012 kg of CO₂ equivalent. To analyse in detail the high percentage represented by this stage, the network diagram shown in Figure 5.1 is studied. This network diagram shows the main material and energy flows of the different processes and stages of the LCA for flash banger (FB). These flows are represented by arrows indicating the direction of material and energy transfer. Thicker arrows indicate higher flow values. In this case, the highest value corresponds to the raw material acquisition and distribution stage.

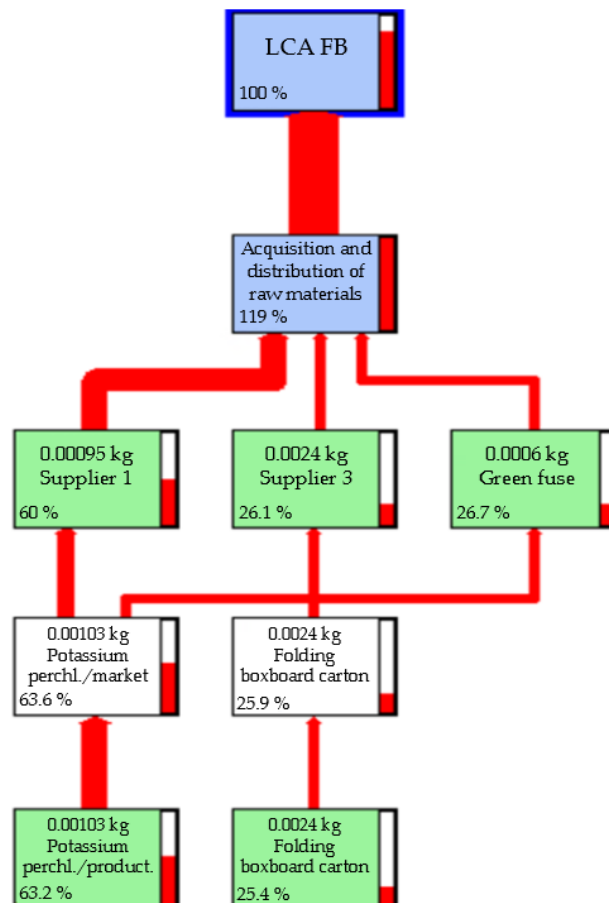


Figure 5.1. Network diagram of the LCA for flash banger (FB).

Figure 5.1 shows a higher percentage impact for stage 1 (119%) than for the total process (100%). This is due to the negative impact value obtained at the end-of-life (stage 5), as indicated above. The impact derived from this stage, approximately

19% of the total, counterbalances the impact of the other stages, giving an overall value of 100%.

It can be seen that the supplier of hazardous materials and cotton (supplier 1) is responsible for most of the environmental impact, namely 60%, followed by the green fuse which has an impact of 26.7% and 26.1% for the cardboard supplier. These percentages are obtained due to the fact that the potassium perchlorate provided by supplier 1 to elaborate the flash composition is the element with the greatest impact in the climate change category for the flash banger. As can be seen in Figure 5.1, it accounts for 63.6% of the impact, while it represents only 20% of the weight of the banger studied. However, cardboard, which represents almost 50% of the weight of the product, only accounts for 25.9% of the environmental impact.

Due to the manual manufacture of this type of article, the impact generated by the energy consumption stage (2) is null, which is environmentally beneficial, due to the absence of electricity consumption.

Finally, stages 3 and 4, corresponding to the transport of pyrotechnic articles from the factory to the place of firing and the emissions generated during this transport, present a minimal impact, barely existing. In the case of the distribution stage, this is due to the situation analysed, where the products are manufactured in workshops close to the final destination (Valencia City Council) and the impact of their transport has hardly any relevance in the total impact. On the other hand, the high level of export of pyrotechnic products from the Chinese market to the rest of the world is well known. This export implies a greater impact due to the distance travelled, depending also on the means of transport used [165].

Looking at the emissions stage, it can be seen that, although emissions are one of the biggest criticisms facing the pyrotechnics sector, they have a negligible impact compared to the first stage of raw material acquisition. The emissions generated by the flash banger under study are minimal, demonstrating that pyrotechnic devices generate far fewer emissions during firing than other emitters present in society [52].

Pyrotechnic shell (CPS and PPS)

The second item under analysis, the pyrotechnic shells, show very similar results to those of the flash banger, both in their cardboard and plastic versions.

The main difference is an increase in impacts for all stages, due to the significantly higher amount of regulated and inert material present in the shells. The functional units of plastic and cardboard shells weigh 1,435.45 g and 1,358.15 g, respectively, while the flash banger only weighs 5.15 g. Furthermore, it can be seen that in this case, due to the fact that the shells have mechanised manufacturing processes, such as the production of the colour producing stars, the energy consumption stage does have a certain impact, which is 0.18 kg of CO₂ equivalent for both types of shell.

The stage of acquisition of raw materials and their distribution is still generating the highest impact, but represents a lower percentage than in the flash banger (around 90% of the total for the climate change impact category) due to the existence of an impact derived from energy and a higher amount of emissions corresponding to stage 4, due to the fact that the shell's NEC exceeds the FB by around a thousand times, reaching climate change impact values of 0.32 and 0.33 kg CO₂ eq. for cardboard and plastic shells, respectively. The total impact in the climate change category amounts to 4.65 kg CO₂ eq. for the cardboard shell and 3.87 kg CO₂ eq. for the plastic shell.

Figure 5.2 shows the network diagram of both pyrotechnic shells. Starting with Figure 5.2 a), corresponding to the cardboard shells, it can be seen that 87% of the impact of the pyrotechnic functional unit comes, as in the FB, from the supplier of the hazardous materials. This is because, chemical compounds are the main ones involved in the environmental impact. Specifically, potassium perchlorate is responsible for 42.1%, while magnalium (aluminium-magnesium mixture) accounts for 29.1%. About the inert material, it can be seen that the impact of the use of cardboard in relation to the total of the procurement stage is 4.17%.

Figure 5.2 b) shows a strong resemblance between cardboard and plastic shells. Chemical compounds used in pyrotechnic compositions still account for the largest product impact. In particular, supplier 1 represents 81.8% of the impact in the climate change category. This value is slightly lower than that observed for the cardboard shell as the pyrotechnic material represents a lower percentage due to a higher weight of inerts. Despite this, potassium perchlorate and the aluminium-magnesium mixture stand out again with percentages of 39.4% and 27.2%, respectively. The main difference can be seen in the material used as packaging. As more plastic is used than cardboard, it also generates a higher impact, accounting for 17.7% of the total impact of the shell.

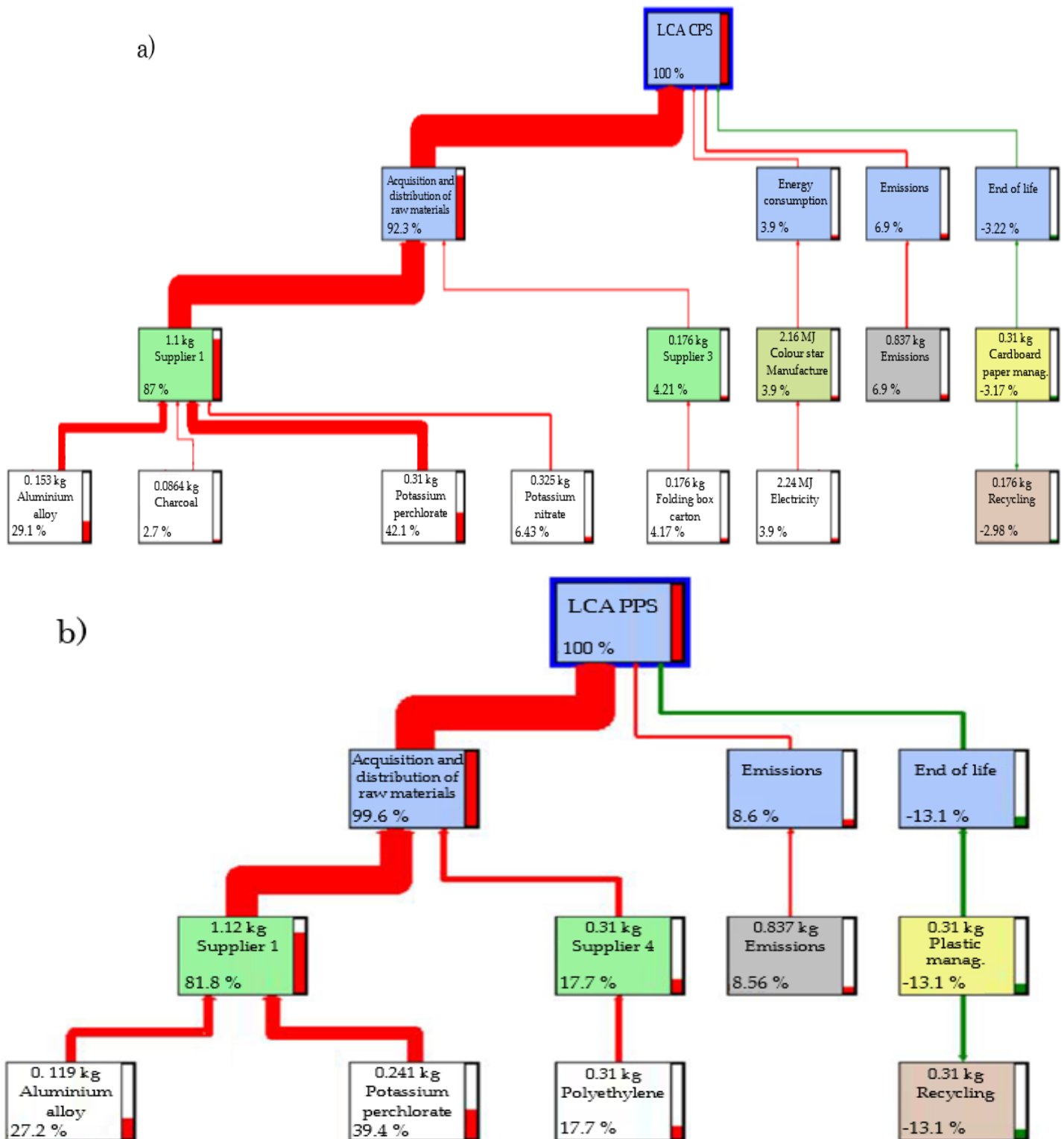


Figure 5.2. Network diagram of the LCA for pyrotechnic shells. a) Cardboard shell (CPS). b) Plastic shell (PPS).

Therefore, when comparing both shells and the impact percentages of each of the materials used as packaging, it may look like plastic has a greater effect on the

environment. However, the result does not only depend on the acquisition of the material but also on the other processes in the model. Analysing the overall process, it can be seen that the cardboard has a higher environmental effect in each of the impact categories analysed. For example, the cardboard shell generates 4.65 kg CO₂ eq. while the plastic shell generates a value of 3.87 kg CO₂ eq. For the category of use of fossil resources, the values are 65.4 and 50.9 MJ, respectively, and for water consumption, 3.28 m³ for the one using cardboard packaging and 2.09 m³ for the plastic one.

These results differ from the expected results and the main reason is the ideal scenario proposed for the end of life stage. Analysing the end of life values, the positive impact is higher for plastic (-13.1%) than for cardboard (-3.17%). This is due to the assumption of full recovery and recycling of the inert materials used in the pyrotechnic articles. The higher positive impact for plastics is explained by a higher recyclability, because paper and cardboard sometimes have limitations in recycling if they have been in contact with certain chemical compositions considered hazardous [166]. In addition, while cardboard has a shorter degradation time, being biodegradable and compostable, plastic has a high contamination potential, taking hundreds of years to decompose [48], so its recovery and recycling will have an even greater positive impact than in the case of cardboard. Another reason for this difference in the impact is the distance between the two suppliers. According to the hypotheses made regarding the location of the factory, while 70 km distance to the factory is assumed for the paper and cardboard supplier, the distance the plastic has to travel from the supplier's premises to the pyrotechnical factory is only 30 km. Previous research shows that this distance is a critical parameter when assessing the impact [167].

This ideal recycling scenario was determined due to the lack of relevant information on the percentage of unburned pyrotechnic products resulting from the firing of pyrotechnic products and the lack of knowledge of the amount of inert material recovered. The reality is far from such a scenario, so the results obtained at the end of life stage may differ significantly from the actual values. If scenarios closer to reality were analysed, it would be observed that, as the percentage of recovered and recycled waste decreases, the total environmental impact from the use of plastic would increase more significantly compared to that of cardboard. This is because the positive contribution of stage 5 to the environmental balance is higher for plastic, as discussed above.

Therefore, this LCA can be considered a preliminary study, with approximate values, which serves to obtain certain important conclusions, but which needs to be refined in order to be able to determine some others. Different recycling scenarios should be evaluated to see their actual influence on the total environmental impact. The direct collaboration of suppliers and manufacturers in the sector will be necessary to provide the unknown information. In addition, analysing different situations of supplier locations, factories and product destinations can add value to the analysis.

5.1.2. Global interpretation

The pyrotechnic sector is harshly criticised socially for the environmental impact generated throughout its life cycle. With the results obtained for the impact on climate change, measured in kg CO₂ eq., comparisons are made with other products and activities of daily use, in order to be able to interpret these values. Figure 5.3 shows the environmental impact on climate change of different products.

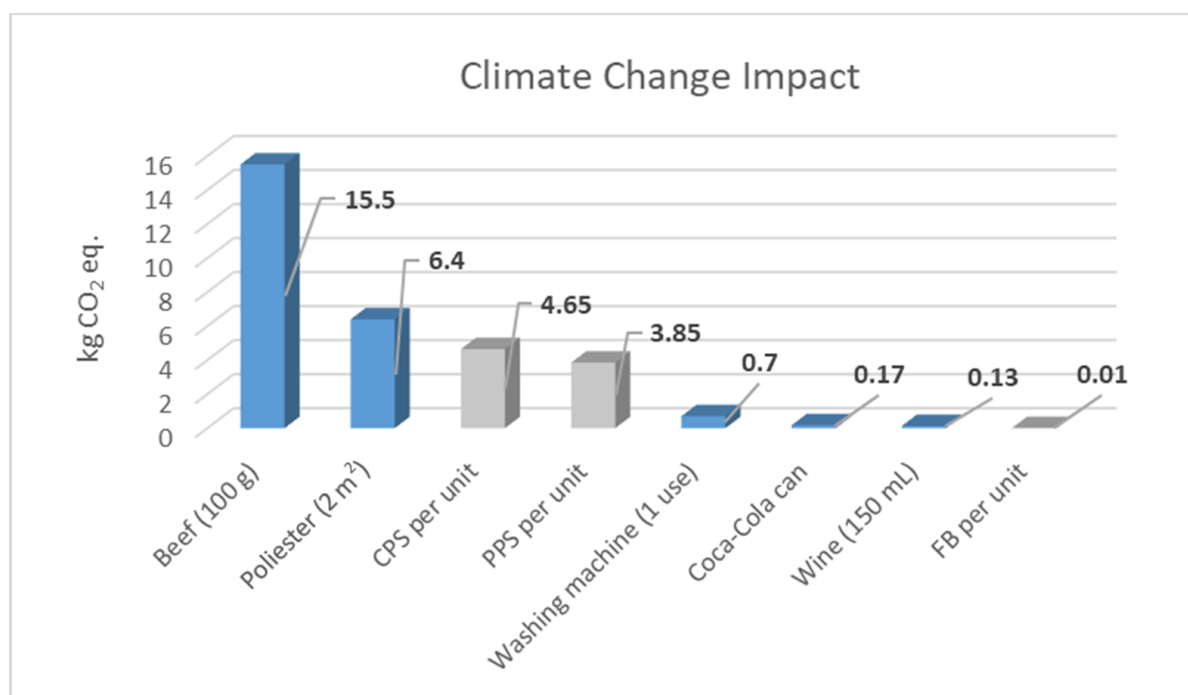


Figure 5.3. Carbon footprint of common products and activities [168].

When comparing the environmental impact values obtained for the pyrotechnic articles studied (in grey colour), it can be seen that they are lower than other products that are well established in society and that are used on a daily basis. For

example, the total impact of a can of Coca-Cola is 17 times greater than that of the flash banger. This shows that the impact of these products is minimal and far from being compared with other more significant sources of emissions in everyday life, and it should be borne in mind that pyrotechnics are a sporadic and localised activity, whereas the other products analysed in the comparison are used on a daily basis.

Nevertheless, in order to obtain a realistic picture of the environmental impact of pyrotechnics in a wider context, it would be essential to carry out a simulation that reproduces a complete fireworks display. Such a simulation would provide an insight into the cumulative impact of various types of pyrotechnic devices, taking into account factors such as the total amount of regulated material or the type of materials used.

However, the LCA has revealed important points for action in order to minimise the impact as much as possible. These measures should focus on the selection and reduction, if possible, of raw materials. Different changes in hazardous materials such as potassium perchlorate or metal compounds will be addressed in this work. Another way to reduce their impact would be to focus on reducing the inert material or substituting it with more sustainable alternatives.

5.2. Theoretical emissions

The analysis of the impact of the different pyrotechnic products production, distribution and use stages shows that atmospheric emissions do not have a major influence on the overall process, but that the raw materials used in the production of explosive mixtures do. In order to establish a relationship between these compounds and their combustion by-products, and due to the social criticism of the pyrotechnic sector for these emissions, theoretical emission studies were carried out, the results of which are shown in the next subsections.

5.2.1. Fireworks professional shows

The main by-products of the use of pyrotechnic articles include greenhouse gases (GHG) and small metallic particles. It is observed in the results of the theoretical analysis of the two professional fireworks displays under study. Tables 5.2 and 5.3 show the total emissions results obtained for the Villaviciosa de Odón show (Spain), and the Macy's Fireworks show (United States), respectively.

Table 5.2. Emissions released during La Pólvara of Villaviciosa de Odón (Spain).

Product	Emissions released		Product	Emissions released	
	Moles	Mass (kg)		Moles	Mass (kg)
CO ₂	13,576	597.5	H ₂ O	3,709	66.8
CO	2,341	65.6	O ₂	1,435	23.0
N ₂	4,011	112.3	SrOH*	205	21.4
K ₂ CO ₃	1,107	153.0	BaOH*	166	25.7
K ₂ S	1,789	197.3	NaOH*	509	20.4
K ₂ SO ₄	327	56.9	CuOH*	350	28.2
KCl	4,436	330.7	CaOH*	433	24.7
MgO	4,851	195.5	OH ⁻	1,663	28.3

Where * represents the excitation of the electron.

Table 5.3. Emissions released during Macy's Fireworks show (United States).

Product	Emissions released		Product	Emissions released	
	Moles	Mass (kg)		Moles	Mass (kg)
CO ₂	326,197	14,356	H ₂ O	89,131	1,606
CO	56,313	1,577	O ₂	34,492	552
N ₂	96,369	2,699	SrOH*	4,917	514
K ₂ CO ₃	26,608	3,677	BaOH*	3,982	619
K ₂ S	42,985	4,739	NaOH*	12,244	490
K ₂ SO ₄	7,837	1,366	CuOH*	8,423	678
KCl	106,601	7,947	CaOH*	10,397	593
MgO	116,579	4,698	OH ⁻	39,963	679

Where * represents the excitation of the electron.

Analysing the results obtained for both shows together, a directly proportional relationship is observed between the emissions generated in each of them and the amount of pyrotechnic composition that composes it. The assumed design of the Macy's Fireworks show, considered the largest pyrotechnic show in the United States, is made up of 24 times the charge contained in the Villaviciosa de Odón show. This implies significantly higher emissions.

Among the products obtained in the combustion of the different pyrotechnic compositions, which participate in the production of the visual and sound effects of the show, several groups can be distinguished. Potassium compounds, and especially those containing sulphur, contribute to the characteristic smell of fireworks and, although they are less toxic than other compounds, if found in high

concentrations they can affect air quality. Water vapour emissions are considerable and are justified by the presence of hydrogen-containing fuels, such as dextrin, generating water vapour during combustion.

However, there are other compounds that present a greater environmental risk. There is a high concentration of different compounds (oxides and hydroxides) that contain a significant amount of metal particles. These metallic particles come from the production of colour or brightness and heat (as in the case of magnesium). The quantities emitted at La Pólvara de Villaviciosa de Odón for these types of compounds are 21.4 kg of SrOH^* , 25.7 kg of BaOH^* , 20.4 kg of NaOH^* , 28.2 kg of CuOH^* and 27.7 kg of CaOH^* , while 195.5 kg of MgO are generated. These quantities are much higher if the case of the Macy's Fireworks show is considered. These metallic particles are a major component of air pollution and can have adverse effects on respiratory health, and heavy metals, such as barium or copper, can fall to the ground and present long-term environmental risks [169].

The products resulting from perchlorate compositions, as well as the pollution related to their production and handling, are one of the most problematic, as they harm humans, micro-organisms and aquatic fauna by leaching into groundwater through the soil via rainfall [45], [47]. In addition, they can affect the thyroid gland, hindering iodide absorption and potentially triggering hypothyroidism [42], [43], [44].

Among the results obtained, it is important to highlight the emissions of gases that directly or indirectly contribute to the greenhouse effect. Emissions of carbon dioxide (CO_2) are the most significant, as it is a common by-product of combustion reactions. Specifically, 597.5 kg and 14,356 kg of this gas are released at La Pólvara and Macy's Fireworks show, respectively. This high volume of CO_2 contributes directly to the greenhouse effect and highlights the environmental impact of these shows. Carbon monoxide (CO), which is another significant product, accounts for 65.6 kg and 1,577 kg of emissions at La Pólvara and Macy's Fireworks show, respectively. This gas, although it does not contribute directly to the greenhouse effect, can favour the creation of other gases that do have a direct influence [65].

When analysing professional shows with large quantities of explosive material, the emissions related to these also represent important values. However, according to previous studies, the average emissions generated do not exceed the limits established by the Ambient Air Quality Standards or only exceed them in the areas closest to the show and at specific periods [55]. Furthermore, it should be taken

into account that this type of shows are performed sporadically, usually once a year (as is the case of the shows under study) and usually last less than half an hour. This means that, despite their high amount of emissions, they cannot be compared to other agents rooted in society, such as tobacco or fossil fuels (heating, vehicles...), which generate emissions constantly all over the world [60].

5.2.2. Comparison with everyday atmospheric emitters

Theoretical analyses have been made of different everyday emitters such as vehicles driving on the M-30 road in Madrid (Spain) and different commercial aircraft flights. Internal combustion engines, in both cases, generate atmospheric emissions, among which carbon monoxide and carbon dioxide predominate, so the comparison focuses on these gases that directly and indirectly influence the greenhouse effect.

Firstly, Table 5.4 shows the daily CO and CO₂ emissions released into the atmosphere by vehicles on the Madrid M-30 ring road, assuming that all of them comply with the limits established by EURO 6 and the reference values of the 2018 WLTP cycle.

Table 5.4. CO and CO₂ emissions released by daily vehicle traffic on the M-30 ring road.

Type of Engine	Emissions (kg)			
	WLTP 2018 levels		EURO 6 Levels	
	CO ₂	CO	CO ₂	CO
Diesel	2,521	10,506	1,996	10,507
Gasoline	1,811	11,316	1,075	11,315
Total:	4,332	21,822	3,071	21,822

Comparing the results obtained for vehicles with respect to fireworks displays, important conclusions can be drawn.

Starting with the most adverse scenario, which analyses the GHG emissions derived from the WLTP cycle according to 2018 data, comparing the carbon dioxide emissions, it can be seen that the daily traffic on the M-30 in Madrid produces 7.25 times the CO₂ generated by La Pólvara fireworks display. This implies that 3.15 h of vehicle traffic, or even 0.5 h if maximum hourly traffic values are taken, are sufficient to equal the carbon dioxide emissions of the show. A comparison with the Macy's Fireworks show exhibits that a single day's traffic generates 30% of the

show's emissions, therefore approximately three days of traffic on this road are sufficient to equal the emissions of one of the world's largest shows. Regarding carbon monoxide emissions, the differences are even more striking in favour of fireworks displays. Comparing the CO emissions of vehicles with La Pólvara, it can be seen that only about 4,000 vehicles are needed to achieve the same amount of emissions. This is 0.30 % of the total number of vehicles on the M-30 ring road every day. Although emissions at the Macy's Fireworks show are significantly higher than those generated at La Pólvara, the differences in CO emitted by traffic are still very significant. The show only accounts for 7.2% of the daily emissions generated by vehicles travelling on the M-30 in Madrid each day.

If the theoretical emissions calculated for fireworks displays are compared with the limits established in EURO 6, which would represent the ideal case of vehicle emissions, the above differences in the case of CO₂ decrease, although greater environmental impact was generated by the daily circulation of vehicles than by the fireworks shows, which are carried out on a one-off, annual basis, is still noticeable. The carbon dioxide emissions generated by daily traffic, taking into account the limits established in EURO 6, are approximately 5 times those of La Pólvara and 21.4% of those emitted in the Macy's Fireworks show, i.e., in less than 5 days, these emissions would be equal.

The actual emission values of vehicles are even higher, as there are older vehicles on the M-30 in Madrid that do not comply with these limits.

In the second place, the carbon dioxide emissions released into the atmosphere on different commercial flights performed by BOEING 737-700 aircraft, all of them departing at Adolfo Suárez Madrid-Barajas airport, are studied. The results are shown in Table 5.5.

Table 5.5. CO₂ emissions released by different commercial flights.

Destination of the flights	Flight distance (km)	CO ₂ emissions per flight (kg)
Valencia Airport (Spain)	286.1	6,607.5
Stansted Airport (London, UK)	1,263.5	20,708.8
Moscow-Sheremetievo International Airport (Russia)	3,439.9	48,691.8

Comparing the emissions produced by the Villaviciosa de Odón fireworks display, the following information is obtained: the flight with the shortest flight distance

(Madrid-Valencia flight) accounts for approximately 11 times the emissions released in the show. When compared with the medium-distance Madrid-London flight, the emissions released are almost 35 times those of the show and, finally, on the Madrid-Moscow flight, which covers the longest distance, more than 80 times the carbon dioxide produced at La Pólvara is released. Again, when comparing the values with Macy's Fireworks show, the differences are reduced. A Madrid-Valencia flight emits about half as much CO₂ as the largest fireworks show in the United States. When compared to a medium-distance flight, a single flight exceeds the emissions of the show and when compared to a long-distance flight, it would be necessary to repeat the show 3 times to equal the carbon dioxide emissions.

A summary of the results obtained from the comparison of CO₂ emissions between pyrotechnic articles and other everyday emitters is shown in Figure 5.4.

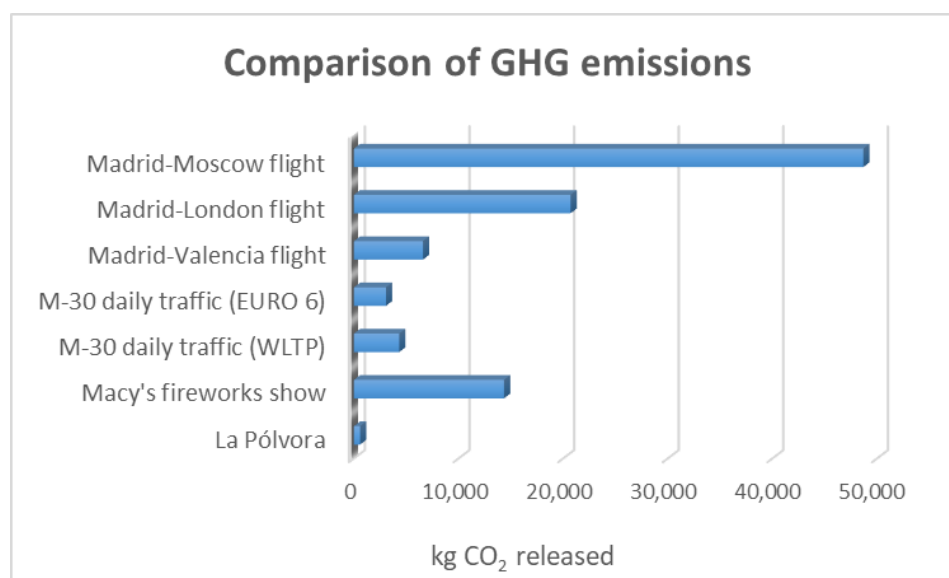


Figure 5.4. Comparison of CO₂ emissions released in different scenarios.

These results demonstrate that established activities in society, which are carried out on a continuous basis in everyday life, can have a much greater environmental impact than fireworks, which occur in one-off situations, without such continuity. Precisely, it has been demonstrated that both internal combustion engines of vehicles circulating on the roads of Madrid and commercial aircraft have high levels of GHG emissions and other gases that indirectly affect the greenhouse effect. Despite this, the pyrotechnic sector is still considered an important pollutant in society and because of this and other aspects analysed in this work,

some assessment is being done with alternative compositions to traditional powders.

