Science of the Total Environment 804 (2022) 150216

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

# Particle release from refit operations in shipyards: Exposure, toxicity and environmental implications

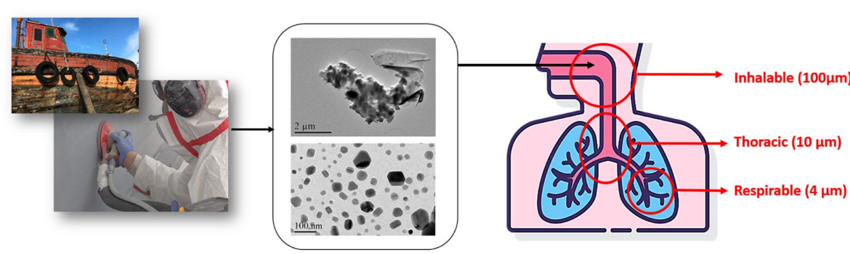
M. López [a,b,*], A. López Lilao [c], C. Ribalta [d], Y. Martínez [e], N. Piña [e], A. Ballesteros [f], C. Fito [f], K. Koehler [g], A. Newton [g], E. Monfort [c], M. Viana [a]

[a] Institute of Environmental Assessment and Water Research (IDAEA-CSIC), C/ Jordi Girona 18, 08034 Barcelona, Spain
[b] Barcelona University, Chemistry Faculty, C/ de Martí i Franquès, 1-11, 08028 Barcelona, Spain
[c] Institute of Ceramic Technology (ITC)- AICE - Universitat Jaume I, Campus Universitario Riu Sec, Av. Vicent Sos Baynat s/n, 12006 Castellón, Spain
[d] The National Research Center for Work Environment (NRCWE), Lersø Parkallé 105, 2100 København, Denmark
[e] Baleari Island University (UIB), Carretera de Valldemossa, km 7.5, 07122 Palma, Illes Balears, Spain
[f] Technological Institute of Packaging, Transportation and Logistics (ITENE), C/ Albert Einstein, 1, 46980 Paterna, Valencia, Spain
[g] Johns Hopkins University (JHU), Baltimore, MD 21218, USA

## HIGHLIGHTS

- Ship refit activities emit ultrafine and engineered nanoparticles in harbour areas.
- Ultrafine and engineered nanoparticles impact human exposure.
- In vitro assays evidenced moderate particle toxicity.
- There is high potential for impacts to the aquatic coastal environment.
- Improvements to safety protocols may minimise exposure and environmental release.

## GRAPHICAL ABSTRACT




## ARTICLE INFO

*Article history:*
Received 29 June 2021
Received in revised form 22 August 2021
Accepted 4 September 2021
Available online 9 September 2021

Editor: Pavlos Kassomenos

*Keywords:*
Ultrafine particles
Harbours
Vessel refit and repair
Maintenance
Ship
Human health
Exposure
Abrasion

## ABSTRACT

European harbours are known to contribute to air quality degradation. While most of the literature focuses on emissions from stacks or logistics operations, ship refit and repair activities are also relevant aerosol sources in EU harbour areas. Main activities include abrasive removal of filler and spray painting with anti-fouling coatings/primers/topcoats. This work aimed to assess ultrafine particle (UFP) emissions from ship maintenance activities and their links with exposure, toxicity and health risks for humans and the aquatic environment. Aerosol emissions were monitored during mechanical abrasion of surface coatings under real-world operating conditions in two scenarios in the Mallorca harbour (Spain). Different types of UFPs were observed: (1) highly regular (triangular, hexagonal) engineered nanoparticles (Ti-, Zr-, Fe-based), embedded as nano-additives in the coatings, and (2) irregular, incidental particles emitted directly or formed during abrasion. Particle number concentrations monitored were in the range of industrial activities such as drilling or welding (up to $5 * 10^5/cm^3$, mean diameters <30 nm). The chemical composition of $PM_4$ aerosols was dominated by metallic tracers in the coatings (Ti, Al, Ba, Zn). In vitro toxicity of $PM_2$ aerosols evidenced reduced cell viability and a moderate potential for cytotoxic effects. While best practices (exhaust ventilation, personal protective equipment, dust removal) were in place, it is unlikely that exposures and environmental release can be fully avoided at all times. Thus, it is advisable that health and safety protocols should be comprehensive to minimise exposures in all types of locations (near- and

* Corresponding author at: Institute of Environmental Assessment and Water Research (IDAEA-CSIC), C/ Jordi Girona 18, 08034 Barcelona, Spain.
*E-mail address:* maria.lopez@idaea.csic.es (M. López).

https://doi.org/10.1016/j.scitotenv.2021.150216

Spray painting
Incidental nanoparticles
Personal protective equipment

far-field) and periods (activity and non-activity). Potential release to coastal surface waters of metallic engineered and incidental nanomaterials, as well as fine and coarse particles (in the case of settled dust), should be assessed and avoided.



## 1. Introduction

European harbours are highly active hubs, as 75% of all goods to or from the EU are transported through harbour areas (EUROSTAT, 2019; Karl et al., 2019). Every additional one million tonnes of cargo handled in a port create an average of 300 new jobs at local level, and the amount of cargo handled in European ports and the size of ships are expected to continue to increase significantly (Mayet, 2017). Globally, maritime transport is expected to increase (Corbett et al., 2010; Faber et al., 2020) in the coming years and up to 2050, despite efforts towards more sustainable consumption patterns. This activity generates air pollutant emissions ($PM_{2.5}$, black carbon, ultrafine particles, $SO_2$) with known impacts on air quality and human health, which have been the target of numerous research studies in Europe and globally (Broome et al., 2015; Cesari et al., 2014; Contini et al., 2011; EEA, 2013; González et al., 2011; Lack and Corbett, 2012; Merico et al., 2016; Moore et al., 2009; Viana et al., 2014, 2020).

While most of the literature available focuses on stack emissions (Cesari et al., 2014; Contini et al., 2011; Ledoux et al., 2018; Mamoudou et al., 2018; Manoli et al., 2017; Viana et al., 2009; Westerlund et al., 2015; among others) or emissions from logistics operations (trucks, lorries for transport of goods within the harbours; Keuken et al., 2012; Lee et al., 2012; Minguillón et al., 2008; Moore et al., 2009), these are not the only sources of air particulates in harbour areas. In addition to transportation of passengers and cargo, a number of harbours specialise in vessel refurbishment activities (refit and repair), which include activities such as abrasive removal of filler and paint, or spray painting with antifouling coatings, primers and topcoats. Examples of maintenance operations are repairing steel damage caused by saltwater corrosion or removing wildlife attached to hulls, which creates drag that reduces fuel efficiency. Across all industries in the US, for example, corrosion costs alone are estimated at more than $1tn a year (STG, 2021). Maintenance activities generate significant particle emissions with potentially large impacts on coastal air and water quality, as well as human health for the workers. The growing maritime industry globally necessarily results in a growing market and impact of ship maintenance activities which, in Europe, are mostly carried out in the Palma de Mallorca harbour (Spain) for recreational ships. The Mallorca harbour hosts 450 ship refurbishment companies, employing 3000 professionals from this sector (Balears, 2021). In general, these activities follow a specific temporal pattern, concentrated roughly between the months of October and April (summer in the northern hemisphere), given that during the warmer months of the year the ships are at sail (as opposed to undergoing refurbishment).

The literature on particle emissions from vessel refurbishment activities is significantly scarcer than for ship exhaust emissions. Particles from ship coatings are known to impact surface water quality and aquatic environments (Miller et al., 2020; Soroldoni et al., 2018), but impacts on air quality and human exposure remain a research gap. Air quality impacts during discharge of dusty materials in harbours were assessed by (Alastuey et al., 2007; Artíñano et al., 2007; Martín et al., 2007). Scrap metal handling was also included as one of the emission sources contributing to PM10 concentrations in the Volos harbour in Greece (Manoli et al., 2017) and in Spain (Sanfélix et al., 2015). Maintenance activities with conventional materials were identified as a relevant source of outdoor particle pollutants with impacts on exposure (Malherbe and Mandin, 2007), while high ultrafine particle (UFP; <100 nm) number concentrations ($>5 * 10^6/cm^3$) were monitored during shipyard sanding operations (Yolanda Martínez-Laserna et al., 2016). Finally, nanoparticle (<50 nm or <100 nm, depending on the literature; Viana et al., 2017) emissions from recreational ship maintenance operations are an emerging environmental and health risk due to the increasing use of ceramic coatings and nanoadditives in surface coatings (e.g., nano-$TiO_2$, carbon black, amorphous nano-$SiO_2$, etc.) in antifouling paints and protective coatings (Miller et al., 2020; Wang et al., 2014). For example, carbon nanotube (CNT) based anti-corrosion coatings are formulated with rope-like carbon structures able to stretch without breaking, making applications easier, with fewer coatings, and a longer life-time (STG, 2021). Nano-enhanced Zn and Cu anti-fouling paints, on the other hand, help solve the issue of marine biofouling by creating coatings capable of simultaneously minimising the attachment of wildlife on ship hulls and the release of Cu and Zn into the aquatic environment (Miller et al., 2020). However, sanding and abrasion of such nano-enabled coatings may result in unexpected (and unwanted) human exposures to engineered nanomaterials. The release mechanisms of engineered and incidental nanomaterials have been studied for diverse mechanical processes (Bressot et al., 2018; Göhler et al., 2010; Morgeneyer et al., 2015, 2019; Shandilya et al., 2014). Models such as that developed by Shandilya et al. (2015a) and Shandilya et al. (2015b) estimate particle emissions from solid surfaces subjected to mechanical stresses similar to the activities described in this work. Finally, the human exposure and environment impacts of ultrafine and engineered nanoparticles have been reviewed, among others, by Clar et al. (2018, dermal transfer and environmental release), Bressot et al. (2015; workplace exposures), Bressot et al. (2018; release to the consumer), Bundschuh et al. (2018; environmental release), Brunelli et al. (2021; release from cultural heritage surfaces), Kuhlbusch et al. (2018; exposures for workers, consumers and the general public), Salmatonidis et al. (2019; workplace exposure mitigation) and Zhao and Zhang (2019; exposure assessment).

The present work aimed to assess particulate matter emissions, including ultrafine particles, from recreational ship maintenance activities and their potential toxicity for human health and the environment. Specific objectives were to (i) identify particle exposures, (ii) understand particle release mechanisms, and (iii) assess potential health risks deriving from particle chemical composition and toxicity.

## 2. Materials and methods

### 2.1. Particle emission scenarios

Particle emissions were monitored and sampled in the Mallorca harbour (Spain), under real-world operating conditions during abrasion of coatings (primer and top-coat paints: D3001 545 Epoxy primer; Snow White #715338; AWLCAT #2 Spray converter; T0001 Fast evap. reducer) in the shipyard and in a workshop. The technical specifications of the coatings are provided in Supporting Information (Table S1). The Mallorca harbour is a representative scenario due to the high rate of refit and repair activities it hosts, when compared to other European harbours. The details of the specific vessel being refurbished cannot be reported due to confidentiality reasons. Two emission scenarios were assessed, aiming to cover the whole chain of activities and scales encountered during abrasive removal of coatings for >70 m long vessels:

- **Workshop**: removable parts of the vessel (e.g., windows, doors, ventilation grids) are typically refit in workshops, as opposed to in the shipyard. The main activities evaluated in the workshop were manual (with sandpaper) and mechanical (with orbital sanders) abrasion of primer and top-coat coatings. Two separate indoor spaces were monitored: area 1, where the deeper coatings were applied and abraded (high-build epoxy resin primer coating, abraded with sanding grain P150; putty and filler material, with 3MP80 and 3MP40) (Fig. 1). Between 3 and 6 workers were exposed on a regular basis in workshop. Measured room ventilation rates (air exchanges per hour, ACH) were 29.4 $h^{-1}$ in, natural (driven by the workshop's open doors) and supported by local exhaust ventilations built into the abrading tables. The workshop doors were open (natural ventilation) and the abrading tables were equipped with local exhaust ventilation. Aerosol sampling took place in the workshop between November 19th to 21st, 2019, during working hours (8:30 am to 14:30 pm).

- **Shipyard**: the vessel's outer surface is refit in the shipyard, inside a tent which is purposely built around the entire vessel (see Fig. S1 in Supporting Information). The purpose of the tent is to minimise particle release to the shipyard air, in terms of air pollution but also to avoid cross-contamination to other vessels. As a result, particle emissions from abrasion of coatings are generated in an enclosed air volume resembling an indoor microenvironment, where workers are exposed (Fig. 1). Between 8 and 10 workers operated simultaneously on the deck that was being worked on, during this study. Abrasion of primer and top-coat paints (a $TiO_2$-based coating, particle size unspecified by the manufacturer, Table S1) was carried out with mechanical abraders (orbital sanders) connected to local exhaust ventilation systems (sanding grain 3MP180, 3MP320, 3MP400). Ventilation was mechanical inside the tent, with 13.1 measured air exchanges per hour (ACH). Aerosol sampling took place in the workshop between January 14th to 16th, 2020, during working hours (8:30 am to 14:30 pm).

Two monitoring locations were set up in each scenario in order to account for background concentrations in parallel with emissions from the activities:

- Far field (FF): representative of average aerosol concentrations indoors, and of a mix of emissions. It was located at approximately 3-5 m from the workers, at 1 m from the ground.
- Near-field (NF): representative of the worker exposure at breathing height, but not directly in the breathing zone (Asbach et al., 2017) due to the size of the monitors. The aerosol instruments were placed on a table as near as possible to the worker but without interfering with their work. The inlets, when it was technically feasible, were at breathing height (1.6 m) and attached to a tripod.

In addition, background concentrations were also monitored during the midday lunch break, when activities were fully stopped (Figs. 2 and 3).

The location of the instruments was sometimes modified, especially in the shipyard, in order to follow the activities of the different teams of workers each day. It should be highlighted that the objective of this work was not to assess compliance with occupational limits, therefore the measurement procedures (locations, sampling times, etc.) did not strictly follow standard protocols.

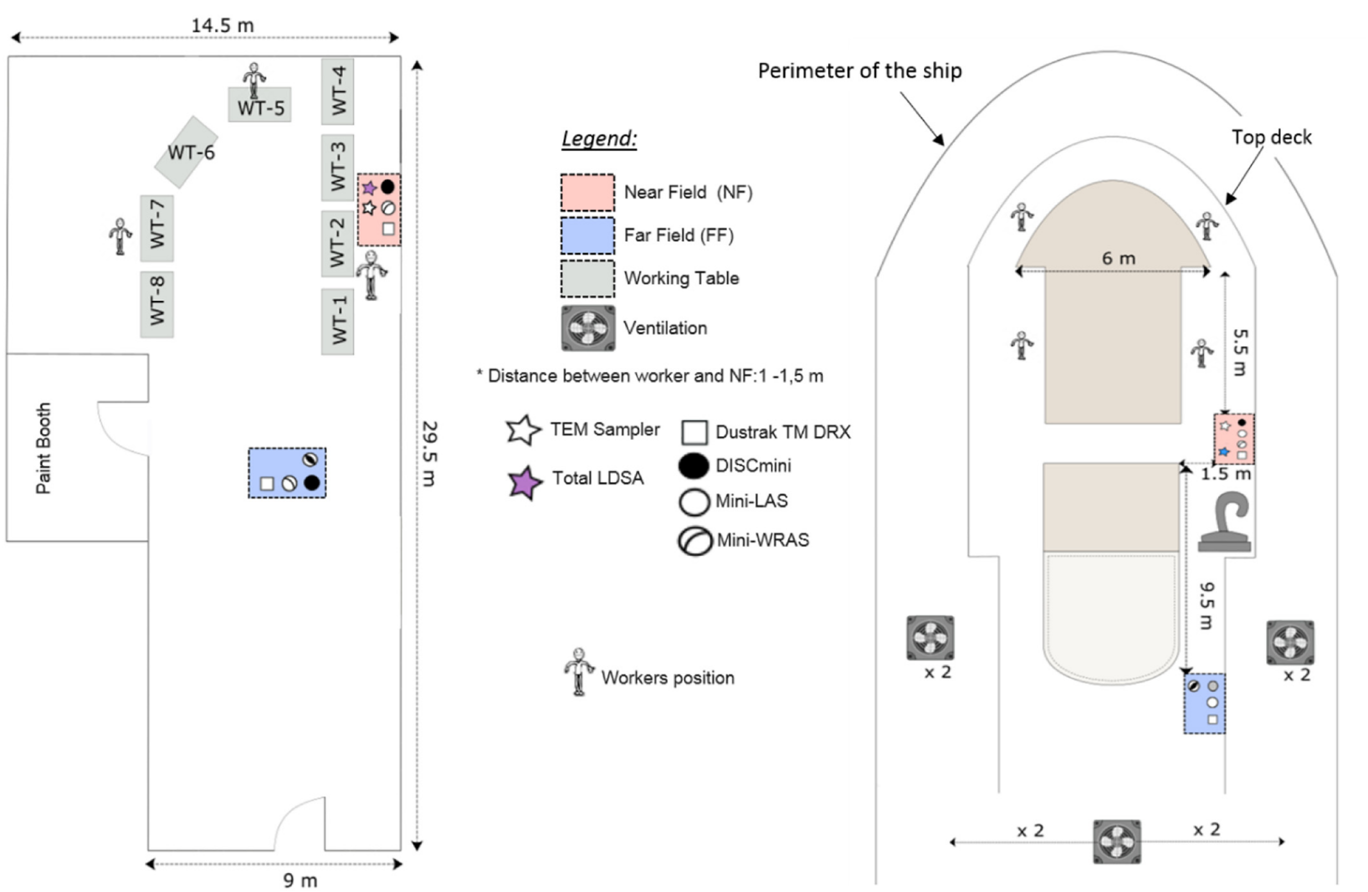



**Fig. 1.** Layout of the workshop (left) and shipyard (right) scenarios monitored, indicating the position of the workers and the aerosol instrumentation deployed.