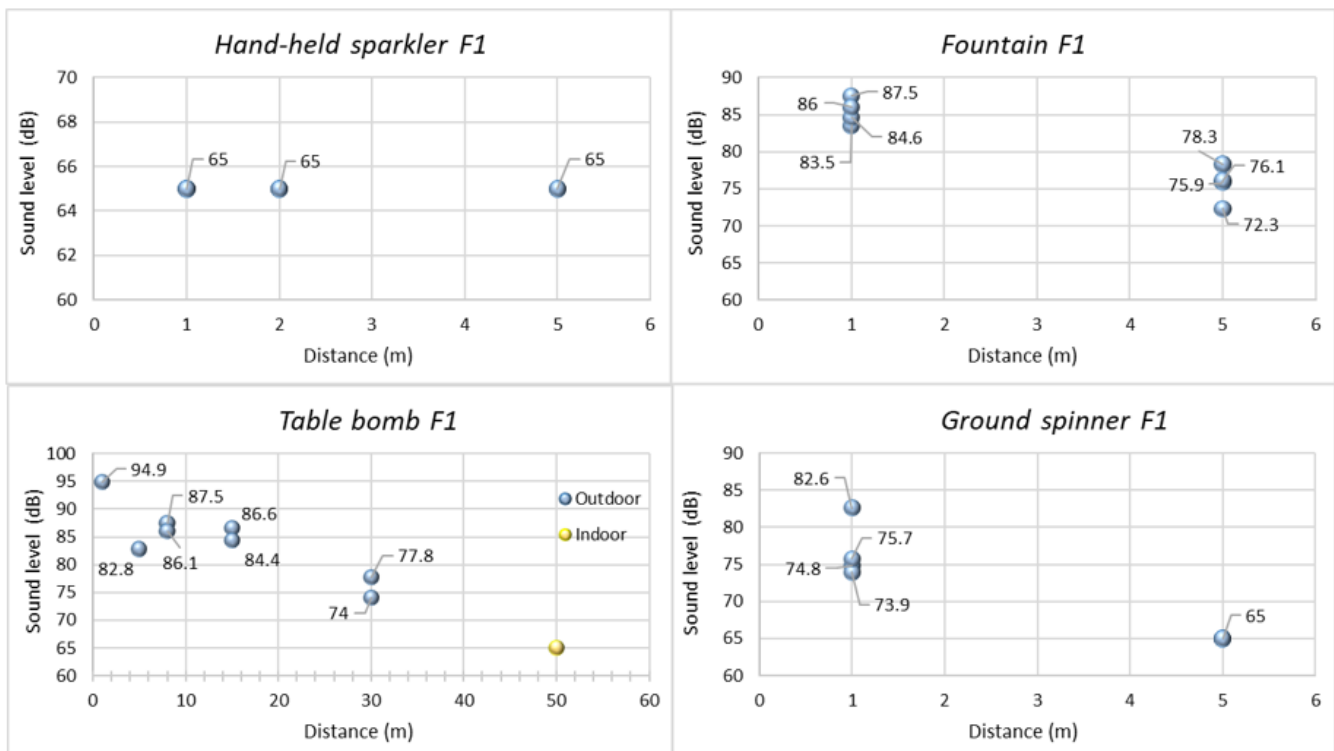
5.3. Sound spectrum of pyrotechnic articles

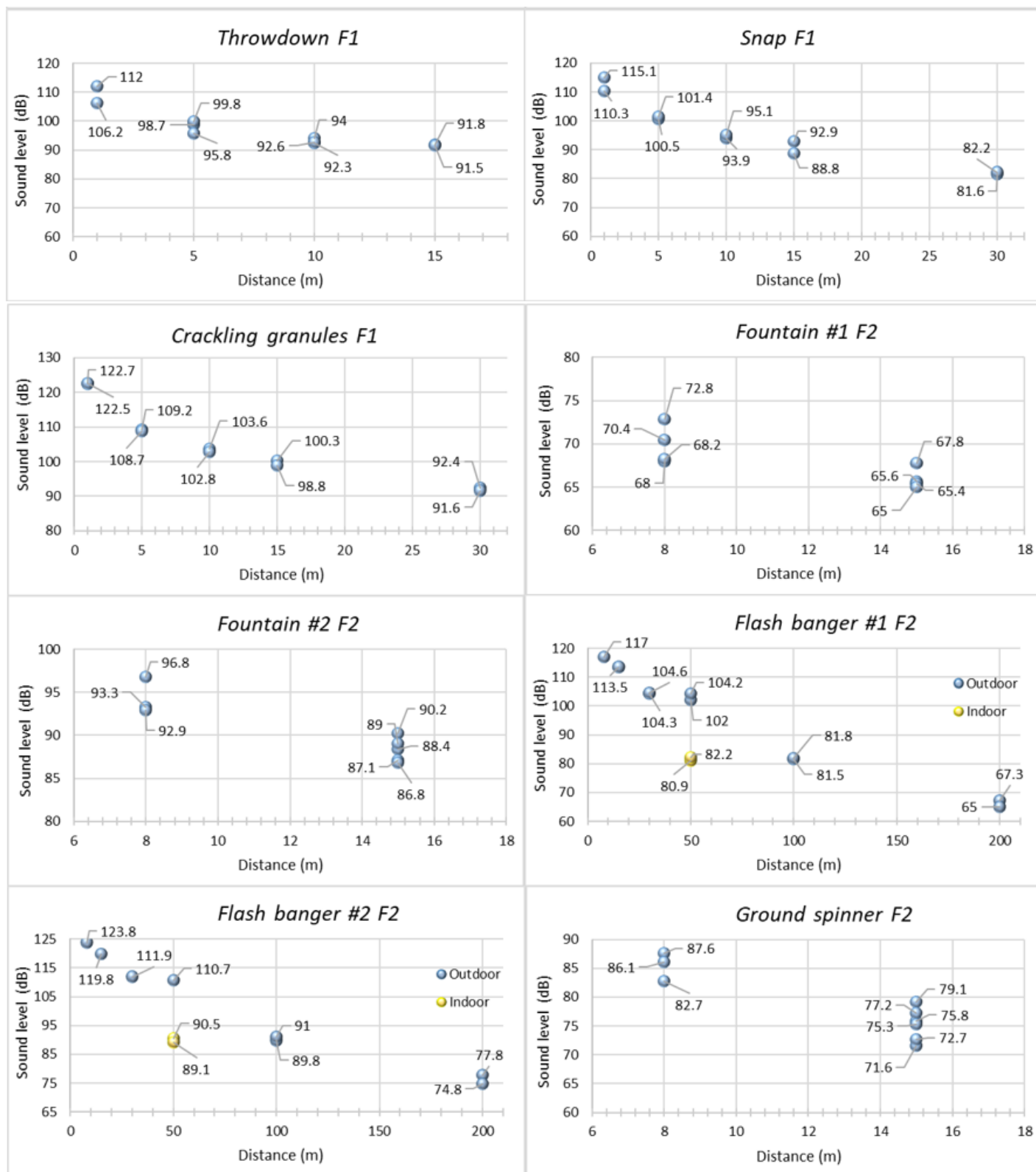
The social difficulties that the pyrotechnics sector has been experiencing in recent years, associated with the effects of sound on animal welfare, is one of the key factors to be analysed and dealt with by the sector, with the aim of achieving coexistence with the rest of society. An analysis of different factors in the transmission of sound and a comparison with other everyday emitters has been carried out in order to understand how pyrotechnic sound affects animals and its main differences, if any, with other sound sources.

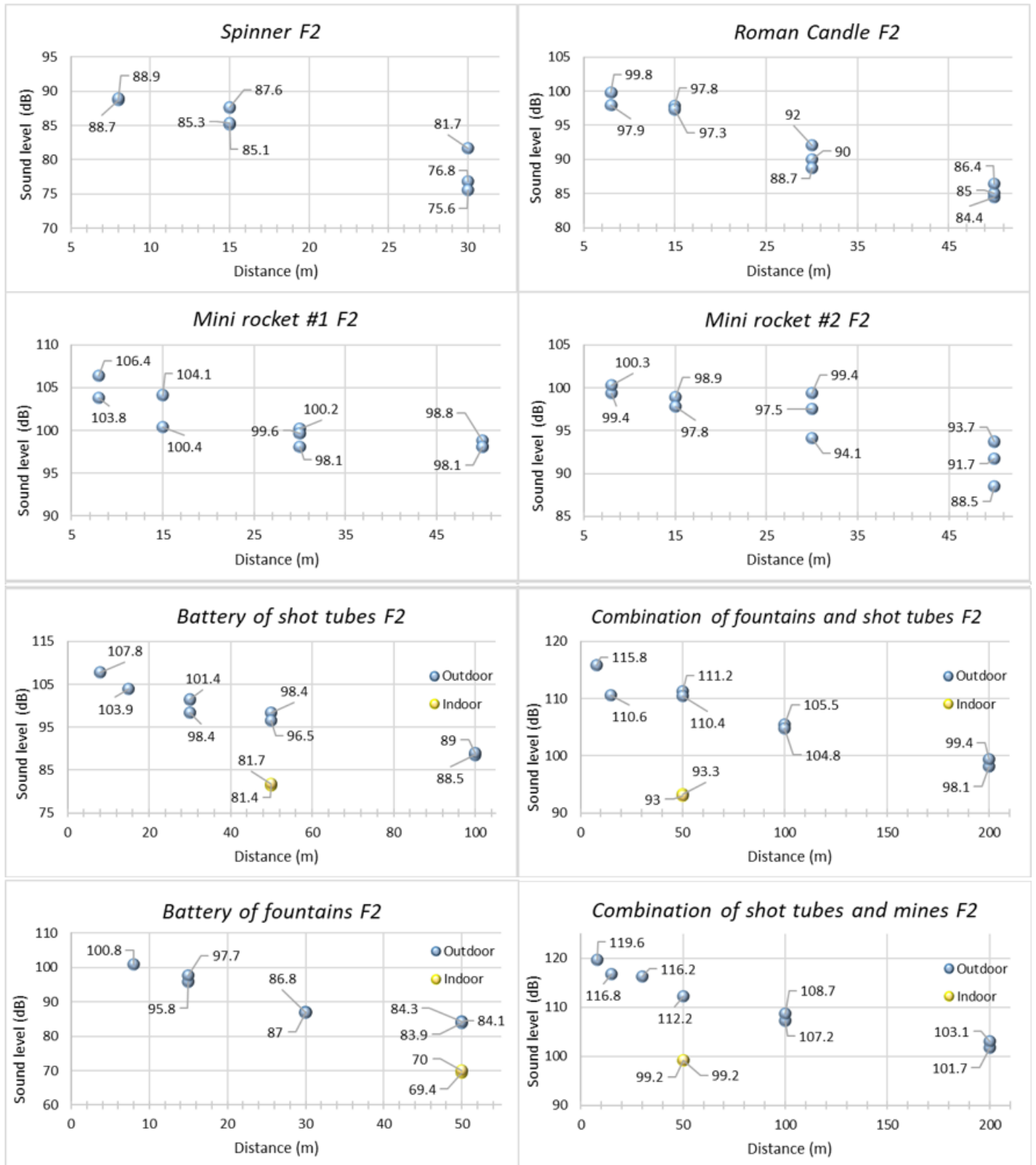
5.3.1. Theoretical and practical results of sound attenuation

Experimental analysis

First, an experimental analysis is carried out with several generic types of different articles for sale to the public categories. This experimental analysis assesses the sound attenuation taking into account certain external factors that affect sound propagation and may therefore differ from the theoretical attenuation. The results obtained in the tests are shown in Figure 5.5.







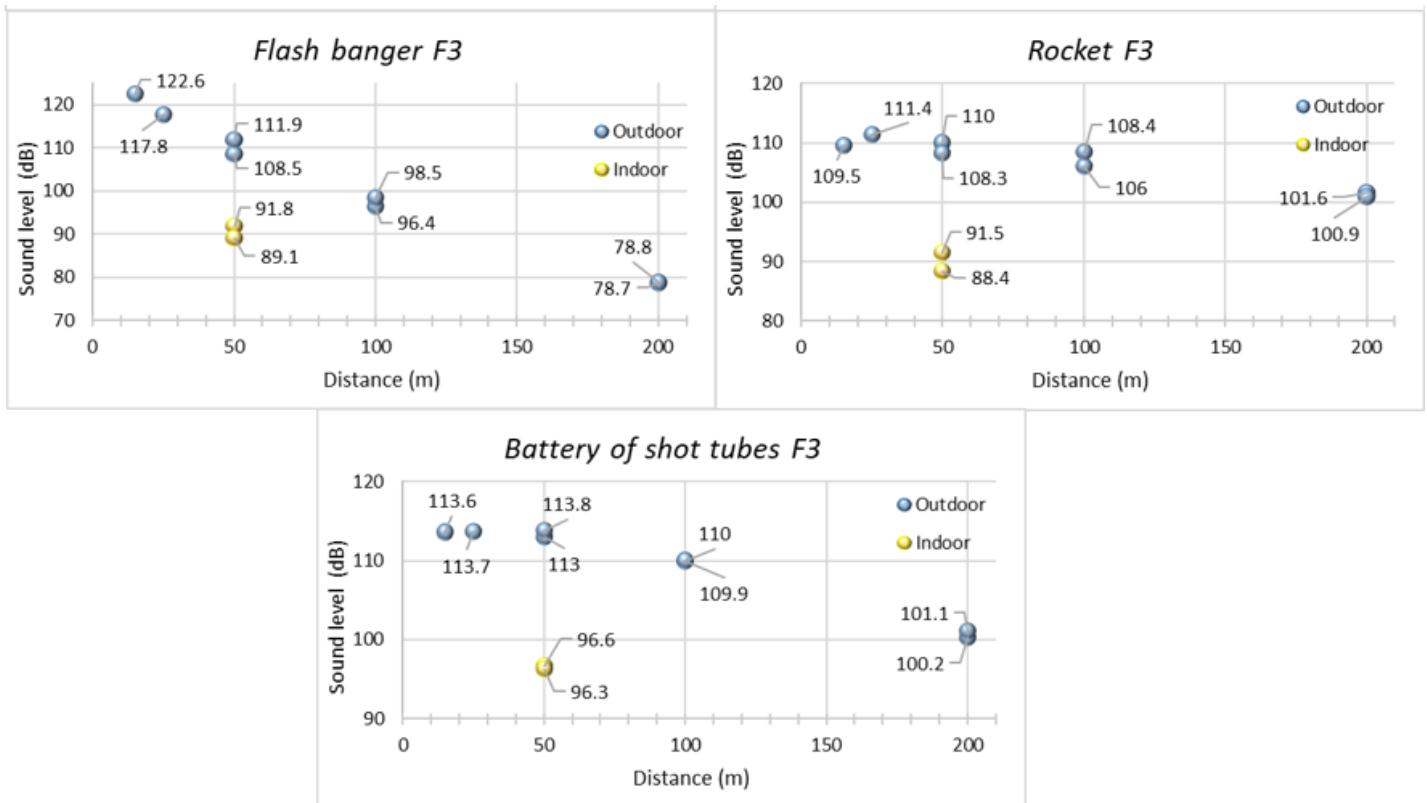


Figure 5.5. Experimental results of sound attenuation for articles to the general public.

It is known from regulations that the category of a pyrotechnic article limits its maximum NEC, being higher in category F3 than in category F2 and in category F2 than in category F1. As can be seen from the results obtained, the articles require a greater minimum distance to reach the 90 dB(AI) reference value as they increase in category. It is also confirmed that the sound or visual effect the article produces directly influences the sound pressure level of the product. Articles intended to produce sound effects such as cracker, whistle or burst have the highest sound pressure level, while those with only black or coloured powder and limited to visual effects have lower sound levels. Therefore, despite being of the same category and containing the same NEC, two articles may have a large variation in the sound emitted depending on the type of pyrotechnic composition they contain.

The measurement points carried out inside a building, represented in yellow colour in Figure 5.5, show that barriers (natural or artificial) have a great influence on sound attenuation. The sound pressure level values measured from this point inside the building at 50 m from the trigger point range from 13 dB(AI) to more than 20 dB(AI) lower than those measured at a point at the same distance in the

open field. This confirms that receivers inside buildings at the time of the pyrotechnic firing are more protected against the sound spectrum than those at the same distance from the item, but without any barrier.

Finally, it was observed that the attenuation depends on the type of article, as it was observed that for ground-based articles there is a greater attenuation of sound than for aerial articles. This is due, among other factors, to the effect of the ground on propagation, which modifies the propagation conditions of sound waves, since the effects of reflections, absorptions and refractions of sound appear, as has been known for many years [170]. Moreover, in the case of ground-based articles, the increase in distance between the receiver and the firing point coincides directly with the distance travelled by the sound. In contrast, for aerial items this is not the case, since doubling the distance between the firing point and the viewer does not double the distance travelled by the sound as shown in Figure 5.6.

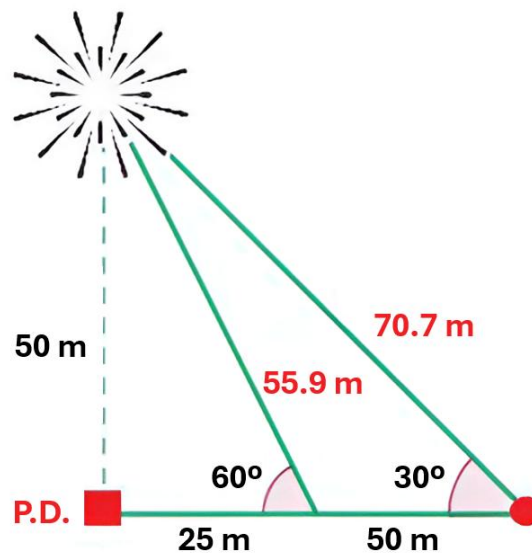


Figure 5.6. Distance between the bursting point of the aerial article and the receiver.

This difference between the sound attenuation of aerial and ground-based articles can be seen in the comparison shown in Table 5.6, which deals with the results obtained for two F3 category items, a flash banger (ground-based article) and a battery of shot tubes (aerial article).

Table 5.6. Comparison of experimental sound attenuation in ground and aerial devices.

Measuring distance (m)	Sound pressure level (dB)	
	Flash banger	Battery of shot tubes
15	122.6	113.6
25	117.8	113.7
50	111.9	113.8
100	98.5	110.0
200	78.8	101.1

As indicated above, it can be seen that the sound pressure level of ground-based fireworks decreases more significantly as the distance increases than in the case of aerial fireworks. In this particular case, the sound attenuation between the measurement points located at 15 m and 200 m for the flash banger is 43.8 dB(AI) while for the battery of shot tubes it is only 12.5 dB(AI). According to these results, it is important to have sound level data also for professional pyrotechnic shows. Therefore, an experimental analysis of sound attenuation in professional fireworks displays is carried out. The maximum values recorded for each of the measurement points in the Ajalvir (Madrid) show are reported in Table 5.7.

Table 5.7. Maximum sound level recorded at the professional show in Ajalvir.

Measurement point	Max. sound level during the show (dB(LC_{Peak}))	Max. sound level before or after (dB(LC_{Peak}))
Sound level meter	142.2	104.4
Dosimeter 1	142.7	116.5
Dosimeter 2	136.1	109.4
Dosimeter 3	122.9	121.6

Analysing these values, relevant information can be obtained. The influx of people in the vicinity of the measuring equipment has a high influence on the sound pressure level in the moments before and after the show. The sound level meter registers the lowest sound level while the show is not taking place. This value is measured just before the start of the fireworks display, because it is located in the safety zone, inside which spectators cannot enter. In dosimeters 1 and 2, a greater intensity is recorded at the end of the show, due to the movement of the spectators present there to other areas of the municipality. In any of the three previous

measurement points, the difference in the sound pressure levels obtained during the show, compared to those measured moments before or after, is notable.

On the other hand, in dosimeter 3, the results do not follow the same logic. This equipment is located in the Plaza de la Villa, the place where there is the greatest influx of people before, during and especially after the show, due to the performance of another small firework display in this location after the end of the measurements. This means that, especially in the post-show measurements, high sound levels are recorded, reaching 121.6 dB (LC_{Peak}), in addition to numerous moments where the noise level exceeds 110 dB (LC_{Peak}). If the maximum values recorded during the show are observed, it can be seen that the difference is not very high. For example, the maximum value recorded at this point during the castle is 122.9 dB (LC_{Peak}).

Focusing the analysis on the measurements recorded during the fireworks display, the values recorded by the dosimeters on the LC_{Peak} scale are transformed to the LAI_{max} scale, in order to evaluate the results on the pyrotechnical measurement scale. The sound spectrum can be seen graphically in Figure 5.7.

It can be seen from the sound spectrum that, due to the phenomenon of attenuation, as the distance from the point where the spectator is located to the firing point increases, the sound pressure level decreases. Despite this, there are some exceptions, such as an instant in the final part of the show, where the highest sound pressure level is reached. At that moment, the values recorded on the LAI_{max} scale are: 125.1, 125.6, 119.0 and 105.8 dB for the sound level meter (70 m), dosimeter 1 (165 m), dosimeter 2 (295 m) and dosimeter 3 (562 m), respectively. As a general rule, sound attenuation can be observed, except for dosimeter 1, where the measured value exceeds that of the sound level meter despite being at a greater distance. This is an exceptional case, since, as can be seen in the rest of the graph, the values obtained in dosimeter 1 are mostly lower than those measured in the sound level meter. Moreover, it should be taken into account that, as it is a completely aerial show, the distance from the opening of the firework (maximum height where the article explodes) to the receiver is not the same as the distance in the horizontal plane, as indicated above.

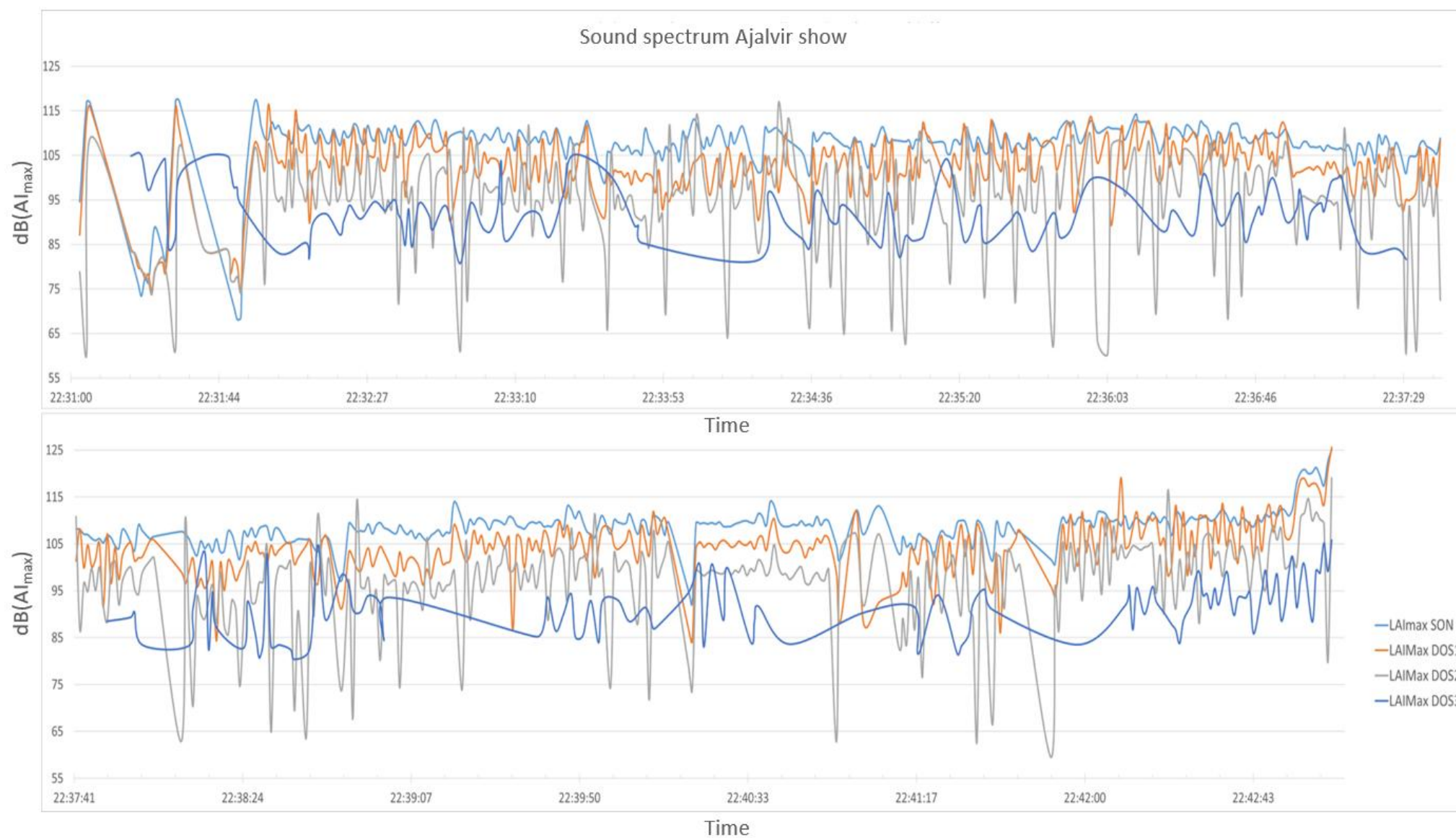


Figure 5.7. Sound spectrum recorded during the fireworks display in Ajalvir.

In order to have data from more than one firework display, this analysis was carried out for the professional show of La Mascletá in Valencia. Similar results were obtained as shown in Table 5.8. First, the influence of the show on the sound pressure level measured at the points where the equipment is located is analysed. To do this, the LC_{Peak} levels recorded before and after the show are compared with those recorded during the show.

Table 5.8. Maximum sound level recorded at the professional show of La Mascletá.

Measurement point	Max. sound level during the show (dB(LC_{Peak}))	Max. sound level before or after (dB(LC_{Peak}))
Sound level meter	145.6	121.6
Dosimeter 1	121.6	90.1
Dosimeter 2	135.1	111.8
Dosimeter 3	135.2	104.5

It is observed that the ambient noise in the moments before and after the show is higher in the location of the sound level meter than in any other place, since once the show is over, the spectators remove the fences that delimit the safety zone and come closer to celebrate, which implies a maximum recorded value of 121.6 dB (LC_{Peak}). In the rest of the locations there is also a notable difference between the values corresponding to the show and those measured in the absence of it. In addition, the difference between the rest of the measurement points and the dosimeter located inside the building is notable, where a notably lower sound level is recorded than in the rest of the locations, again showing the importance of the barriers in the propagation of sound.

The sound spectrum of La Mascletá show is reported in Figure 5.8. It can be seen that the highest sound level recorded corresponds to that measured in the sound level meter, as it is the equipment with the shortest distance to the firing zone. With respect to dosimeters 2 and 3, both located in outdoor areas at 191 and 238 m respectively, there is a slight difference in the sound pressure levels measured, or even at certain times they are higher for the dosimeter that is further away. This fact reveals the importance of the location of the equipment, as dosimeter 2 is located in a narrow area with tall buildings nearby, while dosimeter 3, although located at a greater distance, is located in a wide area with no buildings obstructing the sound propagation.