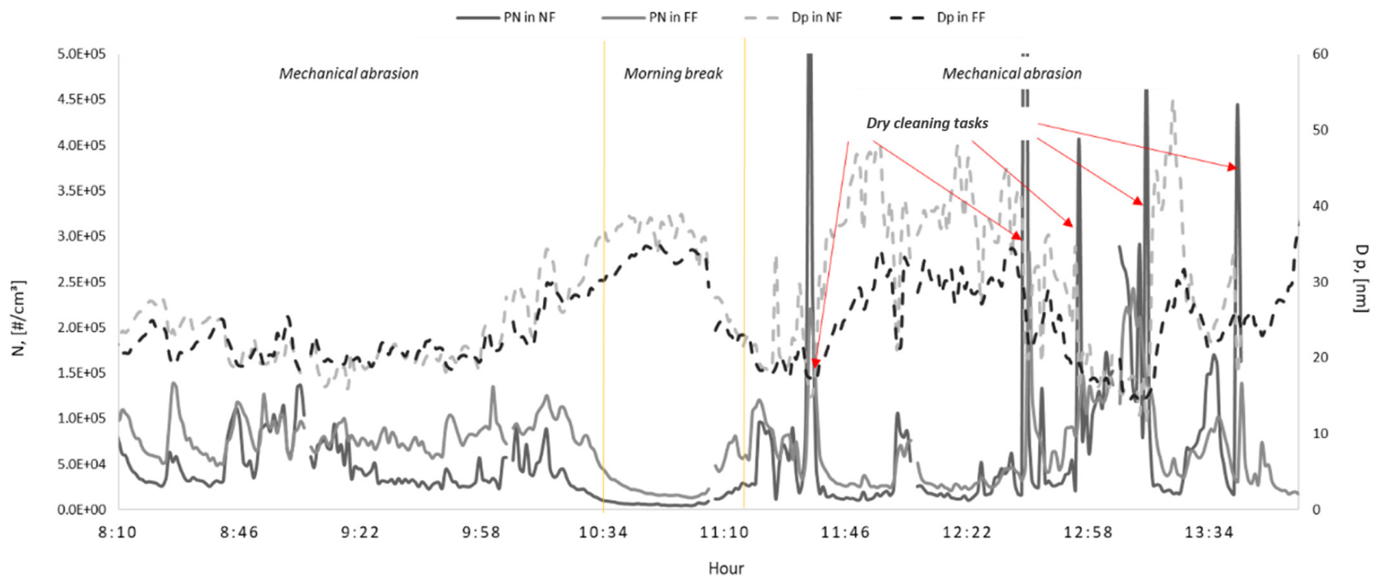



**Fig. 2.** Particle number concentrations (/cm$^3$) and mean particle diameter (nm) in the near-field (NF) and far-field (FF) monitoring locations in the workshop, monitored with DiSCmini on 20/11/2019.

*2.2. Particle monitoring and sampling*

Particle number concentrations (N), mass, size distribution, and mean diameter (Dp) were monitored with online instruments (Table 1):

- Miniature diffusion size classifier DiSCmini (TESTO AG), reporting particle number concentrations and mean particle diameter between 10 and 700 nm, with a 1 min time resolution.
- Mini laser aerosol spectrometer Mini-LAS 11-R (Grimm), for total and size-segregated particle mass concentrations between 0.25 and 32 μm (monitoring inhalable, thoracic and respirable dust, PM values, and particle number concentration), in 31 channels with 6 s time resolution.
- Mini wide range aerosol spectrometer Mini-WRAS (Grimm), for particle mass concentration from 10 nm to 35 μm across 41 channels with 1-min time resolution.
- Electrical mobility spectrometer NanoScan SMPS (TSI Model 3910), monitoring particle size distributions from 10 to 420 nm, in 13 channels with a 1 min time resolution.
- Light-scattering laser photometer DustTrak TM DRX (TSI Model 8533), for total and size-segregated particle mass concentrations in the range 250-3200 nm with 1 min time resolution.

The statistical relevance of increases in particle mass and number concentrations monitored with this instrumentation was assessed following the approach described by Asbach et al. (2012b), based on the comparison with background concentrations +3 times their standard deviation.

*2.3. Aerosol sampling and physical, chemical and toxicological characterisation*

In addition to the online monitors, samplers were deployed at both locations to subsequently analyse the physical, chemical and toxicological aerosol properties:

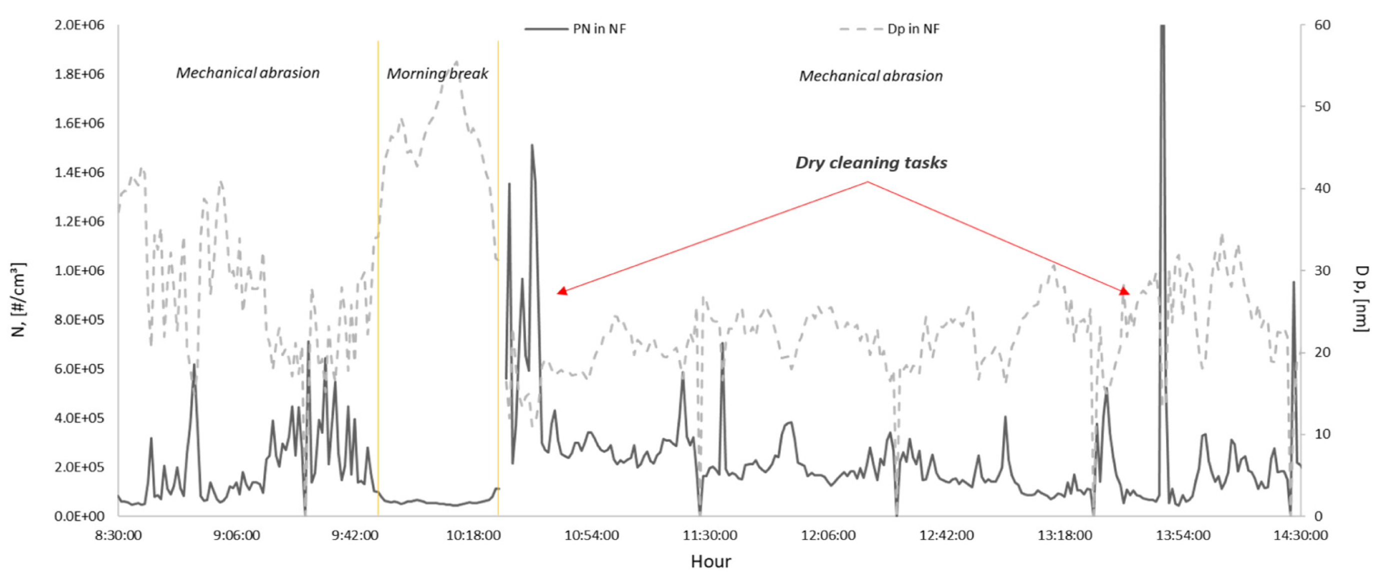



**Fig. 3.** Particle number concentrations (/cm$^3$) and mean particle diameter (nm) in the near-field (NF) and far-field (FF) monitoring locations in the shipyard, monitored with DiSCmini (NF) and NanoScan (FF), on 15/01/2020.

**Table 1**
Monitoring instrumentation deployed in the workshop and the shipyard.

| Instrument | | Manufactured | Sample flow rate (l/min) | Particle size range | Concentration range | Time resolution |
|---|---|---|---|---|---|---|
| Miniature diffusion size classifier (DiSCmini Matter Aerosol AG) | Particle number concentration, mean particle size and alveolar lung deposited surface area | Testo, Wohlen, Switzerland | 1 | 0.3–10 μm (16 channels) | 0–3 × $10^3$/cm$^3$ | 1 min |
| Electrical mobility spectrometer (NanoSacn SMPS TSI Model 3910) | Particle number concentration and particle size distribution | TSI Inc., Shoreview, MN, US | 0.7 | 10–420 nm (13 channels) | 0–$10^5$/cm$^3$ | 1 min |
| Mini wide range aerosol spectrometer (Mini-WRAS 1371) | Particle number and mass concentration and particle size distribution | Grimm Aerosol Technik, Ainring, Germany | 1.2 | 10 nm–35 μm | 0.1–$10^4$ μm/m$^3$<br>3 × $10^3$–5 × $10^6$/cm$^3$ (electrical)<br>0–3 × $10^6$/cm$^3$ (optical) | 1 min |
| Mini laser aerosol spectrometer (Grimm Mini-LAS) | Particle mass concentration | Grimm Aerosol Technik, Airnring, Germany | 1.2 | 0.25–32 μm | 0.1–$10^4$ μm/m$^3$ | 6 s |
| Light scattering laser photometer (DusTrak™ DRX aerosol monitor TSI Model 8533) | Particle mass concentration | TSI Inc., Shoreview, MN, US | 3 | $PM_{10}$, $PM_4$, $PM_{2.5}$ and $PM_1$ | 0.001–150 mg/m$^3$ | 1 min |