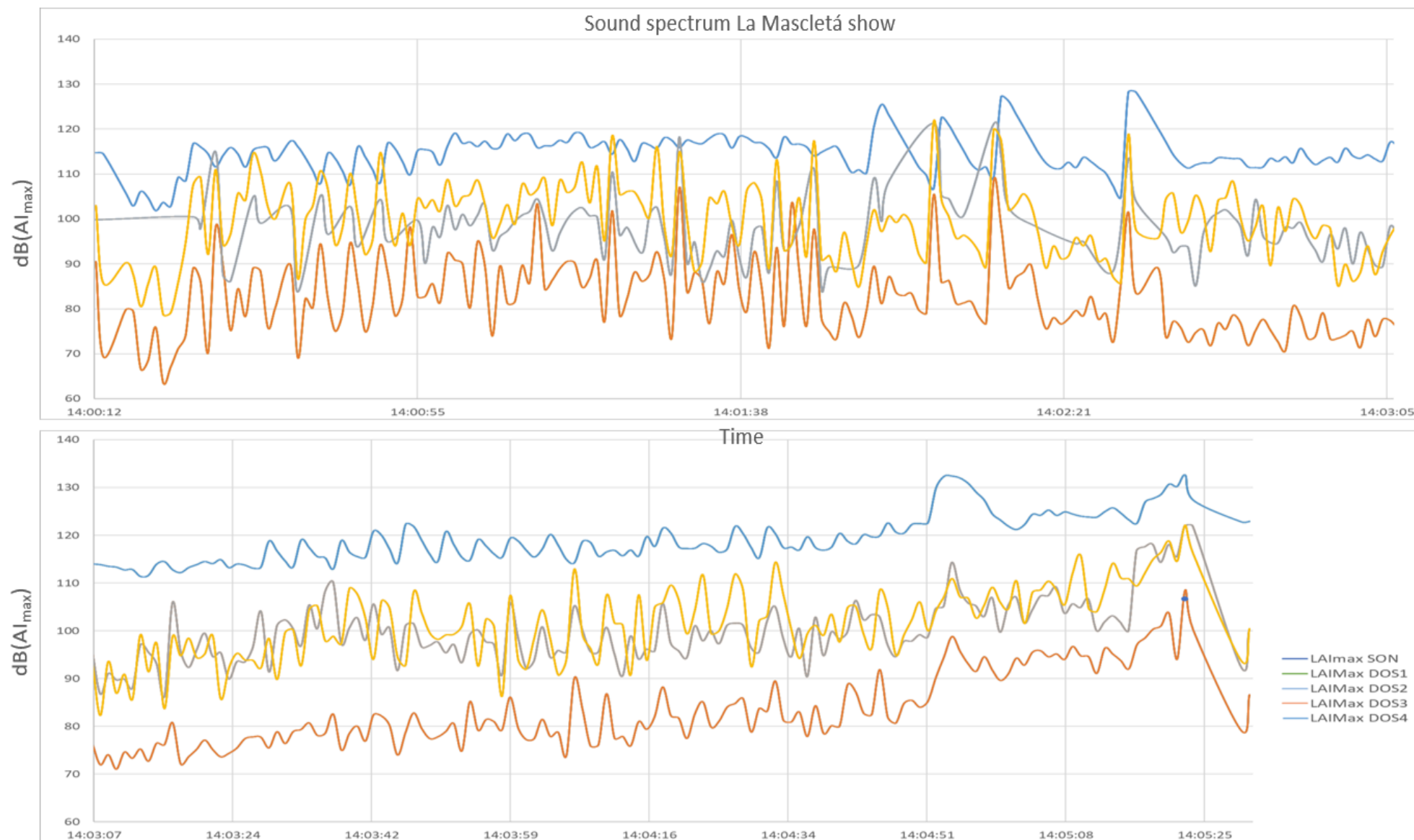


Figure 5.8. Sound spectrum recorded during the fireworks display of La Mascletá.

Dosimeter 4, which only records the instant of the highest sound level of the show, measures the lowest value of all the recording points. This is due to the fact that, in addition to the distance of the spectator, the equipment is located in a park, from which there is no direct view of the show and the sound is obstructed by several rows of buildings. Finally, dosimeter 1, despite being only 105 m away, records a large attenuation of the sound pressure level as it is located inside the Town Hall. The sound pressure level is significantly lower than dosimeters 1 and 2, despite being approximately half the distance from the fire zone.

Comparison between experimental and theoretical analyses

When comparing the theoretical and experimental results, it can be seen that the actual sound attenuation of pyrotechnic articles does not correspond exactly to the theoretical equation which represents the sound attenuation of pyrotechnic articles. Furthermore, the attenuation differs depending on the type of article, mainly differentiating between ground-based and aerial articles.

Therefore, the theoretical and experimental results of an aerial device (F3 battery of shot tube) and a ground-based device (F3 flash banger) are compared. To make these comparisons, the experimental values measured at the different points are taken into account and the theoretical sound pressure level at these distances is calculated, taking as a reference the sound pressure level value recorded at the safety distance. The graphical comparison for the first of these items is shown in Figure 5.9.

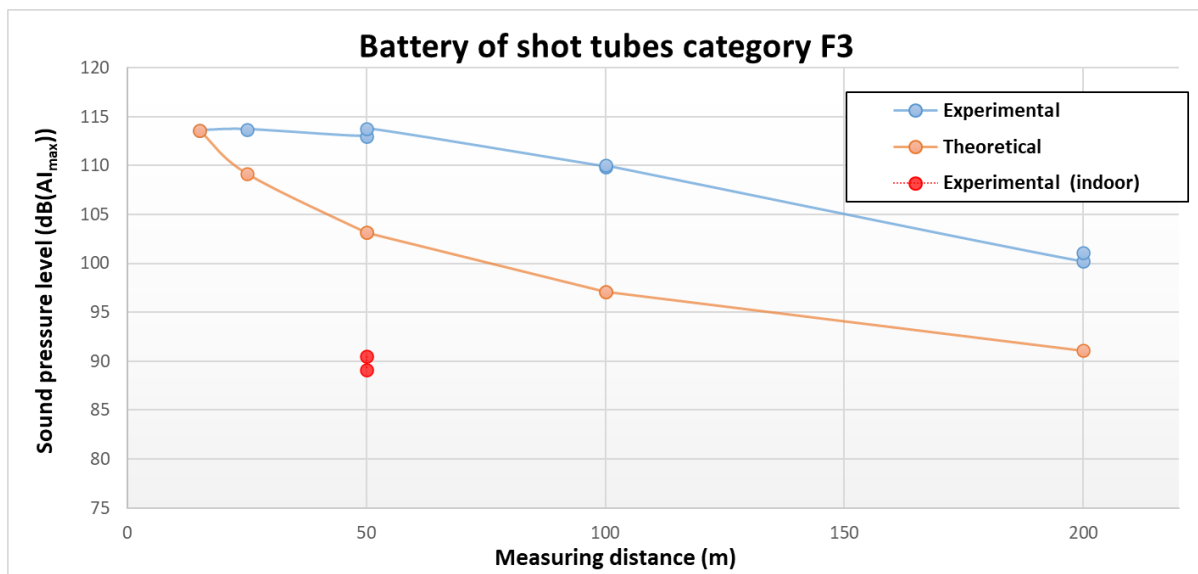


Figure 5.9. Comparison between experimental and theoretical sound pressure level of battery of shot tubes category F3.

As previously mentioned, in the experimental tests, each article was first tested at the safety distance set by the EN 15947:2022 standard, and subsequent testing distances were determined based on the sound pressure level, with louder samples tested more extensively at greater distances to ensure accurate attenuation measurements.

In the case of aerial devices, the actual attenuation of the sound pressure level is lower than the attenuation indicated by the theoretical equation used in the second of the studies carried out. This implies that the necessary distance at which the receiver must be located to receive a specific sound pressure level is greater than that the one presumed by theoretical assessment. However, as the distance increases, the difference between the theoretical attenuation curve and the real attenuation curve becomes smaller, predicting a possible change in the trend that would cause the real attenuation curve to fall below the theoretical curve. Figure 5.9 shows again how the values obtained in the measurement inside the building are much lower than those obtained at the same point in the open field, as well as also being below the value indicated by the theoretical equation, so it is clear that barriers, whether natural or artificial, have a direct relationship with the attenuation of sound pressure levels.

On the other hand, Figure 5.10 shows the comparison between theoretical and experimental results for one of the ground-based articles under study.

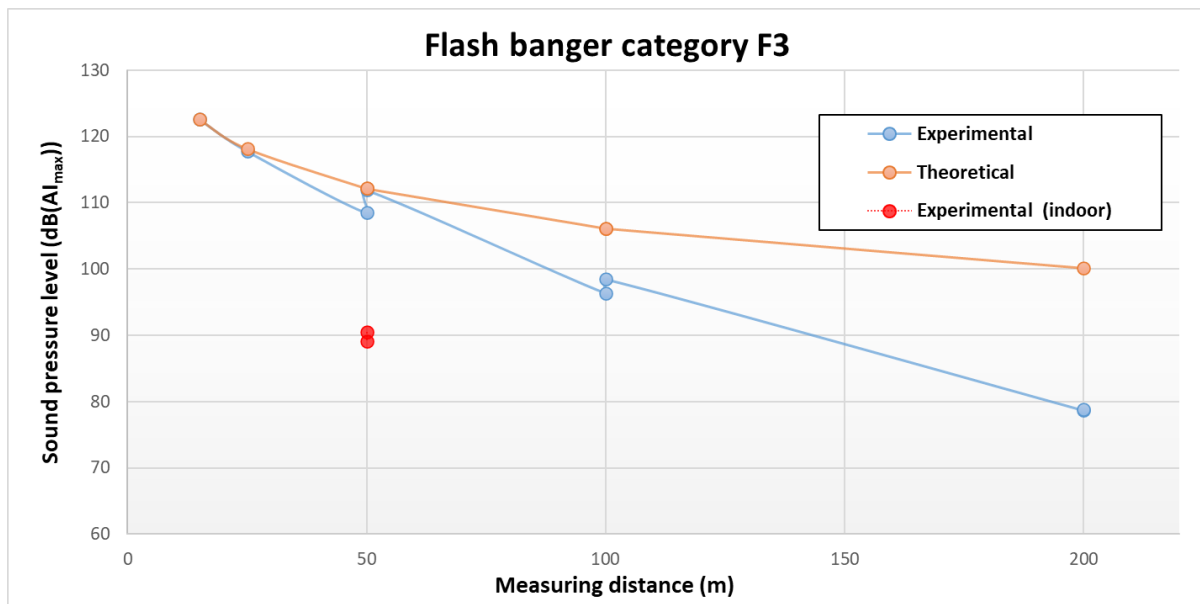


Figure 5.10. Comparison between experimental and theoretical sound pressure level of flash banger category F3.

For ground-based articles, the opposite relationship is observed. The actual sound level values are lower than the theoretical values from early distances. However, the relationship between the actual and theoretical values is very similar at the closest measurement distances, although as the distance between the firing point and the receiver increases, this difference becomes progressively larger. This confirms the effect of the ground on sound propagation, since the greater the distance travelled by the sound wave in contact with the ground, the greater the absorption and reflection of the sound wave.

This comparison is also made for professional performances. When comparing the results obtained in Ajalvir with the attenuation calculated by the theoretical equation, taking as a basis the level recorded in the sound level meter, it can be seen that as the measuring distance from the firing point increases, the sound pressure levels approach the theoretical levels, even observing a greater real attenuation than theoretical in dosimeter 3. This comparison is shown in Table 5.9.

Table 5.9. Comparison between real and theoretical attenuation in Ajalvir's show.

Measurement point	Experimental sound level (dB(LAI_{max}))	Theoretical sound level (dB(LAI_{max}))
Sound level meter	125.1	125.1
Dosimeter 1	125.6	117.6
Dosimeter 2	119.0	112.6
Dosimeter 3	105.8	107.0

Note that, as the reference value in the theoretical analysis is the measured by the sound level meter, both experimental and theoretical sound levels are the same for this apparatus.

These results confirm that, although the actual sound attenuation for aerial fireworks is lower than the theoretical one at close distances, this situation is reversed when the separation between the viewer and the firing point increases, as can be seen in the trend line in Figure 5.9. This might be produced due to the influence of external climatic factors, sound absorption by nearby tall buildings or crowds of people.

Nevertheless, this theoretical equation is used to calculate the necessary distance at which the estimated reference value of 90 dB(AI) is reached in the tests. The

necessary distance would be approximately 3,000 m, a value that would make the use of pyrotechnics unfeasible.

Analysing La Mascletá, it can be seen that the specific moment that provides the maximum sound pressure level value occurs during the final part or closing of the show. The values obtained in each of the measurement locations, as well as their supposed value according to the theoretical calculation of the attenuation, taking the sound level measured in the sound level meter as a reference, are shown in Table 5.10.

Table 5.10. Comparison between real and theoretical attenuation in La Mascletá show.

Measurement point	Experimental sound level (dB(LAI_{max}))	Theoretical sound level (dB(LAI_{max}))
Sound level meter	132.6	132.6
Dosimeter 1	108.5	122.8
Dosimeter 2	122.0	117.6
Dosimeter 3	122.1	115.7
Dosimeter 4	106.7	109.3

According to the results obtained, it is observed that the real attenuation in dosimeter 1 and dosimeter 4 is higher than theoretically expected. This is due to the barrier effect caused by buildings. In addition, the main use of terrestrial artifacts favours sound attenuation, as seen in previous tests.

Theoretically calculating the distance at which the reference 90 dB(AI) would be reached, based on the sound level measured on the sound level meter, gives a distance of approximately 2,800 m with the spectator in the open field. On the other hand, if a spectator is located inside a building, basing the calculation on the value recorded on the dosimeter 1, a necessary distance of 250 m is obtained. These theoretical values are assumed to be lower in reality, given the attenuation results obtained previously, although the distances are still very high and make the use of pyrotechnics impossible.

5.3.2. Influence of climatic factors

The influence of climatic conditions is analysed in order to understand the relationship and how these conditions affect the results previously obtained.

During the replay of the sound attenuation tests of pyrotechnic articles for sale to the general public in spring, an increase of 11.2 °C and a decrease of 35% in relative humidity were recorded. The results obtained are shown graphically in Figure D.1 in Annex D.

The results show that, for all tested families excluding the hand-held sparkler, since for this item the ambient noise is not exceeded, a decrease in sound pressure levels is observed. Nevertheless, meteorological factors do not influence the propagation of the sound level of all pyrotechnic articles in the same way. In particular, the largest differences are found in the three tested families of Fountains (one of category F1 and two of category F2). Table 5.11 shows the results obtained for these articles in both test situations.

Table 5.11. Influence of climatic conditions on Fountains.

Type	Test	Sound Pressure Level (dB(AI _{max}))							
		1 m				5 m			
F1 Fountain	Autumn	87.5	86.0	84.6	83.5	78.3	76.1	75.9	72.3
	Spring	83.1	82.5	78.0	76.1	73.1	69.3	66.5	<65
F2 Fountain 1	Autumn	72.8	70.4	68.2	68.0	67.8	65.6	65.4	<65
	Spring	<65	<65	<65	<65	<65	<65	<65	<65
F2 Fountain 2	Autumn	96.8	93.3	92.9	90.2	89.0	88.4	87.1	86.8
	Spring	70.6	68.3	65.5	<65	<65	<65	<65	<65

As can be seen, measurements were repeated for each of the samples four times at each of the distances (1 m and 5 m). The sound pressure levels reach approximately 7 dB(AI) difference at 5 m distance for fountain category F1. Fountain 2 of category F2 is the article with the largest difference. The level reached is up to 25 dB(AI) lower at both measurement distances (1 m and 5 m), with sound levels close to ambient sound.

The effect of the fountain is continuous over time for a certain period. In contrast, for most of the generic types, the sound effects are either single and punctual (as in the case of banger articles) or of short duration (each of the shots of a battery or combination). This duration of the effect may be the main reason for the different influence of weather conditions on sound attenuation.

These findings confirm that warm weather and lower humidity conditions favour sound attenuation. Therefore, holding the professional events measured above at times that meet these conditions would favour a reduction in noise levels. Despite this, it is observed that, for most of the generic types, the differences are not very noticeable. This implies that the distances needed to reach the reference value of the analyses would still be very high and would complicate the continuation of pyrotechnics as they are known today.

5.3.3. Comparison with everyday sound emitters

Since the maximum noise values indicated as advisable in order not to affect animal welfare are based on experience and known sound levels, the sound spectrum of different everyday emitters is compared with fireworks. This comparison is intended to confirm the reference value of 90 dB(A) since, according to the results obtained previously, the safety distances required to achieve this value would make the use of pyrotechnics unfeasible.

The maximum sound values obtained in each of the measurements made are shown in Table 5.12.

Table 5.12. Maximum sound values recorded in the comparison of everyday emitters and pyrotechnic articles.

Sound emitter	Distance of the sound level meter (m)	LAI_{max} (dB)
Flash banger #1 (F2)	15	110.78
Flash banger #2 (F2)	15	112.14
Flash banger #3 (F2)	15	114.44
Flash banger #4 (F3)	15	122.34
Flash banger #5 (F3)	15	123.71
Whistle (punctual)	2	102.58
Whistle (longer period)	2	102.47
Horn (punctual)	2	97.71
Horn (prolonged)	2	98.24
Glorieta de Cuatro Caminos	2	88.93
Cuatro Caminos subway station	2	90.51
Kennel	0.5	124.00

It is observed that a spectator located at a safe distance receives the sound effect produced by flash bangers with a high intensity. In the case of category F3 bangers, the sound pressure levels are higher than those generated by other everyday emitters, such as a whistle, a horn, the traffic itself or the noise perceived on a metro platform. In contrast, the differences in the values measured when exposed to these everyday emitters are smaller when compared to flash bangers of category F2. It should be noted that, while the sounds generated by pyrotechnics are always for entertainment purposes and are based on sound effects and/or opening effects at specific points in time, usually coinciding with annual festivities, the noises generated by the everyday emitters analysed are secondary effects derived from them.

When comparing the sound levels achieved in the kennel, it is observed that barking generates a sound intensity of similar magnitude to F3 articles, and even significantly higher when compared to category F2 flash bangers. While the sound pressure levels for flash bangers reached a maximum value of 114.44 dB(AI) for category F2 and 123.71 dB(AI) for category F3, the maximum value recorded in the kennel reached 124.00 dB(AI). This value is very similar to the maximum sound level recorded at the nearest measuring point at a professional show such as the one in Ajalvir, where 125.1 dB(AI) was recorded.

It is evident that dogs do not show any symptoms of welfare distress to their own barking or that produced by another dog nearby, whereas this is the case for perceived pyrotechnic sound effects of similar intensity. This observation raises important questions about how animals adapt to high sound levels in their natural environment and how this might influence their perception and reaction to external sound events, such as pyrotechnics. But what it does show is that animals, particularly dogs, do not suffer hearing damage when confronted with sounds of this intensity, as they are exposed to the same intensity levels on a daily basis, without any effect on their well-being.

In order to analyse the range of frequencies emitted by pyrotechnic effects and to compare it with other emitters, the results about frequency obtained with the Brüel & Kjaer 2250-Ligth sound level meter are analysed. The exploration of the specific frequencies emitted by each sound emitter is essential, as certain frequencies can differentially influence the perception and reaction of animals. The sound level meter provides information on how much of the total sound intensity comes from each frequency range, so that it is possible to estimate which frequencies are dominant in each of the sounds under study. The frequency data

corresponding to the maximum sound pressure level instants of each situation are processed. In the case of flash bangers, whistle or horn, these moments correspond to each of the ‘shots’ carried out. For everyday situations such as traffic, metro or kennel noise, the five maximum values that are reached during the whole measurement are selected. Table 5.13 shows a summary of the results obtained, indicating the predominant frequency range in each of the situations.

Table 5.13. Frequency range generated by everyday emitters and pyrotechnic articles.

Sound emitter	Predominant frequency range (Hz)
Flash banger #1 (F2)	1k - 2.5k
Flash banger #2 (F2)	630 - 2k
Flash banger #3 (F2)	500 - 1.6k
Flash banger #4 (F3)	250 - 630
Flash banger #5 (F3)	250 - 500
Whistle (punctual)	2.5k - 3.15k
Whistle (longer period)	2.5k - 3.15k
Horn (punctual)	1k - 1.6k
Horn (prolonged)	1k - 1.6k
Subway	50 - 100
Vehicle traffic / Noise from vehicles	80 - 200 / 1.25k - 2k
Kennel	500 - 1k

The frequencies emitted by a given sound source are the same, regardless of the duration of the sound, since the characteristics of the sound wave do not depend on the duration of the sound [171]. This is confirmed by comparing the results obtained in the tests with the whistle and the horn, where measurements were made of punctual and prolonged sounds.

When observing the measurements made on the five flash bangers under study, it can be seen that, as the net charge inside the banger increases, the sounds are more bass and with greater intensity, which causes the predominant frequency range to decrease. According to the study carried out, which includes F2 and F3

category flash bangers, with NEC values close to the limits established by the regulations, it is possible to determine a predominant frequency range that includes all the flash bangers and is located between 250 and 2,500 Hz.

Sounds such as those produced by a whistle, for example, used by traffic officers to regulate the movement of vehicles, generate frequencies in the predominant range between 2,500 and 3,500 Hz. In the case of the entrance and exit of the metro on the platform, the predominant frequencies appear in a lower range and oscillate between 50 and 100 Hz. The same fact is noticed for vehicle traffic itself, which generates a predominant frequency range between 80 and 200 Hz. This type of sound differs from the predominant frequency range of pyrotechnic bangers, but this is not the case for the other sound emitters studied.

Sounds from traffic or vehicle horns generate frequencies in the 1,000 to 2,000 Hz range. In the case of the kennel, where the sounds recorded come only from the barking of the dogs, a predominant frequency range between 500 and 1,000 Hz is found. Comparing these sounds with those produced by fireworks, it is observed that the predominant frequency ranges are similar. Specifically, the entire frequency range generated by flash bangers is present among the rest of the analysed emitters. In this way, it can be confirmed that the frequencies generated by the burst effect of flash banger do not differ from those perceived by the user when exposed to everyday sounds such as the horn, traffic or the barking of a dog. This leads to the conclusion that, just as the animal does not suffer hearing damage or injury from such everyday sounds, neither does it suffer these effects from the sounds generated by pyrotechnics.

Therefore, it is confirmed that the cause of impact to animal welfare when exposed to sounds generated by pyrotechnics is not a damage to hearing, but rather the appearance of fear or stress derived from lack of knowledge and lack of training in the presence of such sounds [172]. There are numerous examples where animals have been observed that, in the presence of this type of sound effects produced by pyrotechnics, do not suffer any type of alteration, due to previous training and knowledge of the emitting source [173].

5.4. Sustainability and technical feasibility of alternative compositions

According to the results obtained, the challenges of the pyrotechnic sector could be met by the substitution of traditional chemical compositions with alternatives that improve the environmental impact and generate less noise impact, maintaining the correct functioning of fireworks.

5.4.1. Evaluation of propellant and perchlorate substitutes

Nitrocellulose is proposed as the first possible substitute for traditional powder. Its use as a substitute for black powder (acting as a propellant) and perchlorate compounds (accompanying colour-producing substances) is analysed due to its composition and properties, and because it is already used in certain types of articles for this purpose, according to EN 15947:2022.

Theoretical emission analysis

First, theoretical analyses comparing the emissions results from the use of nitrogen-base compounds and conventional powder were performed.

The results of the theoretical emissions analysis for the indoor use Fountains of category F1 are shown in Table 5.14. This comparison analyses both types of fountains on the pyrotechnic market, those using perchlorate compositions and those using nitrocellulose compositions.

Table 5.14. Theoretical emissions comparative between nitrocellulose and potassium perchlorate Fountains.

Products	Nitrocellulose article (g)	Potassium perchlorate article (g)
CO ₂	0.880	2.773
CO	2.829	---
N ₂	0.280	---
H ₂	0.143	---
NO ₂	1.840	---
KCl	---	2.311
H ₂ O	---	0.937
TiO ₂	2.476	2.476

It can be seen that nitrocellulose significantly reduces carbon dioxide emissions, but generates new harmful combustion by-products such as carbon monoxide and nitrogen oxides, specifically NO_2 . Furthermore, the elimination of perchlorates in the whole process, not only in its combustion, but also in its production and handling, avoids the most damaging pollution generated by today's pyrotechnics.

In the case of Table bombs and Mines, nitrocellulose is used as a propellant and acts as a substitute for black powder. The results of the emission comparison between the two compositions are shown in Table 5.15.

Table 5.15. Theoretical emissions comparative between nitrocellulose and black powder Table bombs/Mines.

Products	Nitrocellulose article (g)	Potassium perchlorate article (g)
CO_2	0.119	0.204
CO	0.378	0.130
N_2	0.038	0.087
H_2	0.019	---
NO_2	0.247	---
K_2CO_3	---	0.213
K_2S	---	0.170

Again, a decrease in CO_2 emissions released is observed, although CO emissions increase, and nitrogen oxides appear. This trend obtained by substituting black powder as propellant is verified in the results obtained by theoretically replacing all the black powder used as propellant in the Macy's Fireworks Show by nitrocellulose. The results obtained are shown in Table 5.16.

Table 5.16. Theoretical emissions comparison of nitrocellulose and black powder as propellants in a professional show assuming 9,732 kg of NEC.

Black powder			Nitrocellulose		
Product	Moles	Mass (kg)	Product	Moles	Mass (kg)
CO	56,313	1,577	CO	163,767	4,587
CO_2	56,313	2,478	CO_2	32,753	1,441
N_2	37,542	1,052	H_2	114,637	232
K_2CO_3	18,771	2,594	N_2	16,377	459
K_2S	18,771	2,070	NO_2	65,507	3,013

The results obtained reveal a significant decrease in carbon dioxide emissions, with an approximate reduction of 42%. However, there has been an increase of around 190% in the release of carbon monoxide into the atmosphere as a result of the chemical reactions involved. It is important to note that carbon monoxide does not contribute directly to the greenhouse effect, as its impact on the atmosphere lies in its ability to react and form other compounds [67], [174]. In addition, its residence time in the atmosphere is significantly shorter than that of carbon dioxide [66].

Moreover, the black powder does not only produce GHG but also potassium compounds that, at high levels can produce health problems such as skin and eyes irritation, and even severe health problems if their concentration significantly increases [175]. The results reported in Table 5.16 show that nitrocellulose combustion does not produce K_2CO_3 neither K_2S , therefore, the problems associated to the potassium compounds do not have to be considered. On the other hand, when addressing nitrogen by-products it is noticed that the use of nitrocellulose reduces nitrogen emissions in more than 43.6% although, it is important to note that nitrocellulose generates nitrogen dioxide, a compound absent in the combustion of black powder. Nitric oxides are responsible for causing serious environmental problems, such as acidification, eutrophication and toxicity, among other effects [176].

Preliminary results indicate that the use of nitrocellulose as a propellant in pyrotechnic products could be an effective strategy to reduce emissions of gases that have a direct impact on the greenhouse effect and represent a higher risk compared to those that have an indirect influence, such as CO_2 [63]. Therefore, by focusing the comparison only on gases that directly or indirectly affect the greenhouse effect, together with the fact that nitrocellulose combustion produces less smoke and soot and, therefore, better pyrotechnic effect visibility [72], nitrocellulose-based pyrotechnic devices could be considered a proper substitute for traditional powder pyrotechnic articles.

Experimental emission analysis

Due to the existence of articles of the same type using both conventional powder and nitrocellulose, such as Fountains using perchlorate or nitrocellulose, their emissions are evaluated experimentally. The results are shown in Table 5.17. These results also include emissions generated by the ignition mean, but these can

be considered negligible if compared to the emissions produced in the combustion of the main composition.

Table 5.17. CO and CO₂ concentrations measured in the comparison of F1 Fountains .

Samples	NEC per tests (g)	Test 1		Test 2	
		CO (ppm)	CO ₂ (% vol.)	CO (ppm)	CO ₂ (% vol.)
A	2.2	2,458	0.26	2,798	0.17
B	4.1	3,866	0.20	4,725	0.24
C	4.1	7,600	0.37	9,581	0.51
D	2.8	2,350	0.68	3,835	0.62
E	6.1	3,460	0.61	3,937	0.55
F	4.5	3,602	0.22	4,043	0.41

For each of the samples, two tests are carried out in order to obtain more reliable results. As shown in Table 4.21, samples A, B and C contain nitrocellulose, while samples D, E and F contain perchlorate. Each of the samples comes from a different manufacturer and, although their design is similar, they have different NECs. The average concentrations of the gases released by each of the fountains under study are calculated and represented graphically in Figures 5.11 and 5.12.

Important conclusions can be drawn from the results obtained. It is observed that the nitrocellulose used by the second manufacturer (sample C) produces higher emissions of carbon monoxide and carbon dioxide compared to the first nitrocellulose sample analysed. Compared to sample B, which contains the same NEC as sample C, the concentrations of both gases are about twice as high. This suggests that, although they are the same type of article and composition, the specific properties of each nitrocellulose (such as the percentage of nitrogen, the quality of the components or the method of synthesis) have a significant impact on the emissions generated. A similar pattern is observed when analysing the perchlorate fountains, as seen in sample D. Despite having the lowest NEC, this sample has the highest CO₂ content among the three perchlorate fountains evaluated.

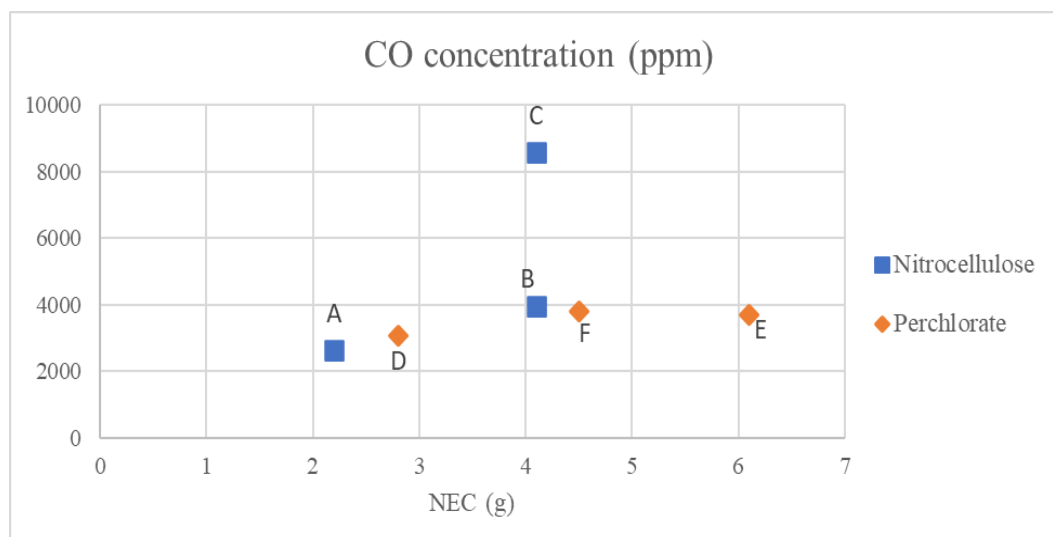


Figure 5.11. CO concentration (ppm) measured in Fountains comparison.

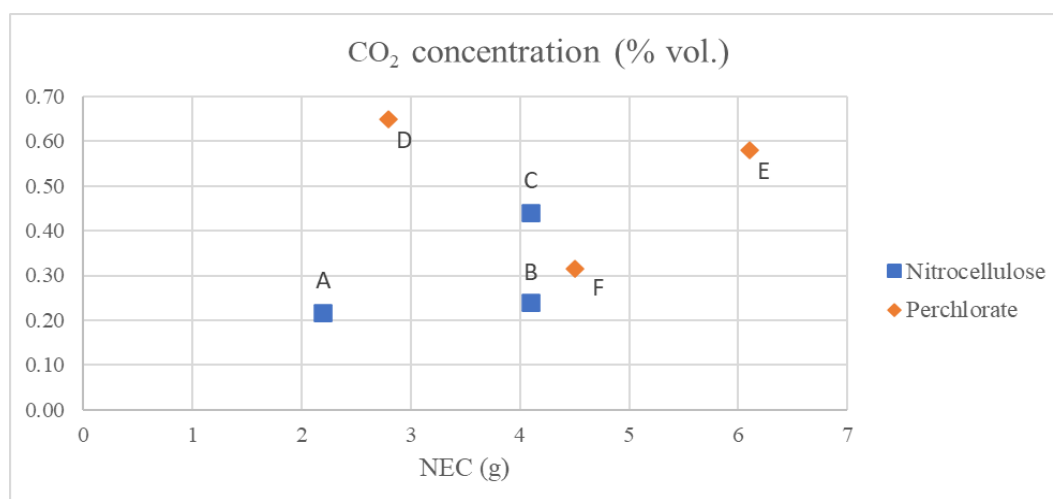


Figure 5.12. CO₂ concentration (% vol.) measured in Fountains comparison.

A general comparison of nitrocellulose and perchlorate fountains yields results that are in line with theoretical predictions. Perchlorate-based compositions tend to show slightly higher CO concentrations than nitrocellulose formulations, while CO₂ emissions are higher for perchlorate-based samples. However, these differences become less remarkable in the case of sample C, probably due to the lower quality of its composition.

In comparison, both nitrocellulose and perchlorate fountains release similar amounts of CO₂, although in the case of perchlorate, emissions tend to be slightly higher. In contrast, CO emissions are somewhat higher for compositions containing nitrocellulose. To analyse this phenomenon in more detail, Table 5.18

presents the standardised emissions of each gas studied, expressed per gram of NEC.

Table 5.18. CO and CO₂ concentrations for each gram of sample.

Samples	CO/NEC (ppm/g of NEC)	CO ₂ /NEC (%/g of NEC)
A	1,195	0.10
B	965	0.06
C	2,095	0.11
D	1,104	0.23
E	606	0.10
F	849	0.07

As can be seen in Table 5.18, CO emissions for the nitrocellulose fountains are higher than the emissions of the perchlorate ones, as can be also deduced from Figure 5.11. On the other hand, CO₂ emissions released by the perchlorate composition are, in general, slightly higher than in the nitrocellulose composition. This difference is especially noticeable in sample D.

Furthermore, it should be noted that the use of nitrocellulose not only helps to reduce greenhouse gas emissions (mainly carbon dioxide), but also eliminates perchlorate-based compounds, which are considered to be one of the most harmful compounds in pyrotechnics, due to the environmental pollution they produce during their production, handling and use, mainly in groundwater [42], [71].

Thermogravimetric Analysis (TG) and Mass Spectrometry (MS)

Once the environmental analysis of nitrocellulose is known, thermogravimetric analysis is carried out to determine the thermal properties of the composition and compare it with the literature on black powder.

The results obtained for the nitrocellulose analysed in the TGA and DTG are shown in Figure 5.13 a). On the other hand, DTA curve is shown in Figure 5.13 b). In both figures are also represented the black powder results curves under helium atmosphere reported by Turcotte et al. [177], in order to compare the results between both compositions used as propellant.

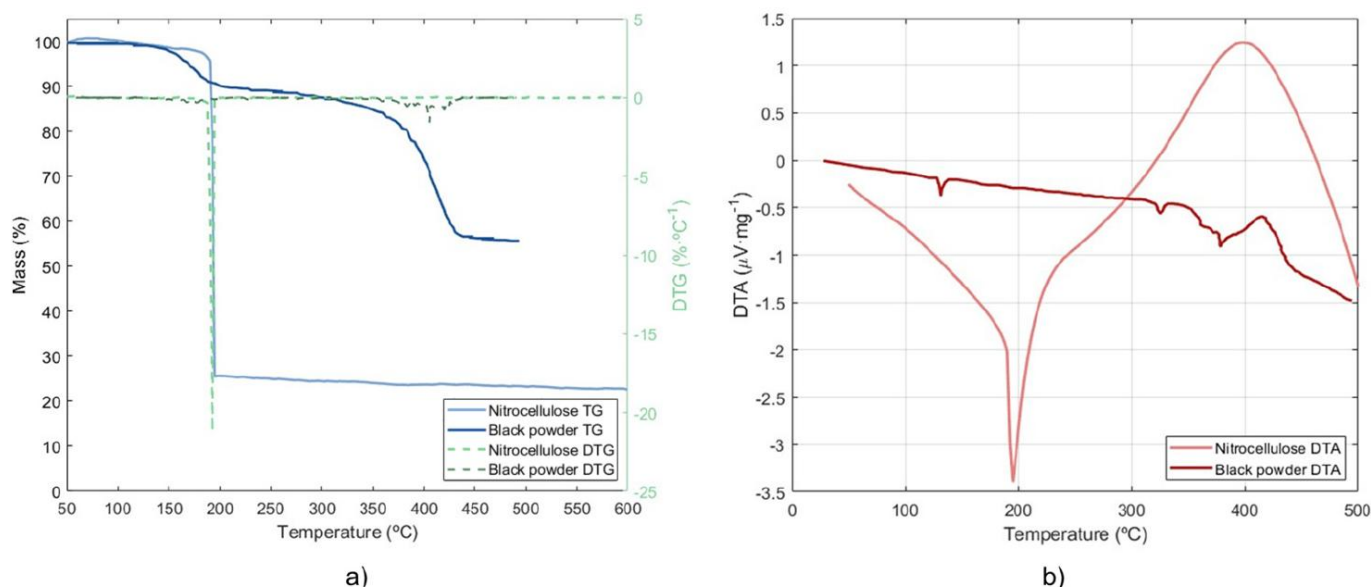


Figure 5.13. Thermogravimetric curves for nitrocellulose (using argon atmosphere) and black powder (using helium atmosphere). a) TG and DTG curves. b) DTA curves.

The TGA curve of nitrocellulose reveals that the moisture content of the sample can be considered negligible, as it does not cause a significant mass loss during its release, which occurs up to about 120 °C. Above 200 °C, a single step reaction is observed, which results in a considerable mass loss, reducing it to about 77% of the initial mass. This reaction corresponds to the decomposition of nitrocellulose, a process that has been shown to occur near 200 °C in previous studies [76], [178]. In particular, the maximum mass loss rate is recorded at 192.5 °C, which is reflected in a peak in the DTG curve and an inflexion point in the DTA curve. On the other hand, when examining the results of the black powder, two distinct stages in its decomposition process can be identified. It can be seen that the decomposition of the black powder occurs at higher temperatures, as the mass loss associated with this process starts at approximately 350 °C. In addition, a small initial mass loss, attributed to the vaporisation of sulphur, is detected, which reaches about 10% between 200 and 250 °C. The final residue exceeds 50%, which is consistent with the fact that the black powder contains more ashes than nitrocellulose, resulting in less pronounced effects. Consequently, the DTA and DTG peaks of the black powder are much lower, and the maximum mass loss rate is shifted towards temperatures close to 400 °C, due to the rapid oxidation that characterises its combustion.

When analysing the DTA of nitrocellulose, a steady decrease is observed from the beginning of the test up to 187.5 °C. From this point, there is an abrupt decrease

up to 195 °C, followed by a gradual increase leading to positive DTA values from 300 °C onwards. This pattern suggests that initially an endothermic process is present, but once the reaction of the sample starts, it shifts to an exothermic phase. In contrast, the black powder shows a small endothermic peak at the beginning related to sulphur vaporization, followed by a second set of peaks between 300 °C and 400 °C, which are generated when the degradation reaction is accelerated.

It is important to note that nitrocellulose has an inherent instability due to oxygen and chemical bonds in its composition, which allows it to react even under inert conditions. Previous studies [178] have reported thermogravimetric curves of nitrocellulose in which decomposition occurs with progressive mass loss under inert conditions. However, in this study, rapid oxidation is observed, which is more characteristic of combustion than thermal degradation. This behaviour is consistent with the known behaviour of nitrocellulose and can be explained by the oxygen released during thermal degradation, as shown in Figure 5.14, represented by amu (atomic mass unit) 32. This exothermic phase persists up to 400 °C, at which point the DTA starts to decrease again.

When comparing the TGA results of nitrocellulose with data available in the literature on black powder, significant differences can be observed [177], [179]. In cases where the heating rate is not low enough, the different volatilisation stages may not be clearly evident in the TGA curve. Although a heating rate of 10 K/min was used in this study, the results obtained are similar to those of previous studies on the TGA of nitrocellulose, where lower heating rates, such as 2, 4 or 6 K/min, were used [180]. As mentioned above, the decomposition temperature of nitrocellulose is considerably lower than the temperature at which KNO_3 oxidizes the charcoal in black powder, which implies that, from a safety point of view, nitrocellulose requires less energy to detonate. In fact, it is widely recognised that nitrocellulose has a lower thermal stability than black powder and is particularly sensitive to moisture content [181], [182].

Further differences are observed when analysing ash content and reaction time. As mentioned above, the TG curve of the black powder showed an ash content close to 60%, as only 40% of the mass was volatilised in the two stages. In contrast, Figure 5.13 revealed that the ash content of the nitrocellulose was around 20%, a significantly lower value. However, this 20% ash seems high compared to previous studies [159], [178], where the residue after TG analysis is usually lower than 20%. This difference can be explained by the specific composition of the sample and the carrier gas used during the TGA tests. As for the reaction time, the differences are

not so noticeable, as the sharp mass drop observed in Figure 5.13 has also been reported in previous research on the rapid oxidation of black powder. In this study, the reaction was recorded to have a duration of 26.4 seconds.

Figure 5.14 a) and 5.14 b) show the mass spectrometry (MS) results superimposed on the TGA (represented on the left ordinate axis) and DTG (represented on the right ordinate axis) curves. To facilitate the visualisation of the results, the MS curves are presented in two separate graphs. Since the experiment was performed using argon as carrier gas, the thermal degradation of nitrocellulose was simulated, and the products generated in this process are represented in the mass spectrometry. These graphs allow correlating the mass loss with the gaseous products released, helping to understand the thermal degradation mechanisms of nitrocellulose. However, due to the workflow of the mass spectrometer, a small delay is observed between the DTG peaks and the amu peaks, which in both cases correspond to the decomposition reaction of the sample. Mass spectrometry tests facilitate the verification of emission results obtained in previous tests, as they allow both the identification of compounds released during the thermal decomposition and the quantification, by means of the intensity of the peaks in the spectrum.

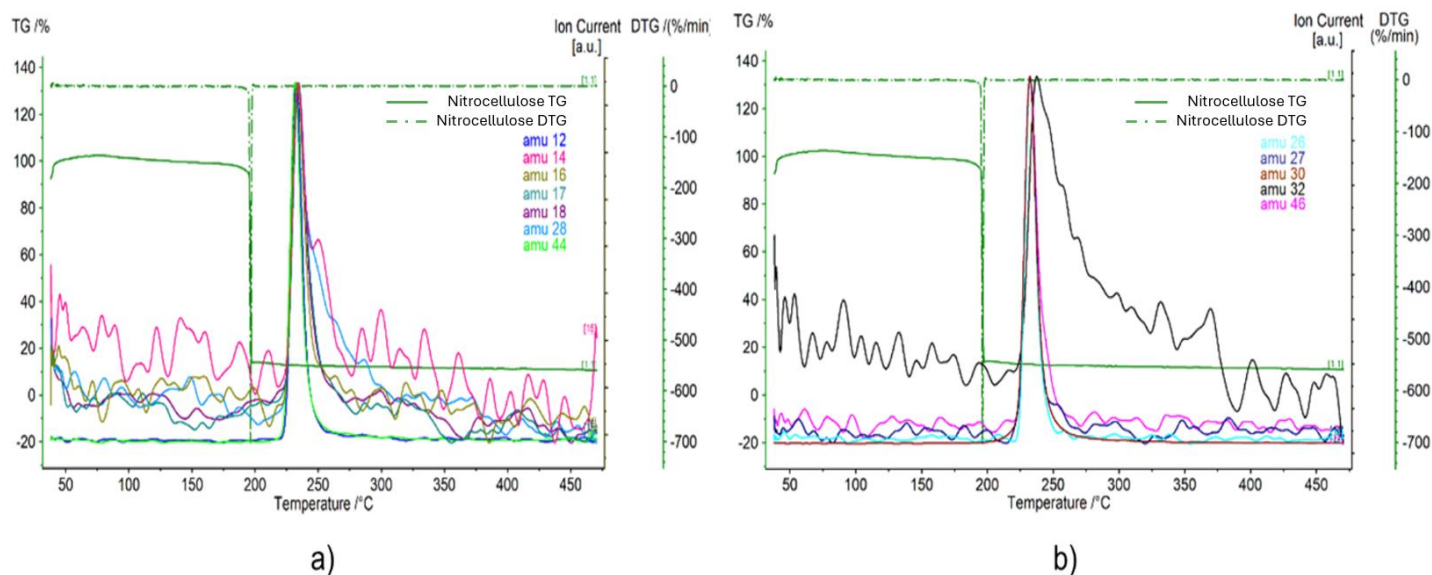


Figure 5.14. a) Mass spectrometry results for amu 12, 14, 16, 17, 28, 44; b) Mass spectrometry results for amu 26, 27, 30, 32 and 46.

Carbon monoxide, carbon dioxide, nitrogen and water are the main components detected. The molecular ion for H_2O is represented by amu 18, while amu 17 corresponds to a fragment ion. Since the curves of the two amu coincide almost

perfectly, it is safe to say that amu 18 reflects the release of H_2O . As for carbon monoxide, it is detected in amu 12, 16 and 28. However, these amu do not only correspond to CO, but also to CO_2 . Carbon dioxide, one of the main products of both combustion and decomposition of nitrocellulose [183], is clearly identified in the sharp peak of amu 44. This peak is confirmed by the fragment ions amu 16 and amu 12. Amu 12 follows the sharp profile of amu 44 with a very short release interval, whereas amu 16 shows a slightly broader peak, influenced by the oxygen fragment ion.

As far as nitrogen is concerned, it is found in both amu 14 and amu 28. Nitrogen release occurs during combustion of nitrocellulose as well as during pyrolysis [184], [185]. As previously mentioned, amu 28 signifies the release of carbon monoxide and carbon dioxide, along with nitrogen. In addition, it can be observed that amu 14 shows an additional peak around 250 °C, which may explain the fact that the peak of amu 28 is broader than the signals of the other components.

In addition to these signals, an additional clear signal represented by amu 32, corresponding to oxygen, is observed. The amplitude of this signal, larger than that of any other amu curve, indicates a continuous release of oxygen at various stages after the decomposition of nitrocellulose. However, oxygen is not among the main products of nitrocellulose pyrolysis, since no mass loss occurs during its release and no alteration is observed in amu 16, which could also represent oxygen. Some studies have reported oxygen release in nano-thermites containing nitrocellulose [186], although the release temperatures in those cases are close to 500 °C. On the other hand, Chai et al. [81] suggested that the decomposition of nitrocellulose involves the fracture of the oxygen bridge, which could be an explanation for the presence of amu 32. However, this observation appears to be an anomaly, suggesting that more tests are needed to properly evaluate it.

The shapes of the peaks in amu 27 and amu 26, could be related to the presence of HCN in the combustion and pyrolysis products of triple-base propellants, which include nitrocellulose, nitroglycerin, and nitroguanidine [187]. Amu 27 corresponds to the molecular ion of HCN, whereas amu 26 is a fragment ion of HCN, and the near perfect match between the shapes of the two curves suggests this relationship. The signals of amu 30 and amu 46 correspond to nitrogen oxides. During thermal decomposition and combustion of nitrocellulose, the predominant nitrogen oxide is nitric oxide [157], which is confirmed by amu 30, which shows a very sharp curve, without “noise” interference, and with a clearly high peak. On

the other hand, nitrogen dioxide (NO_2) is also detected [188], [189], and is represented by amu 46.

The results obtained from TGA and MS tests have provided valuable information on the thermal behaviour and degradation process of nitrocellulose. According to the TGA data, nitrocellulose has an easier tendency to reach explosion reaction compared to black powder, due to its lower decomposition temperatures and higher volatile matter content. This could increase the risk, although the risk could be reduced with higher moisture content. In fact, previous research has indicated that increasing the moisture content improves the thermal stability of nitrocellulose [181]. However, excess moisture can significantly impair the performance of pyrotechnic devices [190], [191]. Therefore, it is advisable to subject nitrocellulose to a drying process before its incorporation into pyrotechnic devices, which would maintain its proper performance and minimize the risk of ignition during transportation and handling.

5.4.2. Evaluation of burst powder substitutes

Different compositions have been evaluated as possible substitutes for flash powder used as burst powder. First, nitrocellulose is raised as an alternative due to its high explosive character. Moreover, the addition of inert compounds to flash powder reduces the risk of ignition and may have other advantages that need to be evaluated.

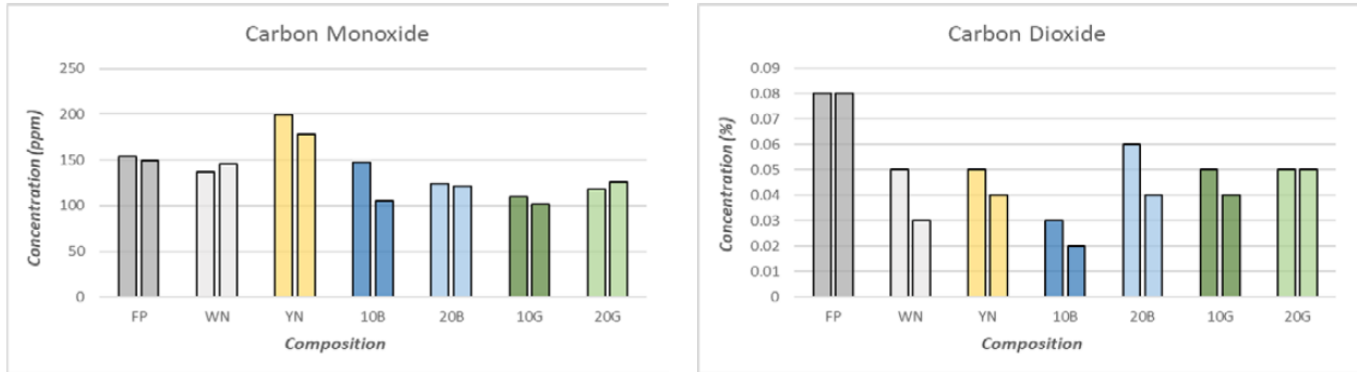
Experimental emission analysis

Measurements made during the combustion of various compositions incorporating nitrocellulose or inert materials allow a comparison of the carbon monoxide and carbon dioxide emissions generated by each formulation analysed. Figure 5.15 shows the results recorded by the gas analyser. The meaning of the abbreviations used in the figure is defined in Table 4.22.

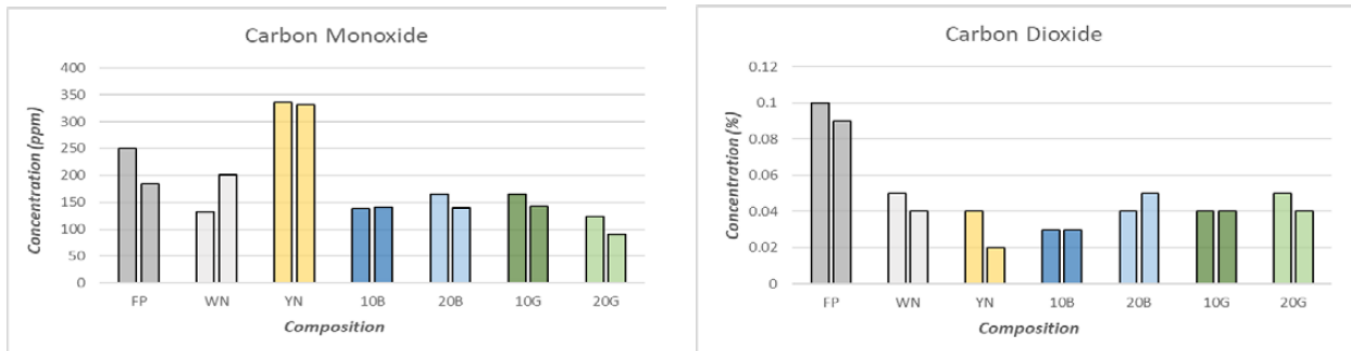
These results provide significant insights into the emissions of gases such as CO and CO_2 produced by flash powder and its potential alternatives. Previous studies on firework emissions [56], [192], [193] indicate a direct correlation between the amount of the new net explosive content (NNEC) in bangers and the levels of these gases. For example, Sample A, which contains 0.08 g of NNEC, reaches maximum emissions of 199 ppm CO for yellow nitrocellulose and 0.08% vol. CO_2 for traditional flash powder. In Sample B, with 0.1 g of NNEC, the maximum concentrations are higher, at 336 ppm CO and 0.10% vol. CO_2 . Finally, Sample C,

using 0.2 g of NNEC, exhibits the highest emissions, with 1612 ppm CO for yellow nitrocellulose and 0.29% vol. CO₂ for flash powder. These results clearly demonstrate that the emissions from combustion are directly proportional to the amount of NNEC used in bangers.

Samples A



Samples B



Samples C

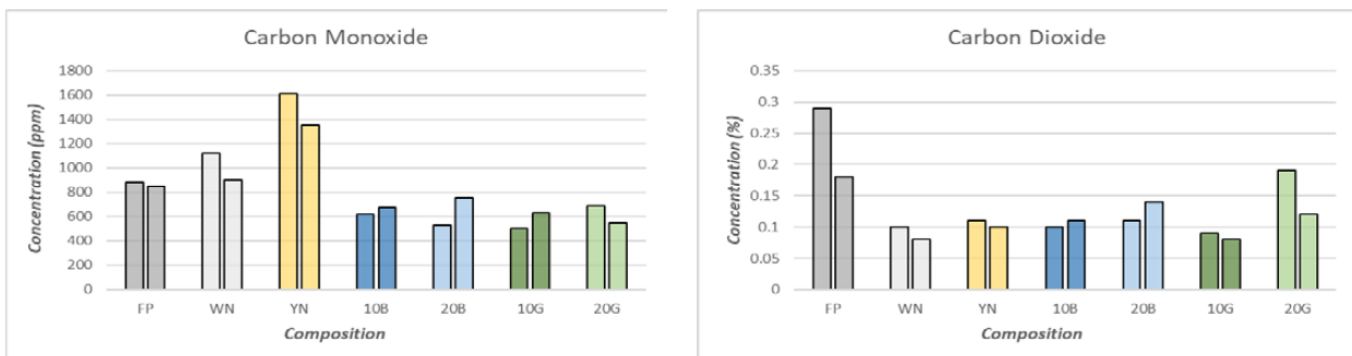


Figure 5.15. CO and CO₂ emissions for flash powder alternatives.

When comparing the three compositions across Samples A, B, and C, a consistent trend is observed. Carbon monoxide emissions, a primary byproduct of nitrocellulose combustion [157], [194], are significantly higher in yellow

nitrocellulose. In contrast, white nitrocellulose, due to its higher purity and more efficient combustion, generates CO levels similar to those of flash powder. The recorded data show that yellow nitrocellulose emits 35-80% more CO compared to flash powder and white nitrocellulose, highlighting the relevance of purity in composition. On the other hand, the addition of inert compounds like sodium bicarbonate and recycled glass reduces CO emissions, as the inert materials addition lowers the NEC while maintaining the same total banger mass. In some cases, CO emissions decrease by nearly 50% compared to the original flash powder. Previous research has already confirmed this fact, indicating that the addition of inert materials to combustible substances reduces the environmental emissions generated in their combustion [129], [130].

Interestingly, emissions from compositions with 20% (w/w) recycled glass are higher than those with 10% (w/w), and a similar pattern is noted for sodium bicarbonate. This could be attributed to moisture loss and CO₂ release during the thermal decomposition of these inert materials, as reported in earlier studies [195]. Additional testing is recommended to establish average values, as observed deviations might also stem from factors like fuse emissions or residual material in the container.

Regarding CO₂ emissions, traditional flash powder generates the highest concentrations of this gas. Similar to CO emissions, the addition of inert materials and the consequent reduction in NEC lead to a significant decrease in CO₂ emissions, with some compositions emitting less than 50% of the CO₂ produced by traditional flash powder.

Sound level analysis

As mentioned above, the sound pressure levels generated by the bursting effects of fireworks represent one of the main concerns of today's society. For this reason, the tests carried out aim to evaluate the sound pressure levels produced by the different compositions analysed, seeking to determine whether it is possible to reduce them without affecting the proper functioning of the devices. To ensure the reliability of the results and to avoid outliers, each test was repeated five times. The average sound pressure values obtained for each type of device and composition studied are presented in Figure 5.16. The meaning of the abbreviations used in the figure is defined in Table 4.22.

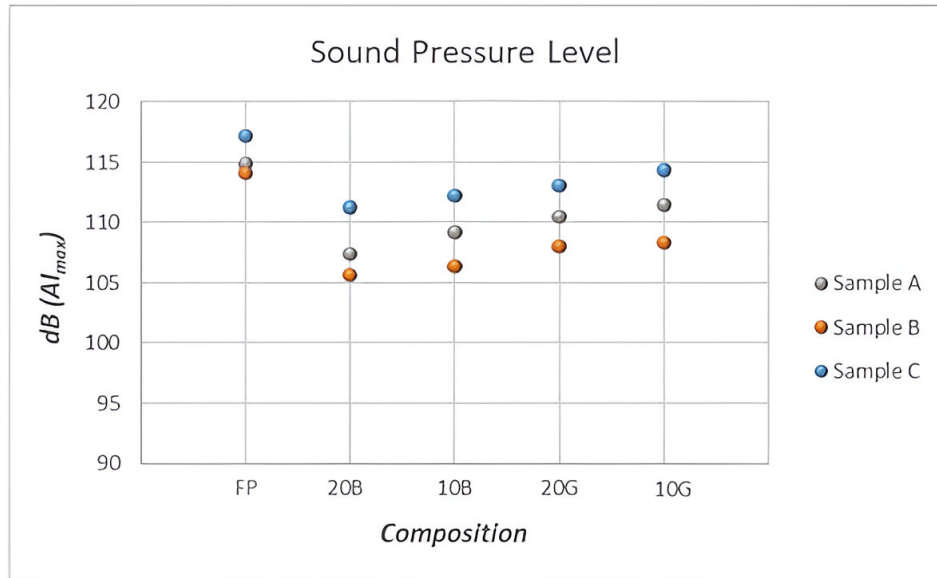


Figure 5.16. Sound pressure level generated by flash powder alternatives.