- **Chemical properties**: total lung-deposited surface area (LDSA) samplers (Koehler et al., 2009) collected particles on polyurethane foams, in the NF locations. The particle chemical composition was determined by acid digestion of the foams and analysis of the extracts by ICP-MS and ICP-OES. Three valid samples were collected from the workshop as well as three from the shipyard scenarios.
- **Physico-chemical properties**: single-particle analysis was carried out by Transmission Electron Microscopy on a J2100 TEM microscope coupled with an energy-dispersive X-ray (EDX) spectrometer, at the Barcelona University. Particles were collected on TEM grids (Quantifolil® Au grids with 1 μm diameter holes - 4 μm separation of 200 mesh) placed in sampling cassettes (SKC INC., USA, inlet diameter 1/8 in. filter diameter 25 mm) following the sampling setup described by Tsai et al., 2008. The cassettes were connected to an SKC Leland pump (3 l/min). Samples were collected from the NF in the workshop, and from the FF in the shipyard. 3 valid samples were collected from the workshop and 3 from the shipyard scenarios.
- **Cytotoxicity**: the potential effect of particles sampled on cell viability (cytotoxicity) was assessed by the MTT in vitro assay (Bessa et al., 2020; Davoren et al., 2007; Y Zheng et al., 2016). Samples were collected using an SKC BioSampler® connected to a sonic-flow BioLite+ pump (12.5 l/min) over 30 min, collecting particles with a <2 μm cutoff in liquid suspension. While the specific collection efficiency for nanoparticles was not determined, previous works have shown high efficiencies for particles around 1 μm (Zheng and Yao, 2017). The aerosol samples were collected directly into liquid suspension to avoid the interference from filter substrates in the subsequent determinations. The suspensions were stored cold after sample collection. A cell culture medium DMEM (Dulbecco's modified Eagle's medium) was used for collection. The collected samples were tested for cytotoxicity (cellular death) through the MTT assay (methylthiazolyldiphenyl-tetrazolium bromide) by using in vitro human lung adenocarcinoma cell line A549 (Type II alveolar epithelium), considering the inhalation route as the main route of entry into the body. The cells were exposed to the particle suspensions, after which cell viability was determined. A549 cells were cultured in DMEM (Thermo Fisher Scientific) with 5% fetal bovine serum (Merck Life Science) and penicillin and streptomycin (100 μl/ml), and the culture were incubated in a humidified cell incubator at 37 °C with 5% $CO_2$. The cells were grown to confluence in 96 well plates, and the airborne particle samples were incorporated using different dilution ratios: 1:1, 1:2; 1:4, and a control. Each concentration was assessed in three replicates per experiment, plates were read at 490 nm with a microplate reader, and statistical analysis was conducted. Two valid samples were collected from the shipyard. Samples from the workshop are not available due to technical issues.

## 3. Results and discussion

### 3.1. Ultrafine particle release and exposure impacts

The results obtained during one representative day in the workshop and shipyard, respectively, are shown in Figs. 2 and 3. The average results from the entire monitoring periods are summarised in Table 2.

In the workshop (Fig. 2), particle number concentrations and diameters varied largely throughout the day as a function of the activities (e.g., mechanical abrasion, dripping). During activity periods, peak (1-min) particle number concentrations reached up to 1.4 $*$ $10^5$/cm$^3$ in the NF and 0.8 $*$ $10^5$/cm$^3$ in the FF, with mean diameters 20 nm and 25 nm, respectively (excluding peaks derived from dry cleaning tasks) (Figs. 2 and 3). Mean particle diameters <20 nm, close to the instrument's lower detection limit (10 nm, according to the manufacturer), were recorded during mechanical abrasion. As expected, concentrations decreased (5–16 $*$ $10^3$/cm$^3$) and mean particle diameters increased (40 nm) during the morning activity break, when aerosol concentrations monitored were similar to ambient air concentrations, characterised by aged diesel soot as a main component (Brines et al., 2015; Viana et al., 2017). Particle number concentrations were highest in the NF (emission source) and decreased towards the FF due to transport and particle agglomeration. Ultrafine particle impacts across the workshop were statistically significant when compared with background concentrations according to Asbach et al. (2012b), even if they were not considered especially high when compared to other industrial scenarios with similar mechanical abrasion and thermal activities (10–60 $*$ $10^5$/cm$^3$ in an automotive grey iron foundry, Evans et al., 2008; 1–100 $*$ $10^5$/cm$^3$ in a metallurgical coke production facility, Weitkamp et al., 2005; 6–8 $*$ $10^5$/cm$^3$ in a sewage sludge industry, Ferge et al., 2004). This was probably the result of relatively low temperature generation process (mechanical abrasion) and the effectiveness of the combination of local exhaust ventilation systems built into each of the abrading tables, and open doors (natural ventilation).

In terms of human exposure impacts, while they were relevant in the NF location (comparable to the breathing zone), workers always wore personal protective equipment (PPE) whenever the mechanical abraders (handheld orbital sanders, in this case) were in operation. In other industrial sectors such as metallurgy, ceramic or pigment (Salmatonidis et al., 2019; Viana et al., 2017), the concentration registered in far field were significantly higher than in the background,

**Table 2**
Mean particle number and mass concentrations, and diameter, monitored in the near-field locations (NF) in the workshop and shipyard. Selected literature studies are shown for comparison.

| | Date | Activities | Particle number[a] (/cm$^3$) | Dp[a] (nm) | Inhalable[b] (μg/m$^3$) | Thoracic[b] (μg/m$^3$) | Respirable[b] (μg/m$^3$) | Statistically significant |
|---|---|---|---|---|---|---|---|---|
| Workshop | 20/11/2019 | Mechanical abrasion | $6.4 * 10^4$–$7.9 * 10^4$ | 20-25 | 6759-7439 | 1987-2329 | 613-771 | Yes (all fractions) |
| | | Background | $0.5 * 10^4$ | 37 | 936 | 591 | 292 | – |
| | 21/11/2019 | Finishing treatment | $2.6 * 10^4$ | 32 | 800 | 253 | 87 | Yes (all fractions) |
| | | Mechanical abrasion | $8.1 * 10^4$ | 23 | 16,374 | 3356 | 967 | Yes (all fractions) |
| | | Background | $1.2 * 10^4$ | 36 | –[c] | –[c] | –[c] | – |
| Shipyard | 14/01/2020 | Abrasion (4 exhaust systems) | $5.0 * 10^5$ | – | 915 | 523 | 114 | – |
| | | Abrasion (8 exhaust systems) | $0.92 * 10^5$ | 24 | 3365 | 1614 | 274 | – |
| | | Background | –[d] | –[d] | –[d] | –[d] | –[d] | – |
| | 15/01/2020 | Abrasion (8 exhaust systems) | $1.8 * 10^5$–$2.1 * 10^5$ | 23-30 | 2357-5926 | 1415-2998 | 287-492 | Yes (all fractions) |
| | | Background | $0.6 * 10^5$ | 35 | 87 | 63 | 22 | – |
| | 16/01/2020 | Abrasion (8 exhaust systems) | $2.7 * 10^5$–$3.9 * 10^5$ | 24-27 | 3546-5047 | 2129-3087 | 565-786 | Yes (all fractions) |
| | | Background | $0.4 * 10^5$ | 48 | 130 | 100 | 49 | – |

Selected literature studies for comparison

| Industrial process | Particle number (N) concentration range monitored (/cm$^3$) | Reference |
|---|---|---|
| Automotive grey iron foundry | $10–60 * 10^5$ | Evans et al., 2008 |
| Sewage sludge industry | $6–8 * 10^5$ | Ferge et al., 2004 |
| Metallurgical coke production facility | $1–100 * 10^5$ | Weitkamp et al., 2005 |

[a] Monitored with DiscMini.
[b] Monitored with Mini-WRAS in the workshop and Mini-LAS in the shipyard.
[c] Instrument failure.
[d] Monitoring started after the morning break.

hence the use of PPE of these areas should be specifically included in the safety and health protocols. In addition, the correct fitting of the PPE should be controlled and monitored to guarantee worker's protection. As a result, it is recommended that, in industrial settings, health and safety protocols should apply a comprehensive approach covering all types of locations (near- and far-field) and periods (activity and non-activity).

A similar pattern was observed in the shipyard (Fig. 3), with statistically significant concentration increases (compared to background) during activity periods and a clear decrease during the morning break. Peak (1-min) particle number concentrations were higher in the tent than in the workshop ($7.2 * 10^5$/cm$^3$ in the shipyard vs. $1.4 * 10^5$/cm$^3$ in the workshop, in the NF), even though workers were using the same type of handheld orbital sanders, probably owing to the lower efficiency of the mechanical ventilation systems inside the tent and to the fact that there was almost no manual abrading in the shipyard. Particle concentrations were relatively stable throughout the day (aside from peaks resulting from dry cleaning), due to the more continuous operation of the sanders and the larger number of workers operating them (8-10 workers in the shipyard vs. 6 in the workshop). Mean concentrations during mechanical abrasion were in the order of $1.8–5.0 * 10^5$/cm$^3$ (23-30 nm; Table 2) in the NF location, indicating high personal exposures to process-generated ultrafine particles. These concentrations were higher than in the workshop and in the range of industrial activities such as drilling, soldering, welding, laser welding and engraving, and thermal spraying (Buist, 2017; Viana et al., 2017; Viitanen et al., 2017).

The activities in both scenarios (workshop and shipyard) resulted in ultrafine particle formation (nucleation of new particles) and release to workplace air, with potential for impacts on personal exposure. Previous works (Fonseca et al., 2015; Ribalta et al., 2019a, 2019b; Salmatonidis et al., 2019) carried out in settings where no nanoadditives were used, detected new particle formation events from high-energy industrial activities, mostly thermal in nature (e.g., thermal spraying, ceramic tile sintering). Conversely, in the scenarios assessed in this work ultrafine particles were released by means of mechanical activities. This type of release was either not detected in previous experiments (Golanski et al., 2011) or only reported by a very limited number of studies (Gonzalez-Pech et al., 2019), under laboratory conditions (Koivisto et al., 2017, and references therein) or in chamber studies (Lee et al., 2016). Therefore, our results provide new evidence on the release of incidental ultrafine particles during high-energy mechanical activities in real-world industrial settings.

### *3.2. Particle emissions in the workshop vs. the shipyard*

The results from the full monitoring campaigns for the near field (NF) are summarised in Table 2. Results are shown for the NF only as the most representative of the abrasion activities and their direct impacts on exposure. In addition to ultrafine particles, particle mass concentrations in various size fractions were also monitored in both scenarios. In terms of particle number, the highest concentrations recorded during the activity were related with dry cleaning operations (on average $8.5 * 10^4$/cm$^3$, with peaks up to $10^6$/cm$^3$, Figs. 2 and 3), indicating that some cleaning activities should be carefully revised and/or redesigned (e.g., by using closed cabins). However, exposure impacts of these peaks may be considered minimal in terms of the cumulative exposure due to their short duration. In contrast, abrasion resulted in the largest increases in particle number concentration when compared to background concentrations, which were higher in the shipyard (up to $3.9 * 10^5$/cm$^3$) than in the workshop ($8.1 * 10^4$/cm$^3$). The ventilation systems in the shipyard improved aerosol concentrations, as evidenced by the contrast between the periods with 4 active extraction systems ($5.0 * 10^5$/cm$^3$) and 8 active extraction systems ($9.2 * 10^4$/cm$^3$). No significant variability was observed regarding mean particle diameters, which ranged between 20 and 32 nm in both scenarios.

Particle mass concentrations, on the other hand, were higher in the workshop (respirable fraction, 613-967 μg/m$^3$) than in the shipyard (114-786 μg/m$^3$). This is probably a result of the air volume in the different scenarios (lower dilution in the workshop, with smaller size than the tent in the shipyard), and to the configuration of the local exhaust ventilation systems, which in the workshop were built in the tables and therefore were less efficient for coarser dust accumulated on the ground (which was accessible for resuspension by the workers). The particle mass emissions generated by the abrasion activities were statistically significant in both scenarios according to Asbach et al. (2012a). In comparison to the literature, particle concentrations were higher than those recorded during industrial activities (150-190 μg/m$^3$ and 40-116 μg/m$^3$ for the respirable fraction in a machining centre and in a foundry, respectively; Gonzalez-Pech et al., 2019; 340 μg/m$^3$ for the thoracic fraction during packaging of carbon black; Kuhlbusch et al., 2004) or comparable to them (150-600 μg/m$^3$ for the respirable fraction during packing of clay materials; Ribalta et al., 2019a, 2019b).

Finally, despite the lower concentrations in the shipyard relative to the workshop, mass concentrations in the shipyard are relevant due to potential impacts in harbour waters and the aquatic ecosystem: fine and coarse particles are deposited on the ground inside and outside the tents and are swept away by the cleaning crews following best practice protocols. These included dry and wet collection of the dust generated and post-treatment of the wastewater generated. However, deposited dust (from the tents but also from other sources such as vehicular traffic across the shipyard) has the potential to reach surface waters (20% of particulate in surface waters originate from man-made sources; Gómez et al., 2015; Koulouri et al., 2008). This is a key potential impact which should be studied in further detail. While dust management protocols and best practices were in place in the shipyard, it is unlikely that this risk can be fully avoided at all times.

### *3.3. Particle morphology and chemical characterisation*

Different particle morphologies and tracers were observed by TEM which related to the main chemical components of the coatings being abraded (Table S1). The most abundant type of particle observed were fine and ultrafine particles of irregular morphology, detected equally in the workshop and the shipyard (Fig. 4a–e). These particles, ranging between 50 nm and >2000 nm in diameter, included key tracers of pigments (Ti, Mg, Si, Zn, Cu) as main components and were therefore interpreted as resulting from mechanical abrasion of the coating materials by the orbital sanders. Similar irregular-shaped fine and ultrafine particles are reported in previous works involving comparable mechanical processes at laboratory scale (Smulders et al., 2014) and in industrial settings (e.g., a machining centre, Gonzalez-Pech et al., 2019).

In addition, fine metallic particles with shapes suggesting the influence of melting, with diameters <1000 nm, were also detected in the shipyard (Fig. 4f, bottom). Examples of tracers were Pb, Zn and Cu. The rounded shapes of these particles suggest partial or total melting, probably caused by the friction of the orbital sanders against the coatings being abraded. The high organic composition of the coatings (Table S1) supports the possibility of melting of the coating materials. The fact that this kind of particle was detected in the shipyard only, and not in the workshop, may point to the duration of the abrasion activity as a relevant parameter (as well as the larger surfaces being treated), given that the activities were longer (in time) in the shipyard than in the workshop, therefore probably reaching higher surface temperatures in the shipyard, while the type of mechanical sanders was common in both scenarios. Also, the coatings being abraded were different, even if they had a similar organic base (toluene- and ethylacetate-based; Table S1). Incidental nanoparticle formation by melting of coating materials and subsequent new-particle formation of comparable spherical metallic particles was previously reported in the framework of thermal spraying activities at industrial scale (Salmatonidis et al., 2019; Viana et al., 2017). Future work will involve real-time monitoring of the actual temperatures reached by the surface being abraded, in order to assess the potential role of chemical components subject to volatilisation in the composition of the coatings.

Finally, in addition to the ultrafine particles incidentally formed during abrasion (through mechanical or thermal processes), markedly regular nanoparticles were also observed (Fig. 5). These particles were only identified in the shipyard, and their regular shapes indicate that they were engineered and probably used as nano-additives in the coatings. The use of engineered nanoparticles (Ti, Zr, Au, Pb, Ag, Cu; Khan et al., 2019; Kittelson et al., 2004; Miller et al., 2020; Morgeneyer et al., 2018, among others) has increased in recent years in the pigment sector, to enhance coating properties such as anti-drip or anti-fogging (Wu et al., 2020). Specifically, in the shipping sector, Ag, Zn and Zr nano-additives are frequently for antimicrobial protection, Ti for absorption of ultraviolet radiation for cleaning and water treatment (Chouirfa et al., 2018), and Cu biocides in anti-fouling paints (Miller et al., 2020). The engineered nanoparticles detected in the shipyard samples showed characteristic triangular and hexagonal shapes (Fig. 5a, c), as well as other polygonal shapes (Fig. 5b), and they were detected as single nanoparticles with diameters <50 nm (Fig. 5d) as well as embedded in larger aggregates formed by the major components of the coatings (traced by Ti, Fe, Zr; Fig. 5a–c). Their main chemical tracers were Ti, Zr and Fe for the oval and hexagonal-shaped particles,