The results show that the highest sound pressure levels correspond to bangers composed of traditional flash powder. Specifically, sample A records an average of 114.85 dB (AI_{max}), sample B reaches 114.03 dB (AI_{max}) and sample C, with a NNEC of 0.2 g, reaches 117.13 dB (AI_{max}). These data show that the sound pressure level does not depend only on the NNEC contained in the banger. For example, although sample A has a lower NNEC than sample B, it generates higher sound levels. This trend is consistently observed in the compositions of samples A and B, indicating that additional factors such as the design of the article, the strength of the paper of the container tube or the compression generated by the gases also have a significant influence on the noise levels [121].

On the other hand, the incorporation of inert compounds, such as sodium bicarbonate or recycled glass, helps to reduce the sound pressure level. Sodium bicarbonate is more effective in reducing the sound effect. In addition, it is observed that higher concentrations of these inert compounds (20 % w/w) achieve lower noise levels than concentrations of 10 % w/w. The composition combining flash powder with 20 % sodium bicarbonate records the lowest sound pressure levels: 107.37 dB in sample A, 105.61 dB in sample B and 111.24 dB in sample C. These compositions achieve a sound reduction in the range of 5 % to 7 %.

Since the decibel scale is logarithmic in base 10 [196], [197], this reduction represents a significant change in the perception of the human ear. For example, a decrease of about 10 dB is approximately equivalent to a 50% reduction in sound

perception. In other words, the bangers including 20% of sodium bicarbonate in their concentrations reduce the perceived intensity of sound by half.

According to the tests carried out with nitrocellulose (white and yellow) on the three types of bangers, adequate performance was not obtained. In all cases, the cardboard tube failed to break, preventing the intended bursting effect. Although the nitrocellulose reacted, the gases released escaped through the silicone plug without generating sufficient pressure to break the cardboard container. This is because nitrocellulose has a less violent reaction than flash powder, and the silicone does not withstand the pressure generated, giving way before the explosion occurs.

Explosion pressure analysis

The explosion pressure produced by explosive charges is one of their main characteristics. This type of powder is characterised by its high reaction speed and the high temperatures it generates, resulting from the presence of metallic compounds [198]. This combination allows the rapid generation of large quantities of gases, which increases the pressure inside the container until it ruptures, triggering the explosion. The explosion process can be represented by a curve relating pressure (kPa) and time (ms), as shown in Figure 5.17. This curve, obtained directly from tests on one of the test samples, shows a sudden increase in pressure, reaching its maximum value in only 0.2 ms.

In the case of pyrotechnic shells, these contain a small container with flash powder. Upon reaching the desired height, the flame ignites this flash powder, which opens the article and transmits the combustion to the chemical compounds that produced the main effects, such as coloured stars, sound effects or crackers [51].

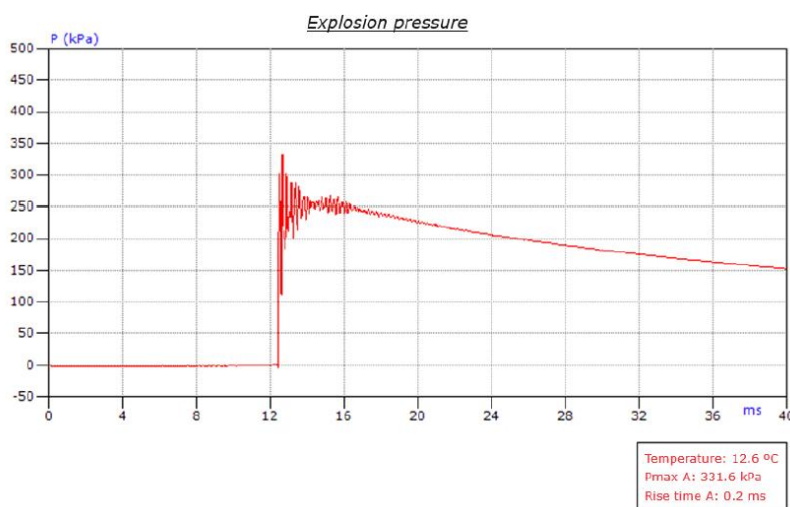


Figure 5.17. Explosion pressure curve generated by a banger under study.

However, the use of flash powder in shells is not intended to produce sound effects. In order to apply alternative compositions in pyrotechnic shells, it is essential to analyse the explosion pressure and determine whether it is sufficient to open the device. The results of the explosion pressure tests, are presented in Table 5.19.

Table 5.19. Maximum explosion pressure registered (kPa).

Composition	Sample A	Sample C	Sample C
FP	320.0	512.0	555.9
	331.6	476.4	589.9
WN	14.4	--	--
	27.5	--	--
YN	--	--	--
	--	--	--
20G	228.6	353.6	497.3
	239.5	240.8	539.6
10G	311.2	404.2	542.3
	291.5	411.7	533.4
20B	132.7	297.8	466.4
	234.7	284.1	423.2
10B	272.1	427.3	520.8
	257.1	369.8	508.6

Note: -- indicates that the banger did not break the tube and no explosion was recorded

Results reveal that some compositions do not perform adequately. In particular, most of the bangers containing nitrocellulose (except the WN in sample A) fail to rupture the cardboard of the tube, as already observed in sound pressure level tests. Although the nitrocellulose ignites, the reaction is less violent, and the gases are released gradually through the plug rather than generating a sudden burst. In contrast, the WN in sample A succeeds in rupturing the cardboard, although the pressures achieved are considerably lower than those of traditional flash powder. For example, while flash powder presents a pressure rise time of 0.2 ms, generating a strong explosion, nitrocellulose presents rise times between 14 and 17 ms, producing a more gradual effect. Increasing the nitrogen content in

nitrocellulose could increase the reaction rate and generate a more explosive character [199], although this would compromise safety conditions.

On the other hand, compositions with flash powder and the addition of inert materials, such as sodium bicarbonate or recycled glass, show satisfactory performance. The data indicates that, in general, the explosion pressure increases as the Net Explosive Content (NEC) increases, although this relationship is not strictly proportional. For example, for FP bangers, sample A (0.08 g NNEC) generates an average pressure of 325.8 kPa, while sample B (0.1 g NNEC) reaches 494.2 kPa. However, sample C, with twice as much NNEC as B, generates only 16% more pressure, reaching 572.9 kPa. This shows that other factors, such as the design of the device, the material of the tube or the volume of the container, also significantly influence the explosion pressure [121]. By adding inert materials to the flash powder, the explosion pressure decreases, with this reduction being more noticeable in sample B than in samples A and C. In addition, sodium bicarbonate is more effective than recycled glass, as seen in the variations of approximately 75 kPa between compositions 20G and 20B of sample C. It is also confirmed that a higher concentration of inert materials further reduces the explosion pressure, as it replaces part of the flash powder and decreases the sensitivity of the composition to ignition [126].

A comparison between previous sound pressure results and explosion pressure reductions in samples with 20% sodium bicarbonate reveals that the sound pressure decreases by about 50%, while the explosion pressure decreases by 23% to 43%, depending on the sample. To compensate for this decrease in explosion pressure, more explosive charge could be added to the banger, provided that similar pressures are achieved to maintain proper operation. This would make it feasible to use these compositions as more sustainable and less noisy alternatives.

However, establishing a direct relationship between NNEC and explosion pressure requires further testing that considers different tube designs, materials and composition percentages. The same applies to nitrocellulose: to make it a viable alternative to flash powder, it would be necessary to increase the energy released during its combustion. This could be achieved by compositions with higher nitrogen content, although it would require further studies to ensure safe and efficient operation.

5.4.3. Fire risk assessment

In order to be able to use alternative compositions to traditional powder, it is necessary to know the properties and associated risks of these compositions. The addition of inert compounds to traditional compositions reduces the risks of ignition and provides greater safety during the handling and storage of the articles, as is well known. On the other hand, the substitution of black powder by nitrocellulose as a propellant has certain associated problems, due to the fact that the nitrocellulose presented low thermal stability. Therefore, it is necessary to properly address the associated risk.

The risk assessment is carried out by comparing nitrocellulose with black powder. Once the process nodes with possible deviations have been located, based on the previous accidents analysed, the risk situations are evaluated using the severity vs. frequency matrix. The detailed results of the risk analysis are shown in Table 5.20, where identical results can be observed for both compositions due to their sensitivity to the same parameters. The severity vs. frequency matrix differentiates between situations of maximum risk (in red colour in Table 5.20), high risk (in yellow colour in Table 5.20) and medium risk (in green colour in Table 5.20).

Table 5.20. Detailed risk analysis by HAZOP methodology results.

Sub-process	Node	GW	Parameter/ Element	Deviation	Consequences	EVALUATION	
						Nitro.	Powd.
Loading process	Product handling by the operator	Low	Stability	Material falling to the ground	Damage to packaging		
				Material falling to the ground	Damage to the product		
				Material falling to the ground	Detonation or ignition of pyrotechnic material		
		Yes	Friction	Temperature increase	Damage to the product or variation in the characteristics of composition		
				Temperature increase	Ignition of pyrotechnic article or packaging		
				Temperature increase	Detonation of pyrotechnic product(s)		
		Yes	Ignition	Contact with ignition source	Ignition of pyrotechnic article or packaging		
				Contact with ignition source	Detonation of pyrotechnic product(s)		
				Temperature increase	Ignition of pyrotechnic article or packaging		
				Temperature increase	Detonation of pyrotechnic product(s)		
				Self-ignition	Ignition of pyrotechnic article or packaging		
				Self-ignition	Detonation of pyrotechnic product(s)		
		More	Static electricity	A spark occurs	Ignition of pyrotechnic article or packaging		
				A spark occurs	Detonation of pyrotechnic product(s)		

		More	Rough	Damaged product	Increased risk of fire or explosion in future phases		
	Product	More	Weight	Incorrect load lifting	Injury to the operator that can lead to falling material		
Transportation	Truck storage	Low	Fastening	Free movement of the load inside the truck	Striking of pyrotechnic material which may damage the pyrotechnic article packaging		
				Free movement of the load inside the truck	Striking of pyrotechnic material which may damage pyrotechnic articles		
				Free movement of the load inside the truck	Striking of the material which may cause detonation of the pyrotechnic product		
	Operator's driving style	More	Rough	Failure of anchoring systems such as: Locking wedges, Corner plates, Panels, Tie bars, Blocking with padding.	Striking of pyrotechnic material which may damage pyrotechnic articles or result in detonation		
				Free movement of the load inside the truck	Striking of pyrotechnic material which may damage pyrotechnic articles		
				Free movement of the load inside the truck	Striking of the material which may cause detonation of the pyrotechnic product		
				Knocking of cargo inside the truck	Striking of pyrotechnic material which may damage pyrotechnic articles		
				Knocking of cargo inside the truck	Striking of the material which may cause detonation of the pyrotechnic product		
				Increased friction between stored goods	Striking of pyrotechnic material which may damage pyrotechnic articles		
				Increased friction between stored goods	Striking of the material which may cause detonation of the pyrotechnic product		
	Route	Yes	Irregularities in the terrain	Failure of anchoring systems such as: Locking wedges, Corner plates, Panels, Tie bars, Blocking with padding.	Movement of cargo inside the truck		
				Knocking of cargo inside the truck	Striking of pyrotechnic material which may damage pyrotechnic articles		
				Knocking of cargo inside the truck	Detonation of pyrotechnic product(s)		
				Increased friction between stored goods	Detonation or ignition of pyrotechnic material		
		Late	Time	Delay on the route due to various causes	Packaging deterioration		
				Delay on the route due to various causes	Deterioration of the product or of the composition characteristics		
		More	Moisture	Increased humidity due to weather conditions during the journey	Packaging deterioration		
		More		Increased humidity due to weather conditions during the journey	Decrease in final product quality		
		Less		Increased humidity due to weather conditions during the journey	Drying of the product which may promote ignition		
		More	Temperature	Increase in temperature due to weather conditions during the journey	Damage to the product or variation in the characteristics of composition		
				Increase in temperature due to weather conditions during the journey	Ignition of pyrotechnic article or packaging		

		Yes	Accident	Increase in temperature due to weather conditions during the journey	Detonation of pyrotechnic product(s)		
				Product spillage	Soil and water pollution		
				Detonation of the product	Damage to third parties		
				Detonation of the product	Occurrence of polluting clouds		
Transfer to storage	Product handling by the operator	Low	Stability	Product fire	Occurrence of polluting clouds		
				Material falling to the ground	Damage to packaging		
				Material falling to the ground	Damage to the product		
				Material falling to the ground	Detonation or ignition of pyrotechnic material		
		More	Friction	Temperature increase	Damage to the product		
				Temperature increase	Ignition of pyrotechnic article or packaging		
				Temperature increase	Detonation of pyrotechnic product(s)		
		Yes	Ignition	Contact with ignition source	Ignition of the container, article or detonation of the pyrotechnic article can occur		
				Temperature increase	Ignition of the container, article or detonation of the pyrotechnic article can occur		
				Self-ignition	Ignition of the container, article or detonation of the pyrotechnic article can occur		
		More	Rough	Damaged product	Increased risk of fire or explosion in future phases		
	Product	More	Weight	Incorrect load lifting	Injury to the operator that can lead to falling material		
		More	Chemical composition	The product is defective and contains a higher quantity of explosive	Has an increased risk of ignition or detonation		
		Yes	Damaged	Material has been damaged and explosive material has been spilled	A product damaged during the transport phase inflames		
		Yes		El material se ha dañado y se ha derramado el material explosivo	A damaged product during the transport phase detonates		
	Packaging	Yes	Damaged	El material se ha dañado y se ha derramado el material explosivo	The pyrotechnic material is more exposed, and ignition occurs.		
		Yes		The packaging is damaged	Pyrotechnic material is more exposed, and the detonation occurs		
	Fire protection system	No	Flow rate	The flow rate is less than the design flow rate.	The flow is not sufficient to stop the early stages of the fire.		
		Inverse	Flow rate	The extinguishing fluid is in poor condition or not properly designed for the type of fire.	The type of fluid used to charge the fire is not suitable for the type of fire studied.		
		Less	Pressure	The fluid has a low pressure and therefore does not flow out of the disperser with sufficient force.	Pressure not enough to stop the early stages of the fire		
		Less	Flow rate	Spreaders blocking	The flow is not sufficient to stop the early stages of the fire.		
		No	Electricity	Fire detection system does not start	The extinguishing emulsion is not emitted, and the fire cannot be stopped.		
Storage	Fire protection system	No	Flow rate	The flow rate is less than the design flow rate.	The flow is not sufficient to stop the early stages of the fire.		
		Inverse	Flow rate	The extinguishing fluid is in poor condition or not properly designed for the type of fire.	The type of fluid used to charge the fire is not suitable for the type of fire studied.		

		Less	Flow rate	Spreaders blocking	The flow is not sufficient to stop the early stages of the fire.		
		Less	Flow rate	The detection system is not connected to the mains and the supply is interrupted.	The flow is not enough to stop the fire.		
		Less	Flow rate	Detection system is connected to the grid and there is no supply	No extinguishing agent so the fire does not stop.		
		Less	Pressure	The fluid has a low pressure and therefore does not flow out of the disperser with sufficient force.	Pressure not enough to stop the early stages of the fire		
		No	Electricity	Fire detection system does not start	The extinguishing emulsion is not emitted, and the fire cannot be stopped.		
	Detectors	Inverse	Flame detection	Detector does not detect flame in the initial phase	Fire starts without being extinguished		
				Detector does not detect flame in the initial phase	The fire does not stop, and the stored pyrotechnic material is detonated.		
		No	Electric current	Detectors cannot operate and do not detect the flame	Fire starts without being extinguished		
				Detectors cannot operate and do not detect the flame	The fire does not stop, and the stored pyrotechnic material is detonated.		
		No	Calibration	The detection setting is not adequate and does not pick up flames until a later stage.	Fire starts without being extinguished		
				The detection setting is not adequate and does not pick up flames until a later stage.	The fire does not stop, and the stored pyrotechnic material is detonated.		
		Storage of material	More	Temperature of the warehouse increases	Self-ignition of pyrotechnic material occurs		
				Warehouse pressure increases	The conditions for detonation are worsened.		
	Product handling by the operator	Low	Stability	Material falling to the ground	Damage to packaging		
				Material falling to the ground	Damage to the product		
				Material falling to the ground	Detonation or ignition of pyrotechnic material		
		Yes	Ignition	Contact with ignition source	Ignition of the container, article or detonation of the pyrotechnic article can occur		
				Temperature increase	Ignition of the container, article or detonation of the pyrotechnic article can occur		
				Self-ignition	Ignition of the container, article or detonation of the pyrotechnic article can occur		
		More	Rough	Damaged product	Increased risk of fire or explosion in future phases		
		More	Static electricity	A spark occurs	Ignition of pyrotechnic article or packaging		
				A spark occurs	Detonation of pyrotechnic product(s)		

As can be seen, 21 situations of maximum risk and 50 of high risk were identified. This number is higher than in other sectors due to the high reactivity of the explosive material [200]. On the other hand, the situations shown in green correspond to those with the lowest risk.

Figure 5.18 a) shows the risk distribution for both compositions for each of the parameters analysed. Figure 5.18 b) shows that most of the risk situations occur during storage and transfer to the storage, due to increased exposure of the pyrotechnic material. As shown in Figure 5.18 a), the most critical aspects of the process are related to impact (14.3%), friction (9.5%), static electricity (19.0%) and contact with ignition sources (19.0%), although the importance of the proper functioning of safety systems stands out, with a probability of 28.6%.

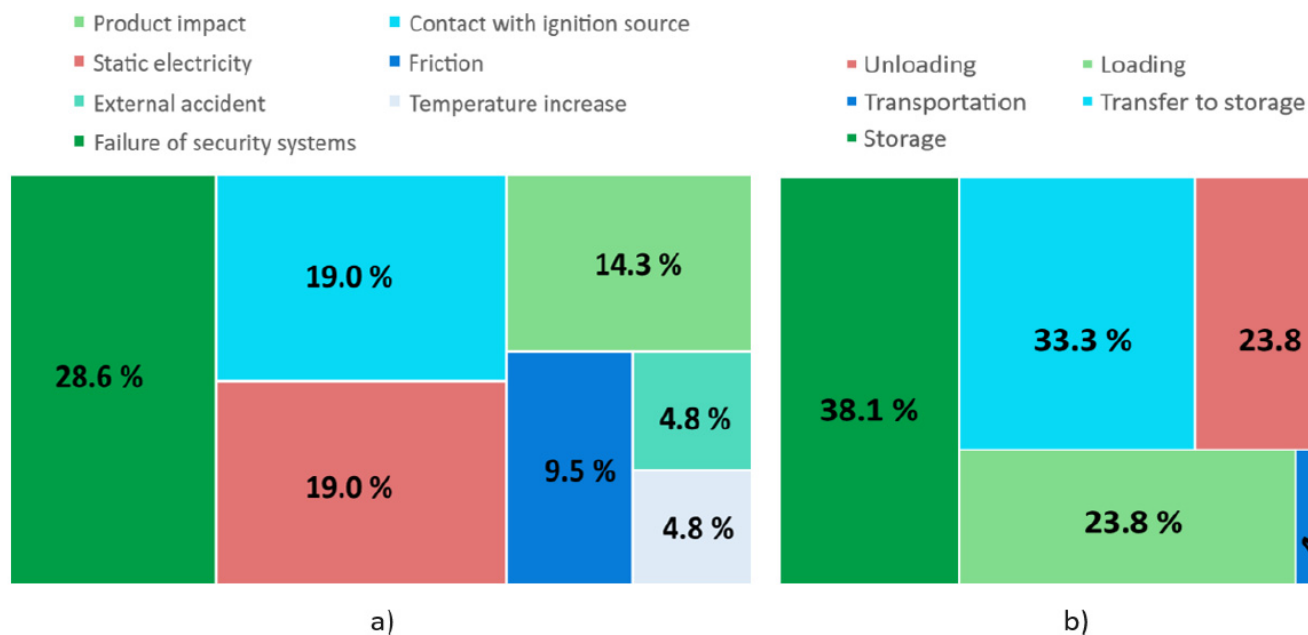


Figure 5.18. a) Distribution of risk on the causes analysed. b) risk distribution according to the sub-process studied.

Although both compounds share the same risk situations, thermogravimetric analysis allows differences between them to be identified. According to this analysis, the risk of self-ignition is low for both compounds due to their high self-ignition temperatures. However, in inert atmospheres, nitrocellulose reacts at 200°C, while black powder reacts at approximately 400 °C, indicating that nitrocellulose is more easily able to initiate the reaction. Thus, although the consequences of an accident are similar for both compounds, nitrocellulose is more likely to be the cause. This does not mean that it cannot be used, but it does require adapting safeguards and protective measures for its handling.

6. Conclusions

The pyrotechnics industry faces the need to address several socioecological challenges in order to continue to coexist with the rest of society. These challenges drive the sector towards a more sustainable model for society and the environment, in line with the Sustainable Development Goals (SDGs) contained in the 2030 Agenda. The results obtained in the research showed important tools with which the sector can adjust its materials and processes towards manufacturing and use in order to generate a lower impact.

One of the main problems faced by the pyrotechnic sector is the emissions generated during the use of fireworks. A large number of compounds are released into the atmosphere as a result of the combustion of the pyrotechnic mixtures inside these devices, intended to create the desired effects. Among the most important and problematic emissions are gases that directly affect the greenhouse effect, such as CO₂, others that indirectly affect it, such as CO, and perchlorate compounds. The latter are the most unsafe products generated by pyrotechnics, due to the contamination of groundwater, not only during their use, but also during their production and handling. These emissions have been demonstrated by the theoretical study of the emissions released by the fireworks displays at Villaviciosa de Odón in Spain and the Macy's Fireworks Show during Independence Day in New York, one of the largest pyrotechnic shows in the world.

However, there are other socially accepted emitters that are used on a daily basis and produce a considerable number of emissions, much larger than the fireworks displays studied. Internal combustion vehicles circulating inside the M-30 ring road in Madrid, according to the theoretical analysis carried out, based on the limits defined in the EURO 6 standard, produce five times the carbon dioxide and 33,285% of the carbon monoxide produced in the Villaviciosa de Odón fireworks display, every day. Furthermore, the CO₂ emissions generated by a fully loaded Boeing 737-700 commercial aircraft compared to the CO₂ released at La Pólvara in Villaviciosa de Odón gave the following data: A Madrid-Valencia flight represents 1,172.7% of emissions, the Madrid-London flight 3,675.4% and the Madrid-Moscow flight 8,641.7%.

On the other hand, pyrotechnics generate a noise impact that causes a certain degree of discomfort to society and, in particular, to pets. The study reveals a direct connection between the sound pressure level of pyrotechnic articles and their category. Furthermore, it is observed that cracker, whistle, opening or bursting

effects generate higher levels than those limited to visual effects, such as lights, sparks and colour. This relationship is key to understand the intensity of the effects in the environment.

However, there is a discrepancy between the actual attenuation of these effects and the current theoretical formula representing such attenuation. This actual attenuation varies according to the type of article and the distance to the receiver. As the distance increases, an exponential increase in sound attenuation was observed, but this variation was not reflected in the theoretical calculations. In particular, it was noted that aerial articles exhibit slower sound attenuation than ground-based articles, the latter requiring a greater separation to achieve an equivalent reduction in decibels.

In addition to the factors inherent to sound, sound propagation is also affected by environmental factors such as relative humidity and temperature. It was found that the higher the temperature and the lower the humidity, the lower the sound pressure level recorded. Additionally, it was verified that barriers, both natural and artificial, play a crucial role. This was evidenced in measurements made during La Mascletá, where it was shown that the receivers inside buildings were more protected against the sound effects than those exposed directly, as the measurements recorded values of 15 dB(LC_{Peak}) lower for the point located in the interior of the building.

By analysing the sound spectrum in everyday activities where the animals are not affected in any way, it was found that pyrotechnics do not differ significantly in intensity or frequency from other sounds such as barking, traffic noise or horns. It is important to note that the sounds of fireworks displays are of a one-off, short duration and therefore should not be equated with continuous exposure to everyday noise, as may be experienced in urban environments. This serves to determine that the impact on animal welfare due to pyrotechnics does not lie in physical damage to hearing, but in the occurrence of fear or stress due to lack of training and unfamiliarity with such sounds. Animal training is one of the main and most effective strategies to prevent the occurrence of fear and stress in animals. The implementation of this measure in current training programmes would considerably reduce animal welfare problems caused by high intensity, spontaneous and unpredictable noises.

Despite this, the sector can adopt more sustainable measures. The assessment of the environmental impacts associated with two common types of fireworks used in

Spain was carried out using the LCA methodology. The study has revealed that the stage with the highest impact is the acquisition and distribution of raw materials (especially hazardous materials such as potassium perchlorate, potassium nitrate or aluminium-magnesium).

Comparing the climate change impact values of flash bangers and pyrotechnic shells with those of other everyday products it was noticed that those produced by pyrotechnic articles were not significant, emitting 0.0102 kg and between 3.87 and 4.65 kg CO₂ equivalents, respectively. The production of just one can of Coca-Cola emits 0.17 kg of CO₂. The shells, although slightly higher than those of other everyday products, do not reach, for example, 15.5 kg CO₂ per 100 g of beef. Despite this, the analysis highlighted points in the process where a contribution can be made to reduce the impact. In particular, the need to focus on the selection of raw materials and reduce the use of hazardous substances to mitigate fireworks environmental footprint.

After understanding the stages with the greatest impact on the pyrotechnic sector and the social difficulties to which it is exposed, possible alternative compositions were analysed to guide fireworks towards sustainability.

The use of nitrocellulose ($[C_6H_7(NO_2)_3O_5]_n$) as a substitute for black powder and perchlorate compounds in pyrotechnic compositions was investigated. It was shown that nitrocellulose can significantly reduce GHG emissions, in particular carbon dioxide, compared to black powder, when both are used as a propellant. The results showed a reduction in CO₂ emissions of 42%. However, carbon monoxide emissions were higher when nitrocellulose was used, due to the reactions that take place during combustion. Taking into account the residence time in the atmosphere of both gases and their influence on the greenhouse effect, it can be confirmed that nitrocellulose is a composition with advantages in environmental sustainability, as far as the greenhouse effect is concerned. By using nitrocellulose as a substitute for perchlorate oxidants, the same trend in CO₂ and CO emissions was obtained. Furthermore, by eliminating perchlorates from pyrotechnic compositions, groundwater contamination via the soil by precipitation related to the production, handling and use of these compounds can be reduced. The ignition hazard analysis carried out by TGA and HAZOP confirmed that nitrocellulose is less thermally stable than black powder therefore further safeguards and protective measures will be necessary. A solution to this fact during nitrocellulose's transport and storage stages would be to increase its moisture content, which implies

improvements in thermal stability. Therefore, nitrocellulose achieves environmental advantages over black powder but presents greater safety risks.

The addition of inert compounds such as sodium bicarbonate (NaHCO_3) or recycled glass and again nitrocellulose were analysed as possible alternatives to flash powder for bursting effects. Comparisons in the gas analyser showed that the new compositions significantly reduce CO_2 emissions. Moreover, the addition of inert compounds reduces carbon monoxide emissions.

However, nitrocellulose did not achieve a correct functioning of the firework, as it does not release enough energy to achieve the opening of the container tube. This fact makes its application in pyrotechnic shells impossible, as the opening of the container would not be achieved and, therefore, the desired visual effects would not be obtained. The explosiveness of nitrocellulose is directly related to its nitrogen content, so by increasing the nitrogen content above the 12.6% that nitrocellulose used currently in pyrotechnics, the desired performance could be achieved.

On the other hand, the addition of inert compounds is a viable solution to reduce emissions and sound pressure levels, while reducing the storage and transport risks associated with traditional powder or nitrocellulose. According to the results obtained, sodium bicarbonate is more effective than glass powder and reduces sound by approximately 50% when using a 20% of mass concentration of sodium bicarbonate. Although the addition of inerts also reduces the explosion pressure generated, a greater reduction in sound than in pressure is observed. This makes its use in pyrotechnic shells feasible, as increasing the total charge would result in the same explosion pressure and therefore the correct opening of the container, while reducing the sound pressure level. Although more tests are needed to establish a Net Explosive Content (NEC) - Explosion Pressure relationship, due to the influence of other factors such as design, material or percentages of each composition, it can be concluded that the addition of inerts to flash powder is a real alternative that would reduce its emissions and sound pressure level.