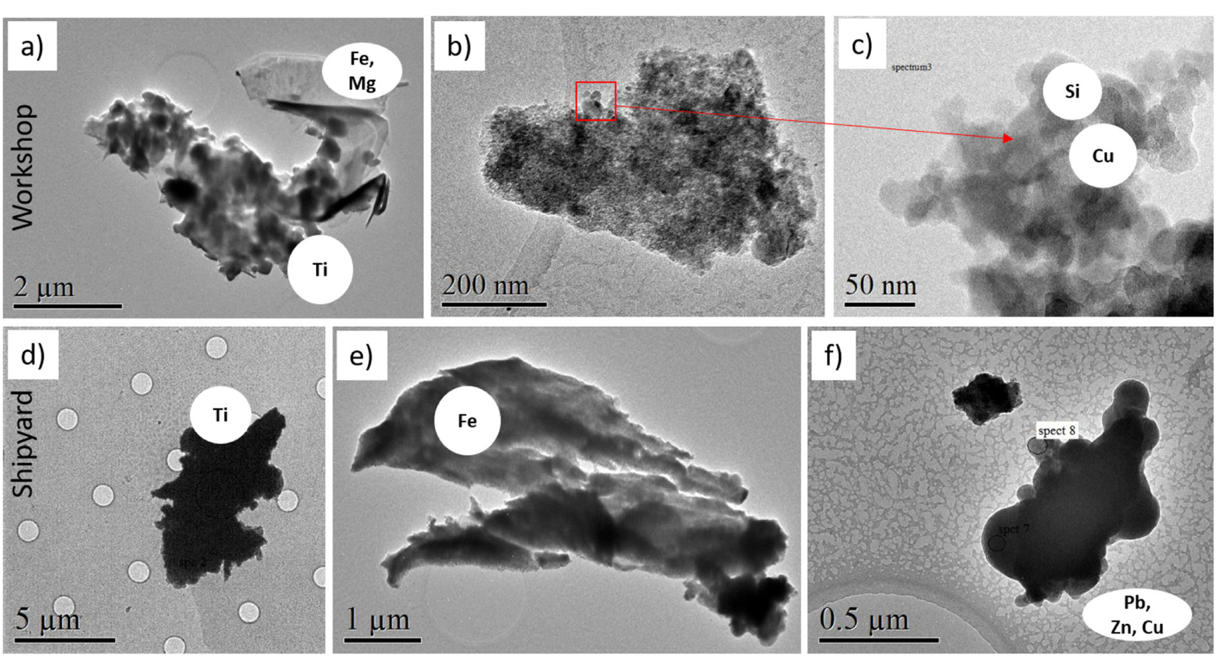



**Fig. 4.** Particles collected on TEM grids in the workshop (top) and in the shipyard (bottom).

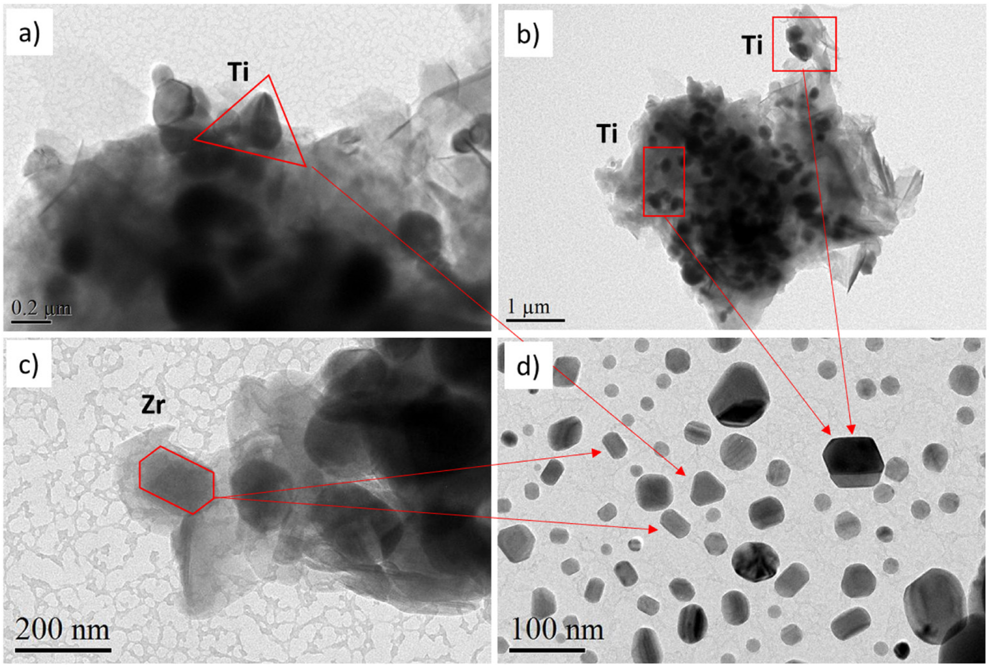



**Fig. 5.** Engineered nanoparticles detected on TEM samples collected in the shipyard.

and Ti for the triangular and polygonal nanoparticles. The specific chemical composition of the coatings being abraded is unknown, as the technical specifications only reported the paint's main components (mostly $TiO_2$, with no reference to the particle size distribution of the pigments). No reference to nano-additives was found in the technical specification sheets. According to the literature (Morgeneyer et al., 2018), the particle morphologies observed in this work are comparable to engineered nanoparticles available on the market for commercial or research use.

In sum, the aerosols released during abrasion in the shipyard contained a mixture of incidental ultrafine and fine particles, generated as a result of mechanical abrasion, and engineered nanoparticles, released together with the coating being abraded. In terms of human health impacts, the incidental and engineered particles detected were found in particle size ranges (<100 nm for engineered nanoparticles, and <500 nm and larger for the aggregates) with major potential health hazard due to their ability to penetrate deepest in the human health respiratory tract (Oberdörster, 2001). Therefore, the release of both types on nanoparticles to workplace air has implications from the point of view of human exposure, if PPE are not adequately implemented. In addition, the potential for ambient air impacts in the harbour area is also relevant, given that the efficiency of the filtration systems in the shipyard tent (connected to the exhaust systems) were not tested in the present study. This is the target of ongoing research in the same shipyard. Finally, potential impacts on the aquatic environment should also be taken into account, as deposited dust may contribute to surface waters in the harbour area, as described above. The release rate of metallic nanoparticles in harbour areas due to mechanical abrasion should be quantified and compared to their release on open sea water from anti-fouling paints (e.g., comparing the active abrasion in the harbour versus the passive abrasion by water during sailing). Further research is necessary on this topic. For example, release rates in the order of <1 to 12 mg/l were reported by Zhang et al. (2017) for $TiO_2$ and $SiO_2$ engineered nanoparticles during weathering of paints in laboratory conditions. Anthropogenic inputs of metal particles have been identified as a significant disruptor of surface water composition in Mediterranean coastal areas (Algül and Beyhan, 2020; Grousset et al., 1995; Heimbürger et al., 2011). While experimental studies have provided evidence for the release of engineered nanomaterials into the environment from nano-enabled products (textiles, paints, etc.) (Gottschalk et al., 2010, among others), the consequences on surface water composition and the aquatic environment of the potential release of engineered metallic nanoparticles to the Mallorca harbour area waters still remain to be evaluated.

### 3.4. Chemical profile of lung-deposited aerosols

Aerosol samples were collected on polyurethane forms to characterise the chemical profile of the total aerosol deposition in the human respiratory tract (Koehler et al., 2009), in the scenarios assessed. In addition to the contribution from ultrafine and nanoparticles described in Figs. 4 and 5, personal exposure and aerosol deposition along the respiratory tract were dominated by the chemical components in coarser particles (Fig. 6). Clear differences were observed between the workshop and the shipyard, in terms of chemical profiles and their repeatability over different days. While the chemical profile of lung-deposited aerosols was mostly constant throughout the different days in the shipyard, large variability was observed across the workshop samples. This was a result of the larger variability in activities in the workshop (mechanical abrasion, manual abrasion, dripping, etc.) which contrasted with the mechanical abrasion carried out throughout the sampling period in the shipyard. In spite of the limited number of samples available (six 8-h samples), these results support the applicability of this sampler, which can be deployed in future real-world high exposure occupational settings. It should be noted that the samples collected were representative of the workers' full 8-hour shifts, and therefore of their actual exposures.

In terms of chemical profiles, particle composition in the shipyard was dominated by the composition of the coating materials, with the largest relative contributions from Ti (43-49%), Mg (29-32%) and Al (8-9%). These are the same tracers observed in Fig. 6, confirming the abrasion of coatings as the main emission source. Ca and Fe were also relevant contributors (7%) to deposited aerosol fraction, in the shipyard. In the workshop, conversely, concentrations were much more variable on the different sampling days and areas of the workshop, with major tracers Ba (12-40%), K (2-41%), Ca (10-44%), Ti (6-26%) and Al (4-14%). When comparing with other studies using the same sampler,

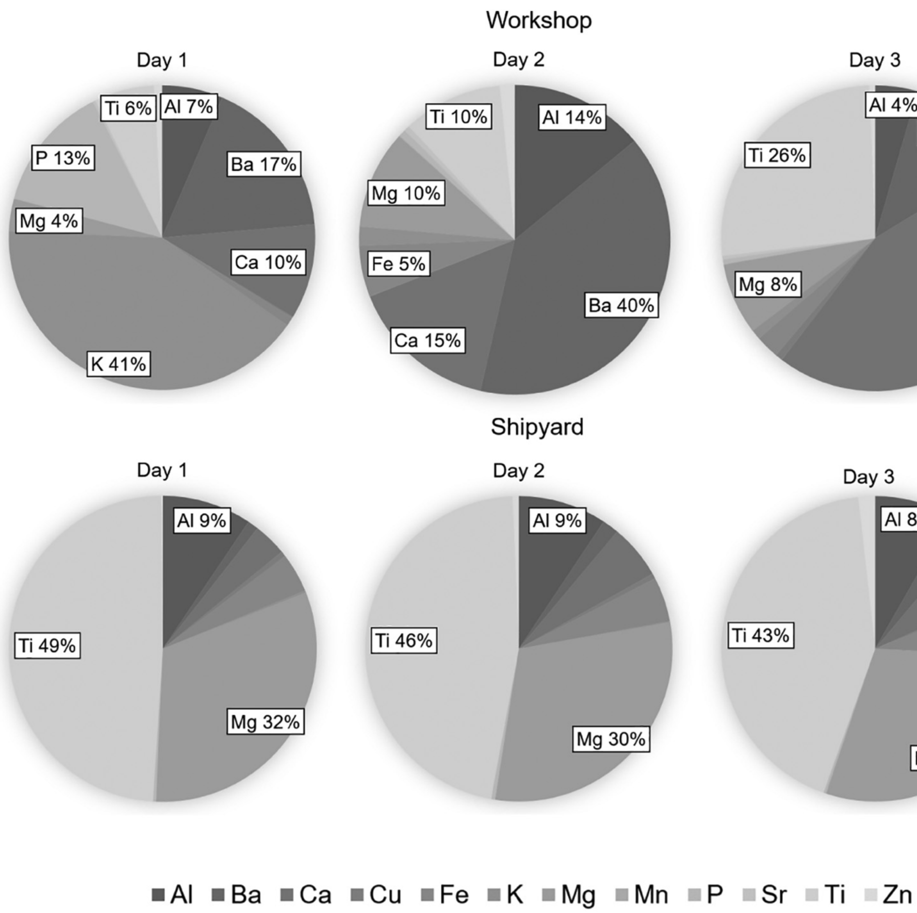



**Fig. 6.** Chemical composition of lung-deposited aerosols sampled on each day in the workshop (top) and the shipyard (bottom).

concentrations were lower than those reported during exposure to stainless-steel welding fumes (Newton et al., 2021) for lung-deposited Ni (0.3-87 μg/m$^3$ vs. 0.4-1.9 μg/m$^3$ in this work) and Cr (0.5-192 μg/m$^3$ vs. 0.5-3.1 μg/m$^3$ in this work), for traditional tracers of welding emissions. Conversely, concentrations of tracers of the coatings were up to one order of magnitude higher than concentrations measured for workers welding stainless steel (8-9 μgTi/m$^3$, 5-6 μgMg/m$^3$, 1-2 μgAl/m$^3$). As with the metallic nanoparticles described in the previous section, the potential release of fine and coarse metal-bearing particles to surface waters may have environmental implications in terms of bio-accumulation in aquatic species (Jitar et al., 2015; Maceda-Veiga et al., 2012; Yigit et al., 2018).

### 3.5. Aerosol cytotoxicity

The results obtained in the MTT assay refer to the average effective concentration ($EC_{50}$), or the concentration affecting 50% of the cell population. The aim of these analyses was to evaluate cell viability after exposure of the cells to the aerosol concentrations sampled, which was only possible in the shipyard due to technical issues with the sampling medium in the workshop. In addition, the complexity of the experimental setup in the shipyard allowed for the collection of only 2 samples, both of them representative of the indoor background aerosol mix (impacted by abrasion and dust resuspension emissions). Cell viability was evaluated after exposure of the cells to the aerosol concentrations monitored in the shipyard, in such a way that concentration-dependent results could only be assessed by diluting the original sample (Fig. 7), in a similar approach to (Lu et al., 2015).

Reduced cell viability was observed after exposure to the original PM samples (without dilution; 35.5-36.8%), when compared to the internal control (which showed no decrease), suggesting that exposure to the particles collected had an effect on cell function. This decrease was comparable and even larger than the one reported by Lu et al. (2015) for exposure to ZnO engineered nanoparticles (40%, for concentrations of 100 μg/ml), who concluded that the local concentration effect of heavy metals in A549 cells (as well as the induction of oxidative stress by the particles) may be responsible for the observed cellular damage. The lower cell viability in our work (testing environmental, or incidental, particles) is also consistent with the conclusion by Lu et al. (2015)

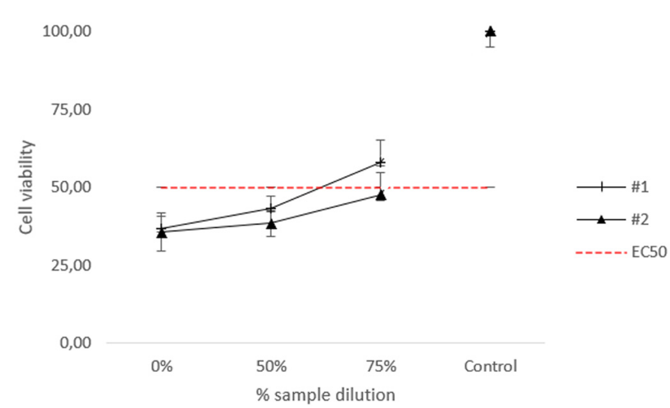



**Fig. 7.** Cell viability (in %) for the two particle samples (with particle diameters <2 μm in suspension) collected in the shipyard, as a function of sample dilution (0% dilution: raw sample as collected in the shipyard; 50% dilution: sample diluted by 50%; etc.). Both samples correspond to repetitions of the same aerosol mix.

that engineered nanoparticles were not as toxic to lung cells as environmental particles. However, a larger dataset is necessary to extract statistically significant conclusions. The comparability between the results from both samples was high, supporting the robustness of the analyses as both samples were collected during similar abrading activities.

Cell viability increased as the sample was diluted, suggesting that the observed effect is dose-dependent. However, as stated above, these are only preliminary results based on the 2 available samples. Only after diluting the sample by a factor of 1:4 (75% dilution) did cell viability increase above the $EC_{50}$, highlighting the relevance of PPE to avoid potential exposures in the NF and FF locations.

## 4. Conclusions

Recreational ship refit and repair operations are relevant sources of potentially health and environmentally hazardous ultrafine particles. Two different types of ultrafine particles were observed during mechanical abrasion of surface coatings: (1) regular (triangular, hexagonal) engineered nanoparticles (Ti-, Zr-, Fe-based) which were originally embedded as nano-additives in the coatings, and (2) irregular, incidental particles emitted directly or formed during the abrasion activity. Particle number concentrations monitored were in the range of industrial activities such as drilling, welding or laser engraving, and were also statistically significant in terms of increases in particle mass concentrations. The chemical composition of particles <4 μm (with major components Ti, Al, Ba and Zn) evidenced that the emission source were the coatings being abraded. In vitro toxicity assessments showed reduced cell viability and a moderate potential for cytotoxic effects, which were comparable to results on engineered nanoparticle toxicity in the literature. These results are relevant in terms of health and environmental impacts.

Despite best practices in place in the scenarios evaluated regarding general exhaust ventilation systems and personal protective equipment, it is unlikely that exposures can be fully avoided at all times. Therefore, in order to ensure effective worker's protection in complex real-world scenarios, it is advisable that risk management protocols take a holistic view, with comprehensive protection protocols covering not only activity periods in the NF but also shutdowns and FF locations. This is considered essential to maximise worker protection. Finally, the effectiveness of protocols in place to remove settled dust (from the tents and other shipyard sources) should be monitored to prevent the release of metallic engineered and incidental nanomaterials, as well as fine and coarse particles, to the coastal surface waters.

## CRediT authorship contribution statement

M. López: Formal analysis, Methodology, Data analysis, Writing - original draft
A. López Lilao: Methodology, Fieldwork, Data analysis
C. Ribalta: Methodology, Fieldwork, Data analysis
Y. Martínez: Fieldwork
N. Piña: Fieldwork
A. Ballesteros: Toxicity analysis
C. Fito: Toxicity analysis
K. Koehler: Methodology
A. Newton: Methodology
E. Monfort: Conceptualization, Writing - review of initial draft
M. Viana: Conceptualization, Formal analysis, Methodology, Writing - review of initial draft.

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## Acknowledgements

This work was carried out in the framework of project IDEALPORT (RTI2018-098095-B-C21). It was also supported by the Spanish Ministry of Science and Innovation (Project CEX2018-000794-S) and by AGAUR (project 2017 SGR41). The authors gratefully acknowledge the extensive knowledge of harbour operations and on-site technical support provided by Global Yatching Group plc.

## Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2021.150216.

## References

Alastuey, A., Moreno, N., Querol, X., Viana, M., Artíñano, B., Luaces, J.A., Basora, J., Guerra, A., 2007. Contribution of harbour activities to levels of particulate matter in a harbour area: Hada Project-Tarragona Spain. Atmos. Environ. 41 (30). https://doi.org/10.1016/j.atmosenv.2007.03.015.

Algül, F., Beyhan, M., 2020. Concentrations and sources of heavy metals in shallow sediments in Lake Bafa, Turkey. Sci. Rep. 10 (1), 11782. https://doi.org/10.1038/s41598-020-68833-2.

Artíñano, B., Gómez-Moreno, F.J., Pujadas, M., Moreno, N., Alastuey, A., Querol, X., Martín, F., Guerra, A., Luaces, J.A., Basora, J., 2007. Measurement of particulate concentrations produced during bulk material handling at the Tarragona harbor. Atmos. Environ. 41 (30), 6344–6355. https://doi.org/10.1016/j.atmosenv.2006.12.020.