According to the exhaustive analysis of the processes of the pyrotechnic sector carried out in this thesis, a possible sustainable future for the industry can be envisaged, thus achieving coexistence with the rest of society. However, among other measures, the sector should consider compositions that generate less environmental and noise impact on the environment, such as those evaluated in this study.

7. Future research lines

From the results obtained in this study, some possible research lines were found with the aim of improving and verifying the methods used in this study, enriching it and providing more accurate information and new insights in sustainable pyrotechnics devices design.

The LCA proposed for the different processes of production, transport and use of pyrotechnic articles implies certain aspects that need to be validated with real world data. Therefore, future research should aim to collect comprehensive real-world data, in particular for the end-of-life stage, in order to provide a more accurate and complete assessment of the recovery and recycling of pyrotechnic waste. In addition, extending the analysis to include other types of fireworks and exploring alternative materials and manufacturing processes would be a crucial aspect.

Tests about nitrocellulose offer significant environmental benefits, but these can be improved by analysing full-size prototype articles in order to estimate the actual substitution ratio where the same effects can be achieved. In this way, application and the associated economic analysis can also be analysed. Furthermore, analysing different nitrocellulose compositions, varying the amount of nitrogen, can provide important information on the needs of the compositions contained in the pyrotechnic articles.

Finally, future tests can analyse a larger number of flash powder with inerts samples in order to establish a Net Explosive Content (NEC) - Explosion Pressure relationship. This would require the analysis of different charges as well as studying the influence of other factors such as design, container material, etc.

References

- [1] G. Chichilnisky, “What is sustainable development?,” in *Man-Made Climate Change: Economic Aspects and Policy Options*, Springer, 1999, pp. 42–82.
- [2] “RES/70/1. Transforming our world: the 2030 agenda for sustainable development,” *Seventieth United Nations General Assembly, New York*, vol. 25, pp. 86–97, 2015.
- [3] “Ministerio de Derechos Sociales, Consumo y Agenda 2030 - Conoce la Agenda.” Accessed: Apr. 13, 2023. [Online]. Available: https://www.mdsocialesa2030.gob.es/agenda2030/conoce_la_agenda.htm
- [4] “The European Green Deal - European Commission.” Accessed: Mar. 08, 2024. [Online]. Available: https://commission.europa.eu/strategy-and-policy/priorities-2019-2024/european-green-deal_en
- [5] S. Fukuda-Parr and T. Smaavik Hegstad, “‘Leaving no one behind’ as a site of contestation and reinterpretation,” *Journal of Globalization and Development*, vol. 9, no. 2, p. 20180037, 2018.
- [6] J. J. Sabatini, “Advances toward the development of ‘Green’ pyrotechnics,” *Green Energetic Materials*, pp. 63–102, 2014, doi: doi.org/10.1002/9781118676448.ch04.
- [7] H. T. A. Bressers, “Implementing sustainable development: how to know what works, where, when and how,” *Governance for sustainable development: The challenge of adapting form to function*, p. 284, 2004, doi: doi.org/10.4337/9781845421700.00018.
- [8] G. Croteau, R. Dills, M. Beaudreau, and M. Davis, “Emission factors and exposures from ground-level pyrotechnics,” *Atmos Environ*, vol. 44, no. 27, pp. 3295–3303, 2010.
- [9] R. Camilleri and A. J. Vella, “Emission factors for aerial pyrotechnics and use in assessing environmental impact of firework displays: case study from Malta,” *Propellants, Explosives, Pyrotechnics*, vol. 41, no. 2, pp. 273–280, 2016.

- [10] D. Katoria, D. Mehta, D. Sehgal, and S. Kumar, "A review of risks to workers associated with fireworks industry," *International Journal of Environmental Engineering and Management*, vol. 4, no. 3, pp. 259–264, 2013.
- [11] D. León, B. Castells, I. Amezcua, J. Casín, and J. García-Torrent, "Experimental Quantification of Fire Damage Inside Pyrotechnic Stores," *Applied Sciences*, vol. 13, no. 10, p. 6181, 2023, doi: doi.org/10.3390/app13106181.
- [12] "Energy - United Nations Sustainable Development." Accessed: May 06, 2022. [Online]. Available: <https://www.un.org/sustainabledevelopment/energy/>
- [13] "Modelo de Plan Estratégico Para las Empresas del Sector Pirotécnico Español," 2023. [Online]. Available: <http://www.lom.upm.es/img/Lom/Main/Modelo%20de%20PE%20para%20las%20empresas%20del%20Sector%20Pirot%C3%A9cnico%20Espa%C3%B1ol.pdf>
- [14] J. G. J. Olivier, K. M. Schure, and J. Peters, "Trends in global CO₂ and total greenhouse gas emissions," *PBL Netherlands Environmental Assessment Agency*, vol. 5, pp. 1–11, 2017.
- [15] K. Acevedo-Whitehouse and A. L. J. Duffus, "Effects of environmental change on wildlife health," *Philosophical Transactions of the Royal Society B: Biological Sciences*, vol. 364, no. 1534, pp. 3429–3438, 2009.
- [16] V. Naik and K. C. Patil, "High energy materials: A brief history and chemistry of fireworks and rocketry," *Resonance*, vol. 20, pp. 431–444, 2015.
- [17] J. Akhavan, *The chemistry of explosives 4E*. Royal Society of Chemistry, 2022.
- [18] M. S. Russell, *The chemistry of fireworks*. Royal Society of Chemistry, 2009.
- [19] J. A. Conkling and C. Mocella, *Chemistry of pyrotechnics: basic principles and theory*. CRC press, 1985.
- [20] B. Berger, "Parameters influencing the pyrotechnic reaction," *Propellants, Explosives, Pyrotechnics: An International Journal Dealing with Scientific and Technological Aspects of Energetic Materials*, vol. 30, no. 1, pp. 27–35, 2005.

-
- [21] A. J. Sánchez, “La Química de los fuegos artificiales.” Accessed: Feb. 02, 2022. [Online]. Available: <https://es-static.z-dn.net/files/d17/b4b1c25f7bd4f72bdef0003fc00e8bfd.pdf>
- [22] “Pirotecnia en España. Listado de empresas de Pirotecnia en España.” Accessed: Feb. 07, 2022. [Online]. Available: <https://empresite.eleconomista.es/Actividad/PIROTECNIA/>
- [23] “AEPIRO. Asociación Española de la Pirotecnia.” Accessed: Apr. 17, 2023. [Online]. Available: <https://aepiro.org/>
- [24] “Informe – «Impacto del sector de la pirotecnia en España» | Fundación Civismo.” Accessed: Dec. 08, 2024. [Online]. Available: <https://civismo.org/informes/informe-impacto-del-sector-de-la-pirotecnia-en-espana/>
- [25] “Pyrotechnic Articles | OEC - The Observatory of Economic Complexity,” Pyrotechnic Articles. Accessed: Feb. 07, 2022. [Online]. Available: <https://oec.world/en/profile/sitc/pyrotechnic-articles>
- [26] *Real Decreto 989/2015, de 30 de octubre, por el que se aprueba el Reglamento de artículos pirotécnicos y cartuchería*. Spain, 2015, pp. 1–280. Accessed: Feb. 24, 2022. [Online]. Available: <https://www.boe.es/boe/dias/2015/11/07/pdfs/BOE-A-2015-12054.pdf>
- [27] “DIRECTIVE 2013/29/EU on the harmonisation of the laws of the Member States relating to the making available on the market of pyrotechnic articles,” 2013.
- [28] “Shopgoods fireworks | NT WorkSafe.” Accessed: Dec. 06, 2021. [Online]. Available: <https://worksafe.nt.gov.au/safety-and-prevention/fireworks/shop-goods-fireworks>
- [29] “Firework permits conditions.” Accessed: Dec. 06, 2021. [Online]. Available: <https://worksafe.tas.gov.au/topics/licensing-permits-and-registration/fireworks-permits/firework-permits-conditions>
- [30] “Health and Safety at Work (Hazardous Substances) Regulations 2017 (LI 2017/131) (as at 23 December 2023) Contents – New Zealand Legislation.” Accessed: Sep. 06, 2024. [Online]. Available: <https://www.legislation.govt.nz/regulation/public/2017/0131/latest/DLM7309401.html>

- [31] Environmental Protection Authority (EPA), “Code of Practice for Outdoor Pyrotechnic Displays (HSNOCOP 30),” Oct. 2012.
- [32] “Fireworks and Pyrotechnic Articles (Scotland) Act 2022”.
- [33] “WHO global air quality guidelines,” 2021.
- [34] “Directive (EU) 2024/2881 of the European Parliament and of the Council of 23 October 2024 on ambient air quality and cleaner air for Europe,” Oct. 2024. [Online]. Available: <http://data.europa.eu/eli/C/2023/251/oj>.
- [35] G. Steinhauser and T. M. Klapötke, “‘Green’ pyrotechnics: a chemists’ challenge,” *Angewandte Chemie International Edition*, vol. 47, no. 18, pp. 3330–3347, 2008.
- [36] A. K. Singh and A. Srivastava, “The impact of fireworks emissions on air quality in Delhi, India,” *Environmental Claims Journal*, vol. 32, no. 4, pp. 289–309, 2020.
- [37] Y. Wang, G. Zhuang, C. Xu, and Z. An, “The air pollution caused by the burning of fireworks during the lantern festival in Beijing,” *Atmos Environ*, vol. 41, no. 2, pp. 417–431, 2007.
- [38] L. Pirker, Ž. Velkavrh, A. Osīte, L. Drinovec, G. Močnik, and M. Remškar, “Fireworks—a source of nanoparticles, PM_{2.5}, PM₁₀, and carbonaceous aerosols,” *Air Qual Atmos Health*, vol. 15, no. 7, pp. 1275–1286, 2022.
- [39] E. F. Kirrane *et al.*, “Associations of ozone and PM 2.5 concentrations with Parkinson’s disease among participants in the Agricultural Health Study,” *J Occup Environ Med*, vol. 57, no. 5, pp. 509–517, 2015.
- [40] Y. Wang *et al.*, “Exposure to PM_{2.5} aggravates Parkinson’s disease via inhibition of autophagy and mitophagy pathway,” *Toxicology*, vol. 456, p. 152770, 2021.
- [41] D. Younan *et al.*, “PM_{2.5} Associated With Gray Matter Atrophy Reflecting Increased Alzheimer Risk in Older Women,” *Neurology*, vol. 96, no. 8, pp. e1190–e1201, 2021.
- [42] N. R. Council, D. on Earth, L. Studies, B. on E. Studies, and C. to A. the H. I. of P. Ingestion, *Health implications of perchlorate ingestion*. National Academies Press, 2005.

-
- [43] O. P. Soldin, L. E. Braverman, and S. H. Lamm, "Perchlorate clinical pharmacology and human health: a review," *Ther Drug Monit*, vol. 23, no. 4, pp. 316–331, 2001.
- [44] J. J. J. Clark, "Toxicology of perchlorate," in *Perchlorate in the Environment*, Springer, 2000, pp. 15–29.
- [45] W. E. Motzer, "Perchlorate: problems, detection, and solutions," *Environ Forensics*, vol. 2, no. 4, pp. 301–311, 2001.
- [46] C. Hogue, "Rocket-fueled river," *Chemical & engineering news*, vol. 81, no. 33, p. 37, 2003.
- [47] B. C. Blount, L. Valentin-Blasini, J. D. Osterloh, J. P. Mauldin, and J. L. Pirkle, "Perchlorate exposure of the US population, 2001–2002," *J Expo Sci Environ Epidemiol*, vol. 17, no. 4, pp. 400–407, 2007.
- [48] L. D. Nghiem, H. M. N. Iqbal, and J. Zdarta, "The shadow pandemic of single use personal protective equipment plastic waste: A blue print for suppression and eradication," *Case Studies in Chemical and Environmental Engineering*, vol. 4, p. 100125, 2021.
- [49] E. J. Blackwell, J. W. S. Bradshaw, and R. A. Casey, "Fear responses to noises in domestic dogs: Prevalence, risk factors and co-occurrence with other fear related behaviour," *Appl Anim Behav Sci*, vol. 145, no. 1–2, pp. 15–25, 2013.
- [50] "China's Fireworks Bans Spark Fiery Debate Ahead of Lunar New Year." Accessed: Jun. 06, 2024. [Online]. Available: <https://www.voanews.com/a/china-s-fireworks-bans-spark-fiery-debate-ahead-of-lunar-new-year/7417364.html>
- [51] R. Lancaster, *Fireworks: Principles and Practice. 3rd edition*. Chemical Publishing Company, 1998.
- [52] "Ministerio para la Transición Ecológica y el Reto Demográfico MITECO | Registro Estatal de Emisiones y Fuentes Contaminantes (PRTR-España)." Accessed: May 12, 2023. [Online]. Available: <https://prtr-es.es/>
- [53] J. Liu, Y. Chen, S. Chao, H. Cao, and A. Zhang, "Levels and health risks of PM_{2.5}-bound toxic metals from firework/firecracker burning during festival periods in response to management strategies," *Ecotoxicol Environ Saf*, vol. 171, pp. 406–413, 2019.

- [54] Y. Zhang, J. Wei, A. Tang, A. Zheng, Z. Shao, and X. Liu, “Chemical characteristics of PM_{2.5} during 2015 spring festival in Beijing, China,” *Aerosol Air Qual Res*, vol. 17, no. 5, pp. 1169–1180, 2017.
- [55] D. J. Seidel and A. N. Birnbaum, “Effects of Independence Day fireworks on atmospheric concentrations of fine particulate matter in the United States,” *Atmos Environ*, vol. 115, pp. 192–198, 2015.
- [56] A. Gonzalez, A. Boies, J. Swanson, and D. Kittelson, “Measuring the effect of fireworks on air quality in Minneapolis, Minnesota,” *SN Appl Sci*, vol. 4, no. 5, p. 142, 2022.
- [57] S. Yang *et al.*, “Profiles, source identification and health risks of potentially toxic metals in pyrotechnic-related road dust during Chinese New Year,” *Ecotoxicol Environ Saf*, vol. 184, p. 109604, 2019.
- [58] X. Huang *et al.*, “Temporal characteristics of atmospheric CO₂ in urban Nanjing, China,” *Atmos Res*, vol. 153, pp. 437–450, Feb. 2015, doi: 10.1016/j.atmosres.2014.09.007.
- [59] C. Hickey *et al.*, “Toxicity of particles emitted by fireworks,” *Part Fibre Toxicol*, vol. 17, pp. 1–11, 2020.
- [60] T. Moreno *et al.*, “Recreational atmospheric pollution episodes: inhalable metalliferous particles from firework displays,” *Atmos Environ*, vol. 41, no. 5, pp. 913–922, 2007.
- [61] T. Moreno *et al.*, “Effect of fireworks events on urban background trace metal aerosol concentrations: is the cocktail worth the show?,” *J Hazard Mater*, vol. 183, no. 1–3, pp. 945–949, 2010.
- [62] U. P. Nasir and D. Brahmaiah, “Impact of fireworks on ambient air quality: a case study,” *International journal of environmental science and technology*, vol. 12, pp. 1379–1386, 2015.
- [63] R. Tuckett, “Greenhouse gases,” in *Encyclopedia of Analytical Science*, Elsevier, 2019, pp. 362–372.
- [64] D. Nong, P. Simshauser, and D. B. Nguyen, “Greenhouse gas emissions vs CO₂ emissions: Comparative analysis of a global carbon tax,” *Appl Energy*, vol. 298, p. 117223, 2021.

-
- [65] K. Kaygusuz, "Energy and environmental issues relating to greenhouse gas emissions for sustainable development in Turkey," *Renewable and Sustainable Energy Reviews*, vol. 13, no. 1, pp. 253–270, 2009.
- [66] L.-J. Liu, L.-C. Liu, and Q.-M. Liang, "Common footprints of the greenhouse gases and air pollutants in China," *J Clean Prod*, vol. 293, p. 125991, 2021.
- [67] S. Banaji, "Nitrogen dioxide, carbon monoxide, natural and anthropomorphic effects, and earth's changing climate," *Atmospheric and Climate Sciences*, vol. 13, no. 1, pp. 62–71, 2022.
- [68] G. Shannon *et al.*, "A synthesis of two decades of research documenting the effects of noise on wildlife," *Biological Reviews*, vol. 91, no. 4, pp. 982–1005, 2016.
- [69] "European Environment Agency. (2017). Annual European Union greenhouse gas inventory 1990–2015 and inventory report 2017."
- [70] E. L. Plambeck, "Reducing greenhouse gas emissions through operations and supply chain management," *Energy Econ*, vol. 34, pp. S64–S74, 2012.
- [71] R. T. Wilkin, D. D. Fine, and N. G. Burnett, "Perchlorate behavior in a municipal lake following fireworks displays," *Environ Sci Technol*, vol. 41, no. 11, pp. 3966–3971, 2007.
- [72] A. Dejeaifve, A. Fantin, L. Monseur, and R. Dobson, "Making Progress Towards «Green» Propellants," *Propellants, Explosives, Pyrotechnics*, vol. 43, no. 8, pp. 831–837, Aug. 2018, doi: 10.1002/prop.201800026.
- [73] E. O. Espinoza and J. I. Thornton, "Characterization of smokeless gunpowder by means of diphenylamine stabilizer and its nitrated derivatives," *Anal Chim Acta*, vol. 288, no. 1–2, pp. 57–69, 1994.
- [74] W. A. MacCrehan, M. R. Reardon, and D. L. Duewer, "A quantitative comparison of smokeless powder measurements," *Journal of Forensic Science*, vol. 47, no. 6, pp. 1283–1387, 2002.
- [75] M. R. Reardon, W. A. MacCrehan, and W. F. Rowe, "Comparing the additive composition of smokeless gunpowder and its handgun-fired residues," *Journal of Forensic Science*, vol. 45, no. 6, pp. 1232–1238, 2000.
- [76] M. N. A. G. Yolhamid, F. Ibrahim, M. A. U. A. A. Zarim, R. Ibrahim, S. Adnan, and M. Z. A. Yahya, "The Novel Usage of Nitrocellulose as a

- Propellant of 5.56 mm Bullet,” *Solid State Phenomena*, vol. 280, pp. 361–367, 2018.
- [77] S. H. Jamal, N. J. Roslan, N. A. A. Shah, S. A. M. Noor, K. K. Ong, and W. M. Z. W. Yunus, “Preparation and characterization of nitrocellulose from bacterial cellulose for propellant uses,” *Mater Today Proc*, vol. 29, pp. 185–189, 2020.
- [78] H. Mattar *et al.*, “Nitrocellulose: Structure, synthesis, characterization, and applications,” *Water Energy Food Environ. J*, vol. 3, pp. 1–15, 2020.
- [79] *EN 15947-5, Pyrotechnic articles - Fireworks, Categories F1, F2, and F3 - Part 5: Requirements for construction and performance*. 2022.
- [80] “CIALFIR – Catálogo online.” Accessed: Dec. 10, 2024. [Online]. Available: <https://catalogo.cialfir.com/>
- [81] H. Chai, Q. Duan, H. Cao, M. Li, and J. Sun, “Effects of nitrogen content on pyrolysis behavior of nitrocellulose,” *Fuel*, vol. 264, p. 116853, 2020.
- [82] J. J. Sabatini and J. D. Moretti, “High-Nitrogen-Based Pyrotechnics: Perchlorate-Free Red-and Green-Light Illuminants Based on 5-Aminotetrazole,” *Chemistry—A European Journal*, vol. 19, no. 38, pp. 12839–12845, 2013.
- [83] J. D. Moretti, J. J. Sabatini, and G. Chen, “Periodate salts as pyrotechnic oxidizers: development of barium-and perchlorate-free incendiary formulations,” *Angewandte Chemie*, vol. 124, no. 28, pp. 7087–7089, 2012.
- [84] G. Young, H. Wang, and M. R. Zachariah, “Application of nano-aluminum/nitrocellulose mesoparticles in composite solid rocket propellants,” *Propellants, Explosives, Pyrotechnics*, vol. 40, no. 3, pp. 413–418, Jun. 2015, doi: 10.1002/prop.201500020.
- [85] T. Lindblom, “Reactions in stabilizer and between stabilizer and nitrocellulose in propellants,” *Propellants, Explosives, Pyrotechnics: An International Journal Dealing with Scientific and Technological Aspects of Energetic Materials*, vol. 27, no. 4, pp. 197–208, 2002.
- [86] J. Yu, L. Chen, and J. Peng, “Thermal hazard research of smokeless fireworks,” *J Therm Anal Calorim*, vol. 109, no. 3, pp. 1151–1156, 2012.
- [87] R. H. B. Bouma, L. N. Kotter, W. J. L. Smit, M. Zebregs, and L. J. Groven, “Mixed colors by combustion of mixed homogeneous pyrotechnics and

- heterogeneous charges,” *Propellants, Explosives, Pyrotechnics*, p. e202300218.
- [88] A. P. Shaw, J. D. Moretti, and W. S. Eck, “Recent progress in the development of less toxic pyrotechnic smoke compositions for military applications,” *Energetics Science and Technology: An integrated approach*, pp. 11–17, 2022.
- [89] M. Damiani, N. Ferrara, and F. Ardente, “Understanding Product Environmental Footprint and Organisation Environmental Footprint methods,” *Publications Office of the European Union, Luxembourg, LUX, 34pp*, 2022.
- [90] C. Ferreira, F. Freire, and J. Ribeiro, “Life-cycle assessment of a civil explosive,” *J Clean Prod*, vol. 89, pp. 159–164, 2015.
- [91] D. Costa, E. Galante, I. Andrade, and J. Cunha, “Environmental life-cycle assessment of a military explosive production unit: a preliminary approach,” *U. Porto Journal of Engineering*, vol. 1, no. 1, pp. 2–10, 2015.
- [92] D. Fraser, D. M. Weary, E. A. Pajor, and B. N. Milligan, “A scientific conception of animal welfare that reflects ethical concerns,” *Animal welfare*, vol. 6, no. 3, pp. 187–205, 1997.
- [93] D. J. Mellor *et al.*, “The 2020 five domains model: Including human–animal interactions in assessments of animal welfare,” *Animals*, vol. 10, no. 10, p. 1870, 2020.
- [94] C. R. Kight and J. P. Swaddle, “How and why environmental noise impacts animals: an integrative, mechanistic review,” *Ecol Lett*, vol. 14, no. 10, pp. 1052–1061, 2011.
- [95] J. Brouček, “Effect of noise on performance, stress, and behaviour of animals,” *Slovak journal of animal science*, vol. 47, no. 2, pp. 111–123, 2014.
- [96] “BVA RESPONSE TO PETITIONS COMMITTEE FIREWORKS INQUIRY,” 2019. Accessed: Nov. 03, 2021. [Online]. Available: <https://www.bva.co.uk/media/3169/bva-response-to-petitions-committee-inquiry-on-fireworks.pdf>
- [97] C. Erbe, R. Dunlop, and S. Dolman, “Effects of noise on marine mammals,” *Effects of anthropogenic noise on animals*, pp. 277–309, 2018.

- [98] A. Hawkins, *The effects of noise on aquatic life*. The Netherlands: Springer; ISBN 978-1-4419-7310-8, 2012.
- [99] P. Scheifele, D. Martin, J. G. Clark, D. Kemper, and J. Wells, “Effect of kennel noise on hearing in dogs,” *Am J Vet Res*, vol. 73, no. 4, pp. 482–489, 2012.
- [100] N. Bueno-Guerra, “How to apply the concept of umwelt in the evolutionary study of cognition,” *Front Psychol*, vol. 9, p. 2001, 2018.
- [101] H. R. Spence, *The importance of bioacoustics for dolphin welfare: Soundscape characterization with implications for management*. City University of New York, 2015.
- [102] P. D. Meek, G.-A. Ballard, P. J. S. Fleming, M. Schaefer, W. Williams, and G. Falzon, “Camera traps can be heard and seen by animals,” *PLoS One*, vol. 9, no. 10, p. e110832, 2014.
- [103] C. D. West, “The relationship of the spiral turns of the cochlea and the length of the basilar membrane to the range of audible frequencies in ground dwelling mammals,” *J Acoust Soc Am*, vol. 77, no. 3, pp. 1091–1101, 1985.
- [104] H. E. Heffner, “Hearing in large and small dogs: Absolute thresholds and size of the tympanic membrane,” *Behavioral Neuroscience*, vol. 97, no. 2, p. 310, 1983.
- [105] R. Dooling, “Avian hearing and the avoidance of wind turbines,” National Renewable Energy Lab.(NREL), Golden, CO (United States), 2002.
- [106] R. R. Fay and A. N. Popper, “Evolution of hearing in vertebrates: the inner ears and processing,” *Hear Res*, vol. 149, no. 1–2, pp. 1–10, 2000.
- [107] H. E. Heffner and R. S. Heffner, “Hearing ranges of laboratory animals,” *Journal of the American Association for Laboratory Animal Science*, vol. 46, no. 1, pp. 20–22, 2007.
- [108] H. Slabbekoorn, R. J. Dooling, and A. N. Popper, “Man-made sounds and animals,” *Effects of anthropogenic noise on animals*, pp. 1–22, 2018.
- [109] A. S. B. Edge and Z.-Y. Chen, “Hair cell regeneration,” *Curr Opin Neurobiol*, vol. 18, no. 4, pp. 377–382, 2008.
- [110] L. M. Storengen and F. Lingaas, “Noise sensitivity in 17 dog breeds: Prevalence, breed risk and correlation with fear in other situations,” *Appl Anim Behav Sci*, vol. 171, pp. 152–160, 2015.

-
- [111] O. N. Larsen, M. Wahlberg, C. Brown, and T. Riede, "Sound and sound sources," *Comparative bioacoustics: An overview*, pp. 3–60, 2017.
 - [112] M. Naguib and R. H. Wiley, "Estimating the distance to a source of sound: mechanisms and adaptations for long-range communication," *Anim Behav*, vol. 62, no. 5, pp. 825–837, 2001.
 - [113] R. J. Peters, *Acoustics and noise control*. Routledge, 2013. doi: doi.org/10.4324/9781315847146.
 - [114] L. Bassett and H. M. Buchanan-Smith, "Effects of predictability on the welfare of captive animals," *Appl Anim Behav Sci*, vol. 102, no. 3–4, pp. 223–245, 2007.
 - [115] J. S. M. Lindstedt, "Fireworks related equine noise anxiety in Finland and Sweden," Estonian University of Life Sciences, 2020.
 - [116] E. Hakanen *et al.*, "Active and social life is associated with lower non-social fearfulness in pet dogs," *Sci Rep*, vol. 10, no. 1, p. 13774, 2020.
 - [117] V. M. Carrieri-Rocha, M. H. L. Duarte, and A. da Silva Vasconcellos, "Acoustic stress in domestic dogs (*Canis familiaris*) living around football stadiums," *Journal of Veterinary behavior*, vol. 37, pp. 27–35, 2020.
 - [118] Royal Society for the Prevention of Cruelty to Animals (RSPCA), "Bang out of Order. Fireworks frighten animals," 2019. Accessed: Nov. 26, 2021. [Online]. Available: <https://www.rspca.org.uk/documents/1494939/0/Bang+out+of+order+-+fireworks+frighten+animals+%28PDF+706KB%29.pdf/ebcfb65c-40f4-58a0-88d2-0896845a3127?t=1571669349793>
 - [119] "Los peores accidentes con pirotecnia en el mundo." Accessed: Feb. 07, 2022. [Online]. Available: <https://www.eleconomista.com.mx/internacionales/Los-peores-accidentes-con-pirotecnia-en-el-mundo-20161221-0047.html>
 - [120] "Principales accidentes pirotécnicos en España - Faro de Vigo." Accessed: Feb. 08, 2022. [Online]. Available: <https://www.farodevigo.es/sucesos/2018/11/12/principales-accidentes-pirotecnicos-espana-15850841.html>
 - [121] A. J. Rajendran and T. L. Thanulingama, "Sound level analysis of firecrackers," *Journal of Pyrotechnics*, no. 27, pp. 60–76, 2008.

- [122] M. R. Sijimol and M. Mohan, “Environmental impacts of perchlorate with special reference to fireworks—a review,” *Environ Monit Assess*, vol. 186, pp. 7203–7210, 2014.
- [123] A. Azhagurajan, L. Prakash, and K. Jeyasubramanian, “Prevention of explosion accidents by employing boron instead of aluminium in flash powder,” *Process Safety and Environmental Protection*, vol. 131, pp. 160–168, 2019.
- [124] M. Rajendran, R. Ramanathan, P. Ganesan, and R. Shanmugavel, “Experimental analysis of tamarind seed powder-based flash powder composition for eco-friendly firecrackers,” *J Therm Anal Calorim*, vol. 143, pp. 3009–3021, 2021.
- [125] V. Duro, R. López, Y. A. del Águila, R. Pardo, and L. M. Debán, “Nitrocellulose Propellants Standard Stability Tests Enhancement Employing Semiconductor Sensors,” *Propellants, Explosives, Pyrotechnics*, vol. 48, no. 2, p. e202200086, 2023.
- [126] I. Amez, B. Castells, D. León, J. García-Torrent, and L. Medic, “Experimental study on inert products, moisture, and particle size effect on the minimum ignition energy of combustible dusts,” *J Loss Prev Process Ind*, vol. 81, p. 104968, 2023.
- [127] B. Castells, I. Amez, N. Fernandez-Anez, D. León, and A. Tascón, “Biomass Inertization to Increase Minimum Ignition Temperature,” *J Loss Prev Process Ind*, vol. 90, p. 105345, 2024.
- [128] Y. Bu, C. Li, P. Amyotte, W. Yuan, C. Yuan, and G. Li, “Moderation of Al dust explosions by micro-and nano-sized Al₂O₃ powder,” *J Hazard Mater*, vol. 381, p. 120968, 2020.
- [129] F. Guerrero, A. Arriagada, F. Muñoz, P. Silva, N. Ripoll, and M. Toledo, “Particulate matter emissions reduction from residential wood stove using inert porous material inside its combustion chamber,” *Fuel*, vol. 289, p. 119756, 2021.
- [130] I. Hudák, P. Skryja, J. Bojanovský, Z. Jegla, and M. Krňávek, “The Effect of Inert Fuel Compounds on Flame Characteristics,” *Energies (Basel)*, vol. 15, no. 1, p. 262, 2021.
- [131] D. León, “Análisis de las Emisiones Producidas por los Artificios Pirotécnicos - Trabajo de Fin de Grado,” Univerisdad Politécnica de Madrid, 2019.

- [132] D. León, “Análisis de Emisiones en Artículos Pirotécnicos,” in *Primer Simposio Internacional de Innovación en Pirotecnia*. ISBN: 978-84-09-18293-0, Pinto, Nov. 2019, pp. 39–40.
- [133] D. León, “Adaptación de los Procesos de la Industria Pirotécnica a los Objetivos Globales de Desarrollo Sostenible - Trabajo de Fin de Máster,” Universidad Politécnica de Madrid, 2021.
- [134] “Simposio de Pirotecnia Sostenible,” Getafe, Apr. 2023. [Online]. Available: <http://www.lom.upm.es/DownloadDocuments?Cat=0&Fam=129>
- [135] J. Pous Cabello, “Modelo de Plan Estratégico Para las Empresas del Sector Pirotécnico Español - Trabajo de Fin de Grado,” Universidad Politécnica de Madrid, 2023. [Online]. Available: <https://oa.upm.es/75718/>
- [136] “Engineering services – Pyrolab.” Accessed: Feb. 28, 2022. [Online]. Available: <http://www.pyrolab.es/en/ingenieria>
- [137] *Texto enmendado de los Anejos A y B del Acuerdo Europeo sobre transporte internacional de mercancías peligrosas por carretera (ADR 2021) con las Enmiendas adoptadas durante las sesiones 105.a, 106.a y 107.a del Grupo de trabajo de transportes de mercancías peligrosas de la Comisión Económica para Europa de las Naciones Unidas (CEPE)*. España, 2021, pp. 1–1093. Accessed: Feb. 19, 2022. [Online]. Available: <https://www.boe.es/boe/dias/2021/04/13/pdfs/BOE-A-2021-5779.pdf>
- [138] *Recommendations on the Transport of Dangerous Goods, vol. I. New York and Ginebra: United Nations*. 2019. Accessed: Feb. 28, 2022. [Online]. Available: https://unece.org/fileadmin/DAM/trans/danger/publi/unrec/rev21/ST-SG-AC10-1r21e_Vol1_WEB.pdf
- [139] “ESPECTÁCULOS – Pirotecnia Turis.” Accessed: Mar. 31, 2022. [Online]. Available: <https://www.pirotecniaturis.com/espectaculos/>
- [140] International Standard Organization, “Environmental management—life cycle assessment, principles and framework, ISO 14040:2006,” *European Committee for Standardization CEN, Brussels, Belgium*, 2006.
- [141] International Standard Organization, “Environmental management—life cycle assessment, requirements and guidelines, ISO 14044:2006,” *European Committee for Standardization CEN, Brussels, Belgium*, 2006.

- [142] R. Abejón, A. Bala, I. Vazquez-Rowe, R. Aldaco, and P. Fullana-i-Palmer, “When plastic packaging should be preferred: Life cycle analysis of packages for fruit and vegetable distribution in the Spanish peninsular market,” *Resour Conserv Recycl*, vol. 155, p. 104666, 2020.
- [143] “Ecoinvent Version 3.8.” Accessed: Dec. 07, 2022. [Online]. Available: <https://support.ecoinvent.org/ecoinvent-version-3.8>
- [144] *EN 15947-2, Pyrotechnic articles - Fireworks, Categories F1, F2, and F3 - Part 2: Categories and types of fireworks*. 2022.
- [145] “Macy’s 4th Of July Fireworks 2022 — By The Numbers.” Accessed: Mar. 30, 2023. [Online]. Available: <https://www.macys.com/social/fireworks/by-the-numbers/>
- [146] *Commission Regulation (EU) No 459/2012 of 29 May 2012 amending Regulation (EC) No 715/2007 of the European Parliament and of the Council and Commission Regulation (EC) No 692/2008 as regards emissions from light passenger and commercial vehicles (Euro 6)*. Official Journal of the European Union, 2012. [Online]. Available: <https://eur-lex.europa.eu/eli/reg/2012/459/oj>
- [147] J. Pavlovic, B. Ciuffo, G. Fontaras, V. Valverde, and A. Marotta, “How much difference in type-approval CO₂ emissions from passenger cars in Europe can be expected from changing to the new test procedure (NEDC vs. WLTP)?,” *Transp Res Part A Policy Pract*, vol. 111, pp. 136–147, 2018.
- [148] E. Y. H. CONSEJERÍA DE ECONOMÍA, *Atlas de la movilidad residencial-trabajo en la Comunidad de Madrid 2017*. 2017. [Online]. Available: <https://www.comunidad.madrid/publicacion/ref/15758>
- [149] “Annual Report 2019, Spanish Association of Automobile and Truck Manufacturers (ANFAC).” Accessed: Jul. 05, 2020. [Online]. Available: https://anfac.com/wp-content/uploads/2020/07/ANFAC_INFORME_ANUAL_2019_VC.pdf
- [150] B. Graver, K. Zhang, and D. Rutherford, “CO₂ emissions from commercial aviation, 2018,” *International Council on Clean Transportation*, Sep. 2019. Accessed: Nov. 21, 2020. [Online]. Available: http://theicct.org/sites/default/files/publications/ICCT_CO2-commercial-aviation-2018_20190918.pdf

- [151] *EN 15947-1, Pyrotechnic articles - Fireworks, Categories F1, F2, and F3 - Part 1: Terminology*. 2022.
- [152] *EN 16261-2, Pyrotechnic articles - Fireworks, Categories F4 - Part 3: Test methods*. 2012.
- [153] “Weather And Environmental Noise Measurements | Brüel & Kjær - HBK.” Accessed: Oct. 13, 2022. [Online]. Available: <https://www.hbkworld.com/en/knowledge/resource-center/articles/sound/noise-measurement-weather>
- [154] *Real Decreto 286/2006, de 10 de marzo, sobre la protección de la salud y la seguridad de los trabajadores contra los riesgos relacionados con la exposición al ruido*. 2006. Accessed: Sep. 22, 2021. [Online]. Available: <https://www.boe.es/buscar/act.php?id=BOE-A-2006-4414>
- [155] A. N. Rimell, N. J. Mansfield, and G. S. Paddan, “Design of digital filters for frequency weightings (A and C) required for risk assessments of workers exposed to noise,” *Ind Health*, vol. 53, no. 1, pp. 21–27, 2015.
- [156] T. B. Brill and P. E. Gongwer, “Thermal decomposition of energetic materials 69. Analysis of the kinetics of nitrocellulose at 50 C–500 C,” *Propellants, explosives, pyrotechnics*, vol. 22, no. 1, pp. 38–44, 1997.
- [157] L. Dauerman and Y. A. Tajima, “Thermal decomposition and combustion of nitrocellulose,” *Aiaa Journal*, vol. 6, no. 8, pp. 1468–1473, 1968.
- [158] B. Kukulski, T. Wszolek, and D. Mleczko, “The impact of fireworks noise on the acoustic climate in urban areas,” *Archives of Acoustics*, vol. 43, no. 4, pp. 697–705, 2018.
- [159] C.-P. Lin, Y.-M. Chang, J. P. Gupta, and C.-M. Shu, “Comparisons of TGA and DSC approaches to evaluate nitrocellulose thermal degradation energy and stabilizer efficiencies,” *Process Safety and Environmental Protection*, vol. 88, no. 6, pp. 413–419, 2010.
- [160] “STA 449 F5 Jupiter - NETZSCH Analyzing & Testing.” Accessed: Sep. 15, 2023. [Online]. Available: <https://analyzing-testing.netzsch.com/en/products/special-offers/sta-449-f5-jupiter>
- [161] “QMS 505 Aëolos - NETZSCH Analyzing & Testing.” Accessed: Sep. 15, 2023. [Online]. Available: <https://analyzing-testing.netzsch.com/en/products/special-offers/qms-505-aëolos>

- testing.netzsch.com/en/products/hyphenated-techniques-evolved-gas-analysis/qms-505-aeolos
- [162] W. Hua, J. Chen, Q. Qin, Z. Wan, and L. Song, “Causation analysis and governance strategy for hazardous cargo accidents at ports: case study of Tianjin Port’s hazardous cargo explosion accident,” *Mar Pollut Bull*, vol. 173, p. 113053, 2021.
 - [163] R. Kuracina, Z. Szabová, L. Kosár, and M. Sahul, “Study into influence of different types of igniters on the explosion parameters of dispersed nitrocellulose powder,” *J Loss Prev Process Ind*, vol. 83, p. 105017, 2023.
 - [164] R. Kuracina, “Comparison of smokeless nitrocellulose powder production accidents in Explosia with the World’s accidents database,” in *New Trends in Research of Energetic Materials*, University of Pardubice, University of Pardubice, Apr. 2005, pp. 613–622.
 - [165] B. Urbano, M. Barquero, and F. González-Andrés, “The environmental impact of fresh tomatoes consumed in cities: A comparative LCA of long-distance transportation and local production,” *Sci Hortic*, vol. 301, p. 111126, 2022.
 - [166] K. Pivnenko, M. E. Olsson, R. Götze, E. Eriksson, and T. F. Astrup, “Quantification of chemical contaminants in the paper and board fractions of municipal solid waste,” *Waste management*, vol. 51, pp. 43–54, 2016.
 - [167] V. G. Lo-Iacono-Ferreira, R. Viñoles-Cebolla, M. J. Bastante-Ceca, and S. F. Capuz-Rizo, “Carbon footprint comparative analysis of cardboard and plastic containers used for the international transport of Spanish Tomatoes,” *Sustainability*, vol. 13, no. 5, p. 2552, 2021.
 - [168] “CO2 Everything | Carbon Footprints of Products & Activities.” Accessed: Jun. 25, 2023. [Online]. Available: <https://www.co2everything.com/>
 - [169] S. Hamad, D. Green, and J. Heo, “Evaluation of health risk associated with fireworks activity at Central London,” *Air Qual Atmos Health*, vol. 9, pp. 735–741, 2016.
 - [170] F. M. Wiener and D. N. Keast, “Experimental study of the propagation of sound over ground,” *J Acoust Soc Am*, vol. 31, no. 6, pp. 724–733, 1959.
 - [171] P. Denes, “Effect of duration on the perception of voicing,” *J Acoust Soc Am*, vol. 27, no. 4, pp. 761–764, 1955.

-
- [172] A. J. Wright *et al.*, “Anthropogenic noise as a stressor in animals: a multidisciplinary perspective,” *Int J Comp Psychol*, vol. 20, no. 2, 2007.
- [173] S. Riemer, “Effectiveness of treatments for firework fears in dogs,” *Journal of Veterinary Behavior*, vol. 37, pp. 61–70, 2020.
- [174] J. C. White, W. R. Wagner, and C. N. Beal, *Global climate change linkages: acid rain, air quality, and stratospheric ozone*. Springer Science & Business Media, 1989.
- [175] X. Cao *et al.*, “Review on physicochemical properties of pollutants released from fireworks: environmental and health effects and prevention,” *Environmental Reviews*, vol. 26, no. 2, pp. 133–155, 2018.
- [176] D. P. Van Vuuren, L. F. Bouwman, S. J. Smith, and F. Dentener, “Global projections for anthropogenic reactive nitrogen emissions to the atmosphere: An assessment of scenarios in the scientific literature,” Oct. 2011. doi: 10.1016/j.cosust.2011.08.014.
- [177] R. Turcotte, R. C. Fouchard, A.-M. Turcotte, and D. E. G. Jones, “Thermal analysis of black powder,” *J Therm Anal Calorim*, vol. 73, pp. 105–118, 2003.
- [178] C. Pu, Y. Luan, M. Yi, and Z. Xiao, “Investigation on thermal characteristics and desensitization mechanism of improved step ladder-structured nitrocellulose,” *Defence Technology*, vol. 20, pp. 93–102, 2023.
- [179] J. Kadarkaraithangam, A. Arumugachamy, P. L. Pandian, and M. Ganapathy, “Monitoring the thermal and safety characteristics of flash and black powder composition containing fructose,” *Science and Technology of Energetic Materials*, vol. 82, no. 5, pp. 128–137, 2021.
- [180] Y. Tang, Z.-P. Li, H.-L. Zhou, C.-F. Miao, J.-C. Jiang, and A.-C. Huang, “Thermal stability assessment of nitrocellulose by using multiple calorimetric techniques and advanced thermokinetics,” *J Therm Anal Calorim*, vol. 148, no. 11, pp. 5029–5038, 2023.
- [181] R. Wei, Y. He, Z. Zhang, J. He, R. Yuen, and J. Wang, “Effect of different humectants on the thermal stability and fire hazard of nitrocellulose,” *J Therm Anal Calorim*, vol. 133, pp. 1291–1307, 2018.
- [182] H. Chai *et al.*, “Experimental study on the effect of storage conditions on thermal stability of nitrocellulose,” *Appl Therm Eng*, vol. 180, p. 115871, 2020.

- [183] E. Lemieux and R. E. Prud'Homme, "Heats of decomposition, combustion and explosion of nitrocelluloses derived from wood and cotton," *Thermochim Acta*, vol. 89, pp. 11–26, 1985.
- [184] K. Aarseth Larsson, "Chemical Characterisation of Nitrocellulose," 2014.
- [185] W. Shen, H. Wang, Y. Liu, Q. Guo, and Y. Zhang, "Oxidization activated carbon fiber through nitrocellulose combustion," *Colloids Surf A Physicochem Eng Asp*, vol. 308, no. 1–3, pp. 20–24, 2007.
- [186] X. Mei, G. Zhong, and Y. Cheng, "Ignition and combustion characteristics of aluminum/manganese iodate/nitrocellulose biocidal nanothermites," *J Therm Anal Calorim*, vol. 138, pp. 425–432, 2019.
- [187] T. Paraschiv, T. V. Tiganescu, G. O. Iorga, R. E. Ginghina, and O. C. Grigoriou, "Experimental and Theoretical Study on Three Combustion Models for the Determination of the Performance Parameters of Nitrocellulose-Based Propellants," *Rev. Chim*, vol. 71, pp. 87–97, 2020.
- [188] R. E. Gosselin, R. P. Smith, H. C. Hodge, and J. E. Braddock, *Clinical toxicology of commercial products*, vol. 1085. Williams & Wilkins Baltimore, 1984.
- [189] M. Á. F. de la Ossa, M. López-López, M. Torre, and C. García-Ruiz, "Analytical techniques in the study of highly-nitrated nitrocellulose," *TrAC Trends in Analytical Chemistry*, vol. 30, no. 11, pp. 1740–1755, 2011.
- [190] S. Bekhouche *et al.*, "Towards understanding the effect of humidity on the degradation of pyrotechnic compositions through spectroscopic data combined with chemometric methods," *Z Anorg Allg Chem*, vol. 647, no. 15, pp. 1547–1559, 2021.
- [191] S. Bekhouche *et al.*, "Insight into the effect of moisture and thermal aging on the degradation of a pyrotechnic igniter composition through thermogravimetric kinetics coupled with deconvolution approach," *ChemistrySelect*, vol. 6, no. 48, pp. 14060–14070, 2021.
- [192] M. B. Karuppasamy, U. Natesan, K. S. Giridharan, and R. V Ravi, "Environmental Assessment of Toxic Gases and Particulate Matter (PM_{2.5}) Monitoring During Fireworks Episodes (Diwali Festival) in Chennai Metropolitan, Southern India," *Sustainable Chemical Engineering*, pp. 169–181, 2024.

-
- [193] B. Pathak, C. Bharali, J. Biswas, and P. K. Bhuyan, “Firework induced large increase in trace gases and black carbon at Dibrugarh, India,” *Journal of Earth Science and Engineering*, vol. 3, no. 8, p. 540, 2013.
- [194] A. E. Finnerty, S. A. Bowers, and M. O. Schroeder, “Ignition of Nitrocellulose in Various Atmospheres,” 1992. Accessed: Sep. 20, 2023. [Online]. Available: <https://apps.dtic.mil/sti/citations/ADA257987>
- [195] M. C. Ball, C. M. Snelling, A. N. Strachan, and R. M. Strachan, “Thermal decomposition of solid sodium bicarbonate,” *Journal of the Chemical Society, Faraday Transactions 1: Physical Chemistry in Condensed Phases*, vol. 82, no. 12, pp. 3709–3715, 1986.
- [196] B. L. Roberts, “The Decibel Scale,” *Department of Physics Boston University*, pp. 2–5, 1984.
- [197] R. W. Young, “Decibel, a unit of level,” *Journal of the Audio Engineering Society*, vol. 19, no. 6, pp. 512–516, 1971.
- [198] K. L. Kosanke and L. Weinman, “From a Technical Standpoint, What Is Firework Flash Powder?,” *Encyclopedic Dictionary of Pyrotechnics:(and Related Subjects)-B&W*, p. 120, 2012.
- [199] K. Cieślak, K. Gańczyk-Specjalska, K. Drożdżewska-Szymańska, and M. Uszyński, “Effect of stabilizers and nitrogen content on thermal properties of nitrocellulose granules,” *J Therm Anal Calorim*, vol. 143, no. 5, pp. 3459–3470, 2021.
- [200] S. N. A. Rusly, S. H. Jamal, A. Samsuri, S. A. Mohd Noor, and K. S. Abdul Rahim, “Stabilizer selection and formulation strategies for enhanced stability of single base nitrocellulose propellants: A review,” *Energetic Materials Frontiers*, 2024, doi: <https://doi.org/10.1016/j.enmf.2024.02.007>.

Annex A: Operations and processes of the pyrotechnic sector.

Table A.1. Hazard Divisions of Class 1 of ADR hazardous materials and articles [137].

Label	Division	Characteristics
	1.1	Substances and objects presenting a mass explosion hazard (a mass explosion is an explosion that affects almost the entire load almost instantaneously)
	1.2	Substances and objects presenting a projection hazard without a mass explosion hazard
	1.3	Substances and articles presenting a fire hazard with slight danger of blast or projection effects or both, but without danger of mass explosion.
	1.4	Substances and articles that present only a small explosion hazard in the event of ignition or ignition during transport. The effects are limited to packages and do not normally result in the projection of fragments of appreciable size or over long distances.

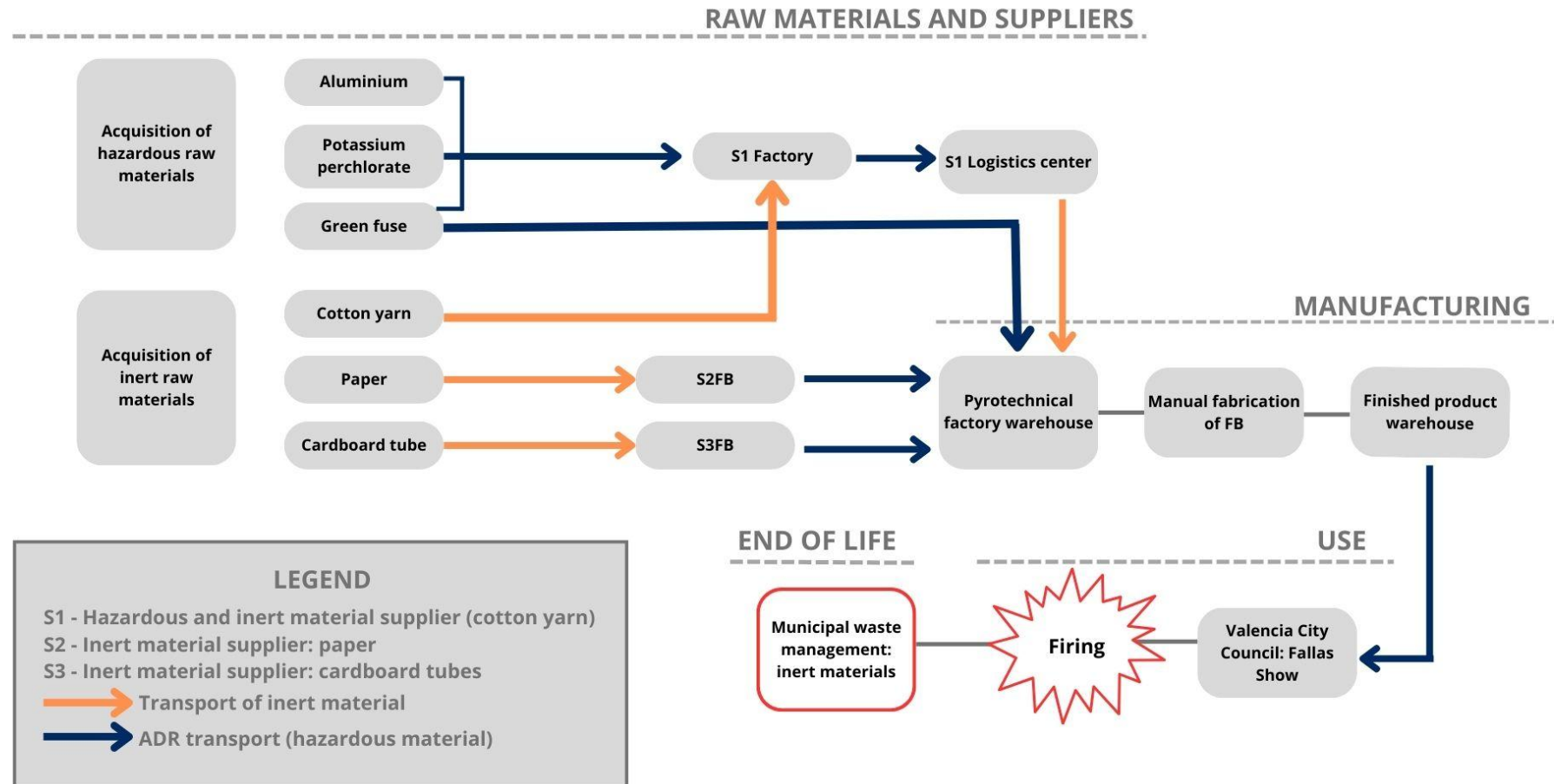


Figure A.1. Detailed flow diagram of Flash Banger (FB) functional unit.

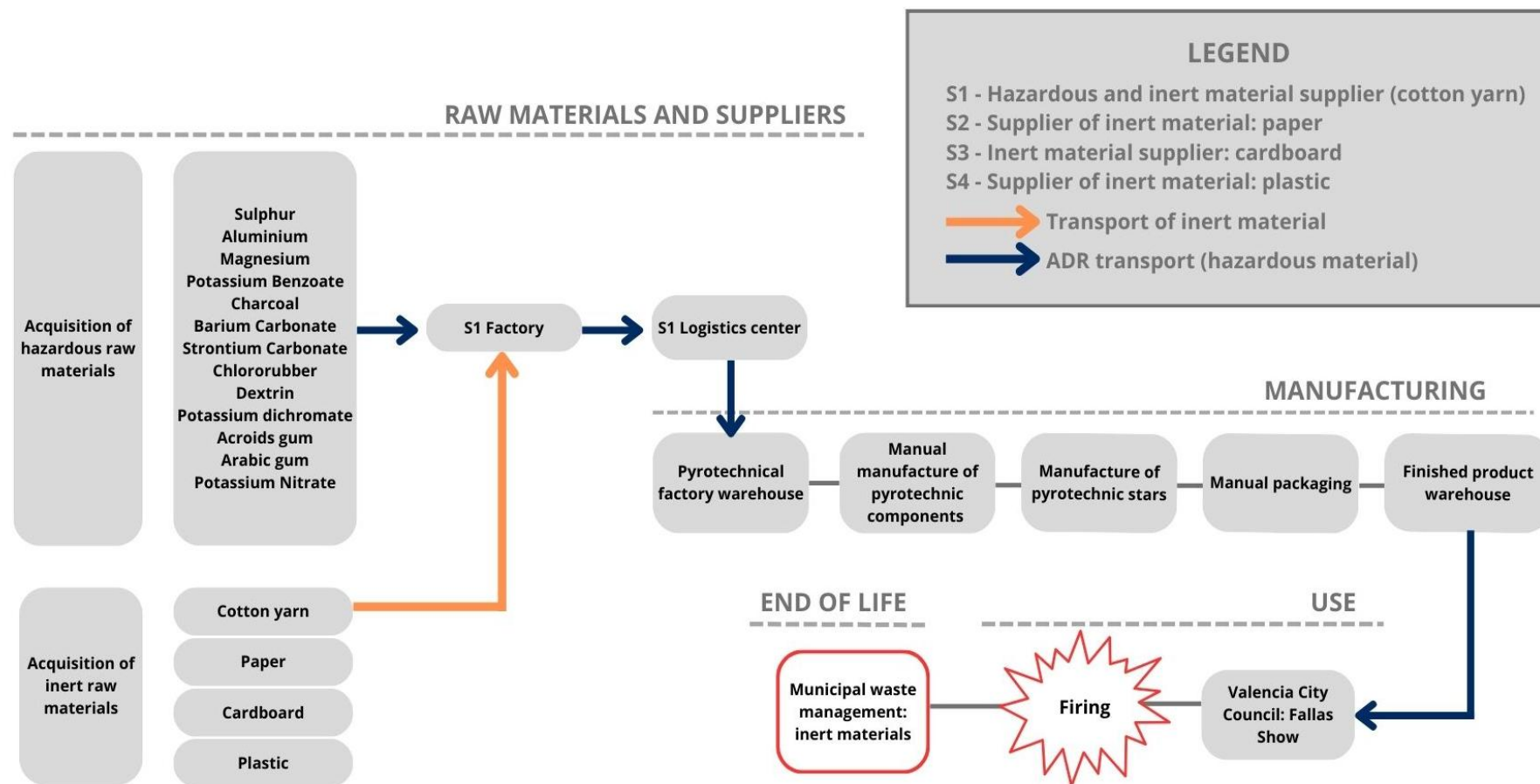


Figure A.2. Detailed flow diagram of Pyrotechnic Shells functional units.

Table A.2. Pyrotechnical reactions for the production of visual colour effects [18], [19].

Colour	Salt dissociation	Colour producing substance	Luminescence effect
Red	$2 \text{Sr}(\text{NO}_3)_2 + \text{heat} \rightarrow 2 \text{SrO}_{(g)} + 2 \text{N}_2 + 5 \text{O}_2$	$\text{SrO}_{(g)} + \text{H}_2\text{O} \rightarrow \text{SrOH}^+_{(g)} + \text{OH}^-$	$\text{SrOH}^+_{(g)} + \text{heat} \rightarrow \text{SrOH}^*_{(g)} \rightarrow \text{SrOH}_{(g)} + \text{photon}$
Yellow	$2 \text{NaNO}_3 + \text{heat} \rightarrow 2 \text{Na}_2\text{O}_{(g)} + \text{N}_2 + 5/2 \text{O}_2$	$\text{Na}_2\text{O}_{(g)} + \text{H}_2\text{O} \rightarrow 2\text{NaOH}_{(g)}$	$\text{NaOH}_{(g)} + \text{heat} \rightarrow \text{NaOH}^*_{(g)} \rightarrow \text{NaOH}_{(g)} + \text{photon}$
Green	$2 \text{Ba}(\text{NO}_3)_2 + \text{heat} \rightarrow 2 \text{BaO}_{(g)} + 2 \text{N}_2 + 5 \text{O}_2$	$\text{BaO}_{(g)} + \text{H}_2\text{O} \rightarrow \text{BaOH}^+_{(g)} + \text{OH}^-$	$\text{BaOH}^+_{(g)} + \text{heat} \rightarrow \text{BaOH}^*_{(g)} \rightarrow \text{BaOH}_{(g)} + \text{photon}$
Orange	$\text{CaCO}_3 + \text{heat} \rightarrow \text{CaO}_{(g)} + \text{CO}_2$	$\text{CaO}_{(g)} + \text{H}_2\text{O} \rightarrow \text{CaOH}^+_{(g)} + \text{OH}^-$	$\text{CaOH}^+_{(g)} + \text{heat} \rightarrow \text{CaOH}^*_{(g)} \rightarrow \text{CaOH}_{(g)} + \text{photon}$
Blue	$\text{CuCO}_3 + \text{heat} \rightarrow \text{CuO}_{(g)} + \text{CO}_2$	$\text{CuO}_{(g)} + \text{H}_2\text{O} \rightarrow \text{CuOH}^+_{(g)} + \text{OH}^-$	$\text{CuOH}^+_{(g)} + \text{heat} \rightarrow \text{CuOH}^*_{(g)} \rightarrow \text{CuOH}_{(g)} + \text{photon}$

Where * represents the excitation of the electron.

Annex B: Sound test specifications.

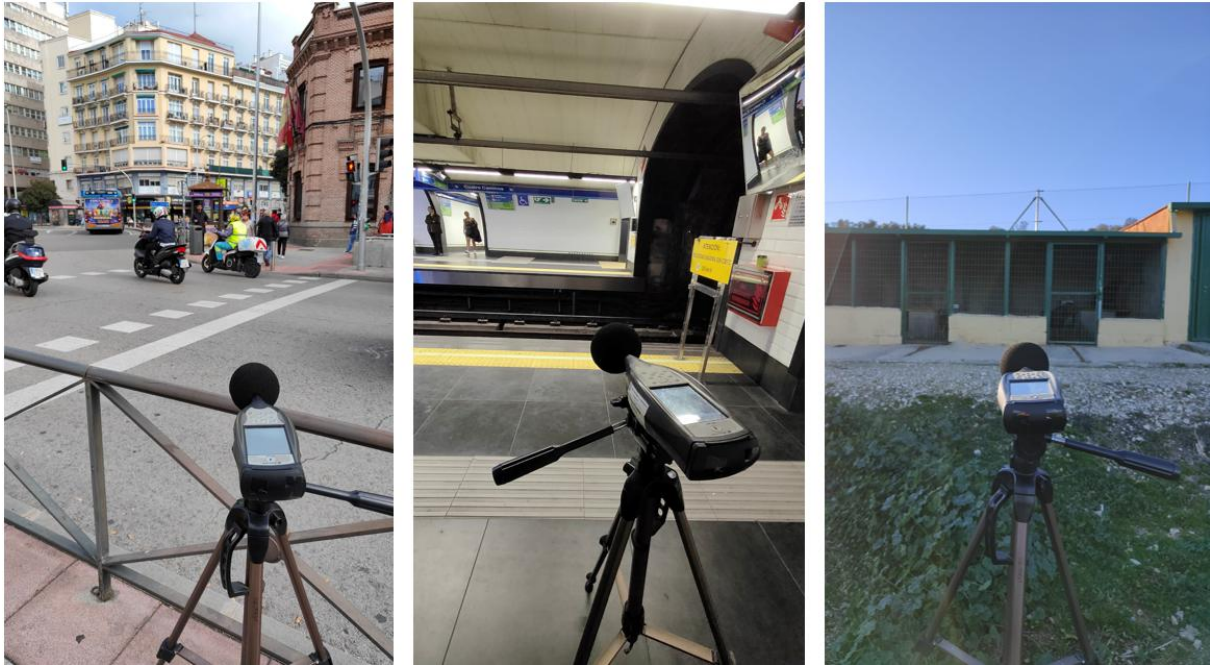


Figure B.1. Locations of measurement points for everyday noise emitters.

Usual Firing structure of La Mascletà

The well-known Mascletà varies depending on the manufacturers who fire it, but they have a similar structure which is detailed below:

Salute shells: they mark the proximity of the start of the pyrotechnic show, in the Plaza del Ayuntamiento one salute is fired 10 minutes before the firing, another 5 minutes before the firing and another just before the firing starts (after the firing order given by the Fallera Mayor de Valencia at 14:00h).

- Traca Valenciana: traditionally the firing begins with the lighting of a common traca Valenciana, which is what starts the initial phase of the mascletà.
- Digital start: this is a different form of firing in which there is a combination of aerial and ground effects fired sequentially, generally around the perimeter of the firing area. In this phase we can find both “pasadas”, which is to turn the square sequentially, and “golpes”, which are simultaneous shots from all around the perimeter of the square. This phase has a variable duration, it can be a single brushstroke combined with the classic aerial initiation or it can be a phase in which the rhythm and intensity of fire is increased and replaces the classic aerial initiation phase. When it replaces

the classic air start, it usually ends with an all-round effects burst that signals the end of the phase and the start of the ground phase..

- Classic aerial start: aerial sound effects phase which is divided into several phases. In each phase, the type of aerial effect and/or the amount of fireworks fired is changed, increasing in intensity. This phase usually ends with an aerial sound effects bang (salute shell) which leads to the next phase.
- Terrestrial phase (main part of the Mascletá): phase in which terrestrial effects of different charges are combined with aerial effects, with the terrestrial effects predominating. This phase lasts the longest, and is subdivided into sub-phases, with between 4 and 6 sub-phases. Each sub-phase is called a “retención” and each retención includes:
 - Ground part (main part): flash bangers of varying intensity fall to the ground at a given rate. As we change subphase (retention), the number of flash bangers per unit of time increases (and flash bangers with a higher charge are also added), thus increasing the intensity of the shot and the sound pressure level at each change of retention
 - Aerial part (accompaniment): in this part, aerial effects are fired to accompany the ground fire. In this case, as a rule, the number of fireworks fired is also increased as the phase changes, so that the intensity is increased.
- Final Terrestrial Phase (Terremoto): this is a phase of very short duration in which a large amount of flash bangers are triggered. It also has several phases (3 to 5) that increase the number of bangers/unit of time, and often the calibre of the bangers, so that it also increases in intensity.
- Final Aerial Phase (Bombardeo): usually fired just as the Terremoto is ending, so that it links one with the other. Depending on the design, it may start together with the terremoto, but either way it always remains the final part of the show. Its structure is also incremental, starting with lower intensity sound effects (smaller aerial bangers) and increasing in type and quantity of sound effects.
- Golpe Final (closing): in general, at the end of the aerial bombardeo, one or more sound effect shots are fired (whistles + aerial banger, buzzer + aerial

banger), which may be combined with a ground part (at the same time or before or after the terremoto).

- Salute shells: the end of the show is marked by two salute shells, one after the other.

The fireworks used in a Mascletá design are generally the following:

- Rastros/Rastres: batteries of small calibre bangers that are ignited one after the other with a delay of between 1 and 2 seconds. They create a background rhythm so that the shot is not left without sound.
- Flash bangers of different calibre and charge (banger with its own entity that stands out from the background sound of the show), can be organised in:
 - Groups: group of 10 bangers separated from each other by a retention of approx. 2.5-3 seconds. They produce a firing cadence.
 - Ramales de terremoto: groups of 20 bangers linked by a fast fuse that produce a rapid sequence of explosions.
 - Digital bangers: fired singly to produce pre-designed sequences or strikes.
- Descargas: clusters of light bangers that start simultaneously and create short bursts of small, low-intensity banger that give a background sound.
- Salute shells (limited in the Plaza del Ayuntamiento to 60 mm calibre).
- Mines/Shot-tubes of sound effects (whistles, buzzers, crackers...).
- Mines/Shot-tubes of visual effects (coloured smoke, crossettes, confetti...).

Annex C: LCA detailed results.

Flash banger (FB)

Impact category	Units	Total	Acquisition and Distribution of Raw Materials	Energy Consumption	Transport	Emissions	End of Life
Acidification	Mol H ⁺ eq.	8.02x10 ⁵	9.46x10 ⁻⁵	---	9.89x10 ⁻⁸	~ 0	-1.44x10 ²
Climate change	Kg CO ₂ eq.	0.01023	0.012168979	---	2.83x10 ⁻⁵	~ 0	-0.001970
Clim. change - biogenic	Kg CO ₂ eq.	0.000360	0.000330568	---	1.06x10 ⁻⁹	~ 0	2.90x10 ⁻⁵
Clim. change - fossil	Kg CO ₂ eq.	0.00981	0.011772376	---	2.83x10 ⁻⁵	~ 0	-0.001992
Clim. change - land use and LU change	Kg CO ₂ eq.	5.94x10 ⁻⁵	6.60x10 ⁻⁵	---	2.29x10 ⁻¹⁰	~ 0	-6.68x10 ⁻⁶
Ecotoxicity, freshwater - part 1	CTUe	0.61065	0.58452537	---	7.36x10 ⁻⁵	0.0964278	-0.07038
Ecotoxicity, freshwater - part 2	CTUe	0.063134	0.14046689	---	4.42x10 ⁻⁵	0.00036407	-0.0778
Ecotoxicity, freshwater - inorganics	CTUe	0.65244	0.69763107	---	9.12x10 ⁻⁵	0.096792	-0.14207
Ecotoxicity, freshwater – organics p. 1	CTUe	0.008731	0.0090481	---	8.03x10 ⁻⁸	~ 0	-0.000317
Ecotoxicity, freshwater - organics - p.2	CTUe	0.012606	0.018313	---	2.65x10 ⁻⁵	~ 0	-0.00573
Particulate matter	disease inc.	6.62x10 ⁻¹⁰	9.80x10 ⁻¹⁰	---	2.13x10 ⁻¹²	~ 0	-3.19x10 ⁻¹⁰
Eutrophic., marine	kg N eq.	2.23x10 ⁻⁵	2.64x10 ⁻⁵	---	3.17x10 ⁻⁸	~ 0	-4.13x10 ⁻⁶
Eutrophic., freshwater	kg P eq.	5.65x10 ⁻⁶	6.47x10 ⁻⁶	---	1.18x10 ⁻¹⁰	~ 0	-8.14x10 ⁻⁷
Eutrophic., terrestrial	mol N eq.	0.000157	0.0001913	---	3.47x10 ⁻⁷	~ 0	-3.45x10 ⁻⁵
Human tox., cancer	CTUh	1.08x10 ⁻¹¹	1.63x10 ⁻¹¹	---	2.29x10 ⁻¹⁵	~ 0	-5.55x10 ⁻¹²

Human tox., cancer - inorganics	CTUh	8.02x10 ⁻¹²	1.11x10 ⁻¹¹	---	1.13x10 ⁻¹⁵	~ 0	-3.06x10 ⁻¹²
Human tox., cancer - organics	CTUh	2.75x10 ⁻¹²	5.24x10 ⁻¹²	---	1.16x10 ⁻¹⁵	~ 0	-2.49x10 ⁻¹²
Human tox., non-cancer	CTUh	1.55x10 ⁻¹⁰	2.09x10 ⁻¹⁰	---	2.06x10 ⁻¹³	1.23x10 ⁻¹¹	-6.62x10 ⁻¹¹
Human tox., non-cancer - inorganics	CTUh	1.49x10 ⁻¹⁰	2.01x10 ⁻¹⁰	---	1.93x10 ⁻¹³	1.23x10 ⁻¹¹	-6.39x10 ⁻¹¹
Human tox., non-cancer - organics	CTUh	6.02x10 ⁻¹²	8.33x10 ⁻¹²	---	1.31x10 ⁻¹⁴	~ 0	-2.33x10 ⁻¹²
Ionising radiation	kBq U-235	0.005613	0.015165	---	1.78x10 ⁻⁶	~ 0	-0.009554
Land use	Pt	0.17089	0.45790015	---	7.94x10 ⁻⁷	~ 0	-0.287015
Ozone depletion	kg CFC ₁₁	5.90x10 ⁻¹⁰	7.29x10 ⁻¹⁰	---	6.76x10 ⁻¹²	~ 0	-1.46x10 ⁻¹⁰
Photochem. ozone formation	kg NMVO C eq.	3.89x10 ⁻⁵	4.92x10 ⁻⁵	---	9.48x10 ⁻⁸	~ 0	-1.05x10 ⁻⁵
Resource use, fossils	MJ	0.180922	0.31964598	---	0.000403	~ 0	-0.13913
Resource use, minerals and metals	kg Sb eq.	1.71x10 ⁻⁷	4.29x10 ⁻⁷	---	1.27x10 ⁻¹²	~ 0	-2.59x10 ⁻⁷
Water use	m ³ depriv.	0.020051	0.033965837	---	-6.49x10 ⁻⁸	~ 0	-0.013915

Cardboard Pyrotechnic Shell (CPS)

Impact category	Units	Total	Acquisition and Distribution of Raw Materials	Energy Consumption	Transport	Emissions	End of Life
Acidification	Mol H ⁺ eq.	0.08186	0.0319921	0.001605	2.61x10 ⁻⁵	0.04930	-0.001061
Climate change	Kg CO ₂ eq.	4.65	4.29	0.1827083	0.007461	0.318971	-0.14976
Clim. change - biogenic	Kg CO ₂ eq.	0.123317	0.1243207	0.0002675	2.80x10 ⁻⁷	~ 0	-0.001272

Clim. change - fossil	Kg CO ₂ eq.	4.52	4.16	0.1808896	0.007461	0.318971	-0.147999
Clim. change - land use and LU change	Kg CO ₂ eq.	0.01125	0.0101866	0.0015512	6.03x10 ⁻⁸	~ 0	-0.000486
Ecotoxicity, freshwater - part 1	CTUe	148	152	0.232026	0.019400	1.44	-5.16
Ecotoxicity, freshwater - part 2	CTUe	87.556	93	0.085597	0.011660	0.198102	-5.69
Ecotoxicity, freshwater - inorganics	CTUe	234	243	0.29440135	0.024046	1.64	-10.4
Ecotoxicity, freshwater – organics p. 1	CTUe	0.48173	0.503678	0.0011837	2.12x10 ⁻⁵	~ 0	-0.02315
Ecotoxicity, freshwater - organics - p.2	CTUe	1.34	1.73	0.0220380	0.00699	~ 0	-0.42011
Particulate matter	disease inc.	3.89x10 ⁻⁷	3.39	3.84x10 ⁻⁹	5.61x10 ⁻¹⁰	6.95x10 ⁻⁸	-2.33x10 ⁻⁸
Eutrophic., marine	kg N eq.	0.031692	0.005839	0.0002521	8.35x10 ⁻⁶	0.025894	-0.000302
Eutrophic., freshwater	kg P eq.	0.001906	0.0018964	6.95x10 ⁻⁵	3.11x10 ⁻⁸	~ 0	-5.96x10 ⁻⁵
Eutrophic., terrestrial	mol N eq.	0.34187	0.0579258	0.002581	9.18x10 ⁻⁵	0.28379	-0.002523
Human tox., cancer	CTUh	8.09x10 ⁻⁹	8.45x10 ⁻⁹	4.61x10 ⁻¹¹	6.04x10 ⁻¹³	~ 0	-4.07x10 ⁻¹⁰
Human tox., cancer - inorganics	CTUh	2.82x10 ⁻⁹	3.01x10 ⁻⁹	2.93x10 ⁻¹¹	2.98x10 ⁻¹³	~ 0	-2.25x10 ⁻¹⁰
Human tox., cancer - organics	CTUh	5.27x10 ⁻⁹	5.44x10 ⁻⁹	1.67x10 ⁻¹¹	3.05x10 ⁻¹³	~ 0	-1.82x10 ⁻¹⁰
Human tox., non-cancer	CTUh	1.81x10 ⁻⁷	1.13x10 ⁻⁷	1.72x10 ⁻⁹	5.44x10 ⁻¹¹	7.12x10 ⁻⁸	-4.86x10 ⁻⁹
Human tox., non-cancer - inorganics	CTUh	1.78x10 ⁻⁷	1.10x10 ⁻⁷	1.70x10 ⁻⁹	5.09x10 ⁻¹¹	7.12x10 ⁻⁸	-4.68x10 ⁻⁹

Human tox., non-cancer - organics	CTUh	2.71x10 ⁻⁹	2.87x10 ⁻⁹	1.99x10 ⁻¹¹	3.44x10 ⁻¹²	~ 0	-1.78x10 ⁻¹⁰
Ionising radiation	kBq U-235	0.89976	1.46	0.138522	0.00047	~ 0	-0.70022
Land use	Pt	198	218	0.3954671	0.000209	~ 0	-20.4
Ozone depletion	kg CFC ₁₁	2.98x10 ⁻⁷	2.99x10 ⁻⁷	1.17x10 ⁻⁸	1.78x10 ⁻⁹	~ 0	-1.48x10 ⁻⁸
Photochem. ozone formation	kg NMVO C eq.	0.076205	0.0328101	0.0006943	2.50x10 ⁻⁵	0.043447	-0.00078
Resource use, fossils	MJ	65.4	71.1	4.49	0.106325	~ 0	-10.3
Resource use, minerals and metals	kg Sb eq.	3.87x10 ⁻⁵	5.76x10 ⁻⁵	6.21x10 ⁻⁸	3.36x10 ⁻¹⁰	~ 0	-1.90x10 ⁻⁵
Water use	m ³ depriv.	3.28	4.17	0.12529007	-1.71x10 ⁻⁵	~ 0	-1.02

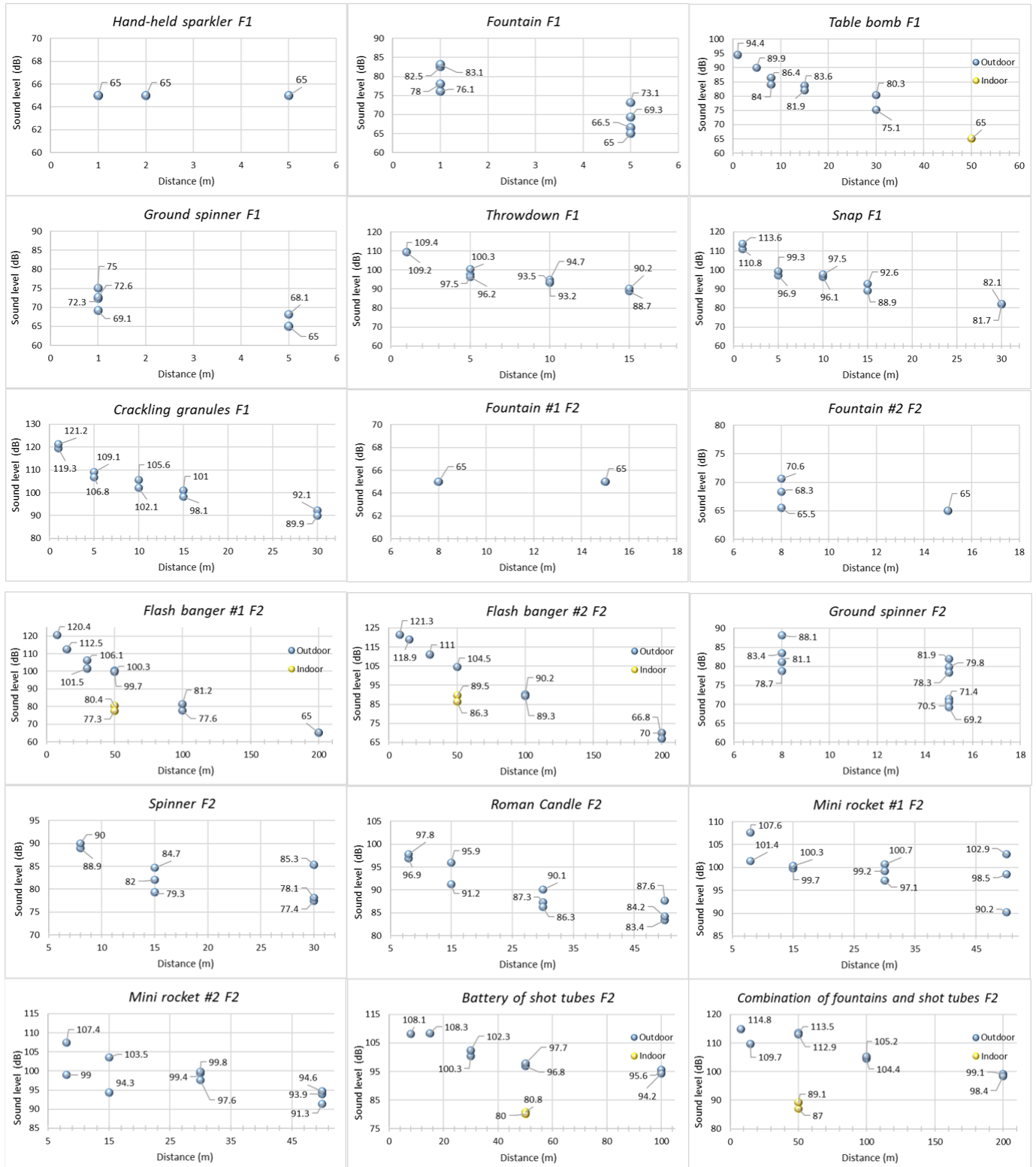
Plastic Pyrotechnic Shell (PPS)

Impact category	Units	Total	Acquisition and Distribution of Raw Materials	Energy Consumption	Transport	Emissions	End of Life
Acidification	Mol H ⁺ eq.	0.07798	0.0264185	0.001605	2.76x10 ⁻⁵	0.05153	-0.00160
Climate change	Kg CO ₂ eq.	3.8705	3.86	0.1827083	0.00789	0.33129	-0.50690
Clim. change - biogenic	Kg CO ₂ eq.	0.09826	0.0984990	0.0002675	2.96x10 ⁻⁷	~ 0	-0.000504
Clim. change - fossil	Kg CO ₂ eq.	3.7633	3.75	0.1808896	0.00789	0.33129	-0.50639
Clim. change - land use and LU change	Kg CO ₂ eq.	0.00897	0.0074002	0.001551	6.37x10 ⁻⁸	~ 0	2.10x10 ⁻⁵
Ecotoxicity, freshwater - part 1	CTUe	114	113	0.232026	0.02050	1.46	-0.12918
Ecotoxicity, freshwater - part 2	CTUe	66.809	66.7	0.085597	0.01232	0.197617	-0.18505

Ecotoxicity, freshwater - inorganics	CTUe	180	178	0.2944014	0.025415	1.66	-0.27346
Ecotoxicity, freshwater – organics p. 1	CTUe	0.36253	0.357500	0.00118367	2.24x10 ⁻⁵	~ 0	0.00382
Ecotoxicity, freshwater - organics - p.2	CTUe	0.8989	0.022038	0.00739007	~ 0	-0.04459	0.89892
Particulate matter	disease inc.	2.67x10 ⁻⁷	3.84x10 ⁻⁹	5.92x10 ⁻¹⁰	7.27x10 ⁻⁸	-1.86x10 ⁻⁸	2.67x10 ⁻⁷
Eutrophic., marine	kg N eq.	0.00471	0.000252	8.83x10 ⁻⁶	0.02706	-0.0003	0.00471
Eutrophic., freshwater	kg P eq.	0.00145	6.92x10 ⁻⁵	3.29x10 ⁻⁸	~ 0	-1.88x10 ⁻⁸	0.00145
Eutrophic., terrestrial	mol N eq.	0.04783	0.0025812	9.70x10 ⁻⁵	0.29662	-0.00315	0.04783
Human tox., cancer	CTUh	6.20x10 ⁻⁹	4.16x10 ⁻¹¹	6.88x10 ⁻¹³	~ 0	-9.0x10 ⁻¹¹	6.20x10 ⁻⁹
Human tox., cancer - inorganics	CTUh	2.16x10 ⁻⁹	2.93x10 ⁻¹¹	3.15x10 ⁻¹³	~ 0	-7.40x10 ⁻¹¹	2.16x10 ⁻⁹
Human tox., cancer - organics	CTUh	4.05x10 ⁻⁹	1.67x10 ⁻¹¹	3.23x10 ⁻¹³	~ 0	-1.59x10 ⁻¹¹	4.05x10 ⁻⁹
Human tox., non-cancer	CTUh	8.43x10 ⁻⁸	1.72x10 ⁻⁹	5.75x10 ⁻¹¹	6.32x10 ⁻⁸	-7.31x10 ⁻¹⁰	8.43x10 ⁻⁸
Human tox., non-cancer - inorganics	CTUh	8.20x10 ⁻⁸	1.70x10 ⁻⁹	5.38x10 ⁻¹¹	6.32x10 ⁻⁸	-3.13x10 ⁻¹⁰	8.20x10 ⁻⁸
Human tox., non-cancer - organics	CTUh	1.95x10 ⁻⁹	2.34x10 ⁻⁹	1.99x10 ⁻¹¹	3.64x10 ⁻¹²	~ 0	-4.17x10 ⁻¹⁰
Ionising radiation	kBq U-235	0.47249	0.350847	0.138522	0.000497	~ 0	-0.01738
Land use	Pt	155	156	0.395467	0.00022	~ 0	-1.385
Ozone depletion	kg CFC ₁₁	-6.14x10 ⁻⁷	2.37x10 ⁻⁷	1.17x10 ⁻⁸	1.88x10 ⁻⁹	~ 0	-8.65x10 ⁻⁷
Photochem. ozone formation	kg NMVO C eq.	0.0716	0.027175	0.000694	2.64x10 ⁻⁵	0.04541	-0.00169
Resource use, fossils	MJ	50.978	66	4.49	0.11238	~ 0	-19.663

Resource use, minerals and metals	kg Sb eq.	4.17x10 ⁻⁶	2.34x10 ⁻⁵	6.21x10 ⁻⁸	3.55x10 ⁻¹⁰	~ 0	-1.93x10 ⁻⁵
Water use	m ³ depriv.	2.09	2.44	0.125	-1.81x10 ⁻⁵	~ 0	-0.48136

Annex D: Sound tests detailed results.



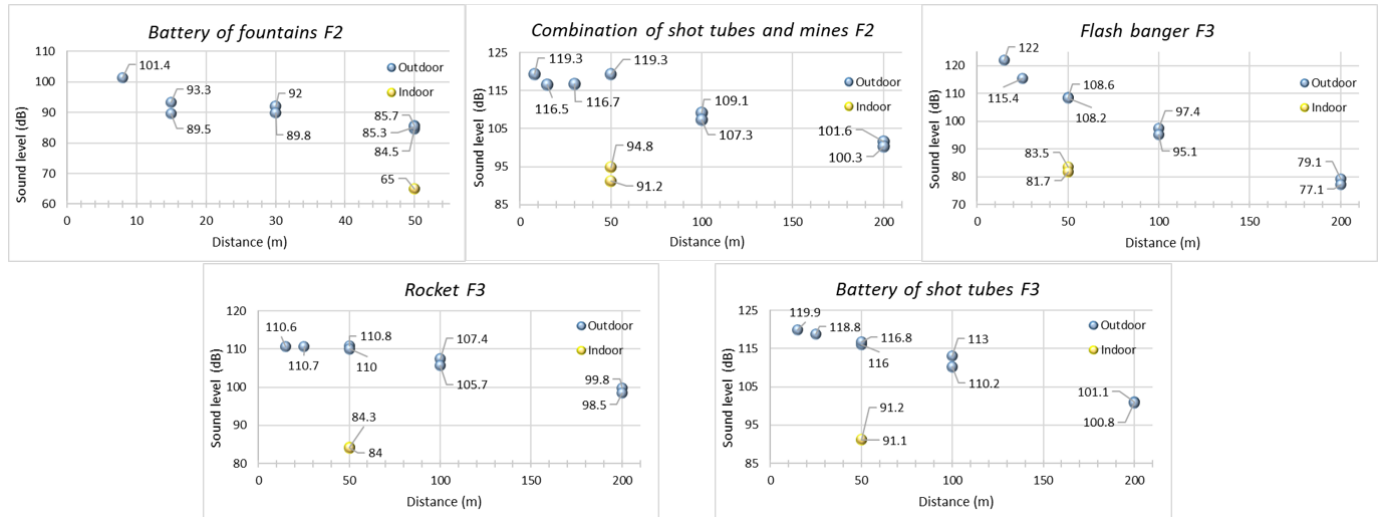


Figure D.1. Results of the influence of climatic factors on sound attenuation.