Asbach, C., Alexander, C., Clavaguera, S., Dahmann, D., Dozol, H., Faure, B., Fierz, M., Fontana, L., Iavicoli, I., Kaminski, H., MacCalman, L., Meyer-Plath, A., Simonow, B., van Tongeren, M., Todea, A.M., 2017. Review of measurement techniques and methods for assessing personal exposure to airborne nanomaterials in workplaces. Sci. Total Environ. 603–604 (October), 793–806. https://doi.org/10.1016/j.scitotenv.2017.03.049.

Asbach, C., Kuhlbusch, T.a J., Kaminski, H., Plitzko, S., Götz, U., Voetz, M., Dahmann, D., 2012. Authors: SOP-Tiered Approach Tiered Approach for the Assessment of Exposure to Airborne Nanoobjects in Work-Places.

Asbach, C., Kuhlbusch, T., Kaminski, H., Stahlmecke, B., Plitzko, S., Götz, U., Voetz, M., Kiesling, H.-J., Dahmann, D., 2012. Standard operation procedures for assessing exposure to nanomaterials, following a tiered approach. http://www.nanogem.de/cms/nanogem/upload/Veroeffentlichungen/nanoGEM_SOPs_Tiered_Approach.pdf.

Balears, P.de, 2021. Ship Refurbishment Stats.

Bessa, M.J., Brandão, F., Fokkens, P., Cassee, F.R., Salmatonidis, A., Viana, M., Vulpoi, A., Simon, S., Monfort, E., Teixeira, J.P., Fraga, S., 2020. Toxicity assessment of industrial engineered and airborne process-generated nanoparticles in a 3D human airway epithelial in vitro model. Nanotoxicology 15 (4), 542–557.

Bressot, C., Shandilya, N., Jayabalan, T., Fayet, G., Voetz, M., Meunier, L., Le Bihan, O., Aguerre-Chariol, O., Morgeneyer, M., 2018. Exposure assessment of nanomaterials at production sites by a short time sampling (STS) approach: strategy and first results of measurement campaigns. Process Saf. Environ. Prot. 116, 324–332. https://doi.org/10.1016/j.psep.2018.02.012.

Bressot, C., Shandilya, N., Nogueira, E.S.D.C., Cavaco-Paulo, A., Morgeneyer, M., Le Bihan, O., Aguerre-Chariol, O., 2015. Exposure assessment based recommendations to improve nanosafety at nanoliposome production sites. J. Nanomater. 2015. https://doi.org/10.1155/2015/931405.

Brines, M., Dall'Osto, M., Beddows, D.C.S., Harrison, R.M., Gómez-Moreno, F., Núñez, L., Artíñano, B., Costabile, F., Gobbi, G.P., Salimi, F., Morawska, L., Sioutas, C., Querol, X., 2015. Traffic and nucleation events as main sources of ultrafine particles in high-insolation developed world cities. Atmos. Chem. Phys. 15 (10), 5929–5945. https://doi.org/10.5194/acp-15-5929-2015.

Broome, R.A., Fann, N., Cristina, T.J.N., Fulcher, C., Duc, H., Morgan, G.G., 2015. The health benefits of reducing air pollution in Sydney, Australia. Environ. Res. 143 (Pt A), 19–25. https://doi.org/10.1016/j.envres.2015.09.007.

Brunelli, A., Calgaro, L., Semenzin, E., Cazzagon, V., Giubilato, E., Marcomini, A., Badetti, E., 2021. Leaching of nanoparticles from nano-enabled products for the protection of cultural heritage surfaces: a review. Environ. Sci. Eur. 33 (1). https://doi.org/10.1186/s12302-021-00493-z.

HE Buist (2017). Applicability of provisional NRVs to synthetic nanomaterials. A study within the frame of the project Update of the NRVs. Tno 2017 R10424, 1–48. doi: 10.13140/RG.2.2.18241.25445.

Bundschuh, M., Filser, J., Lüderwald, S., McKee, M.S., Metreveli, G., Schaumann, G.E., Schulz, R., Wagner, S., 2018. Nanoparticles in the environment: where do we come from, where do we go to? Environ. Sci. Eur. 30 (1). https://doi.org/10.1186/s12302-018-0132-6.

Cesari, D., Genga, A., Ielpo, P., Siciliano, M., Mascolo, G., Grasso, F.M., Contini, D., 2014. Source apportionment of PM2.5in the harbour-industrial area of Brindisi (Italy): identification and estimation of the contribution of in-port ship emissions. Sci. Total Environ. 497–498, 392–400. https://doi.org/10.1016/j.scitotenv.2014.08.007.

Chouirfa, H., Bouloussa, H., Migonney, V., Falentin-Daudré, C., 2018. Review of titanium surface modification techniques and coatings for antibacterial applications. Acta Biomater. 83, 37–54.

Clar, J.G., Platten, W.E., Baumann, E.J., Remsen, A., Harmon, S.M., Bennett-Stamper, C.L., Thomas, T.A., Luxton, T.P., 2018. Dermal transfer and environmental release of CeO2 nanoparticles used as UV inhibitors on outdoor surfaces: implications for human and environmental health. Sci. Total Environ. 613–614, 714–723. https://doi.org/10.1016/j.scitotenv.2017.09.050.

Contini, D., Gambaro, A., Belosi, F., Pieri, S.De, Cairns, W.R.L., Donateo, A., Zanotto, E., Citron, M., 2011. The direct influence of ship traffic on atmospheric PM2.5, PM10 and PAH in Venice. J. Environ. Manag. 92 (9), 2119–2129. https://doi.org/10.1016/j.jenvman.2011.01.016.

Corbett, J.J., Lack, D.A., Winebrake, J.J., Harder, S., Silberman, J.A., Gold, M., 2010. Arctic shipping emissions inventories and future scenarios. Atmos. Chem. Phys. 10 (19), 9689–9704. https://doi.org/10.5194/acp-10-9689-2010.

Davoren, M., Herzog, E., Casey, A., Cottineau, B., Chambers, G., Byrne, H.J., Lyng, F.M., 2007. In vitro toxicity evaluation of single walled carbon nanotubes on human A549 lung cells. Toxicol. in Vitro 21 (3), 438–448. https://doi.org/10.1016/j.tiv.2006.10.007.

EEA, 2013. The Impact of International Shipping on European Air Quality and Climate Forcing.

EUROSTAT. (2019). EUROSTAT. Https://Ec.Europa.Eu/Eurostat.

Evans, D.E., Heitbrink, W.A., Slavin, T.J., Peters, T.M., 2008. Ultrafine and respirable particles in an automotive grey iron foundry. Ann. Occup. Hyg. 52 (1), 9–21. https://doi.org/10.1093/annhyg/mem056.

Faber, J., Hanayama, S., Zhang, S., Pereda, P., Comer, B., Hauerhof, E., Smith, T., Zhang, Y., Kosaka, H., Adachi, M., Bonello, J.-M., Galbraith, C., Gong, Z., Hirata, K., Hummels, D., Kleijn, A., Lee, D.S., Liu, Y., W., S.van der L., Xing, H., 2020. Fourth IMO GHG Study.

Ferge, T., Maguhn, J., Felber, H., Zimmermann, R., 2004. Particle collection efficiency and particle re-entrainment of an electrostatic precipitator in a sewage sludge incineration plant. Environ. Sci. Technol. 38 (5), 1545–1553. https://doi.org/10.1021/es034709s.

Fonseca, A.S., Viana, M., Querol, X., Moreno, N., de Francisco, I., Estepa, C., de la Fuente, G.F., 2015. Ultrafine and nanoparticle formation and emission mechanisms during laser processing of ceramic materials. J. Aerosol Sci. 88, 48–57. https://doi.org/10.1016/j.jaerosci.2015.05.013.

Göhler, D., Stintz, M., Hillemann, L., Vorbau, M., 2010. Characterization of nanoparticle release from surface coatings by the simulation of a sanding process. Ann. Occup. Hyg. 54 (6), 615–624. https://doi.org/10.1093/annhyg/meq053.

Golanski, L., Gaborieau, A., Guiot, A., Uzu, G., Chatenet, J., Tardif, F., 2011. Characterization of abrasion-induced nanoparticle release from paints into liquids and air. J. Phys. Conf. Ser. 304 (1). https://doi.org/10.1088/1742-6596/304/1/012062.

Gómez, A.G., Ondiviela, B., Puente, A., Juanes, J.A., 2015. Environmental risk assessment of water quality in harbor areas: a new methodology applied to European ports. J. Environ. Manag. 155, 77–88. https://doi.org/10.1016/j.jenvman.2015.01.042.

Gonzalez-Pech, N.I., Stebounova, L.V., Ustunol, I.B., Park, J.H., Anthony, T.R., Peters, T.M., Grassian, V.H., 2019. Size, composition, morphology, and health implications of airborne incidental metal-containing nanoparticles. J. Occup. Environ. Hyg. 16 (6), 387–399. https://doi.org/10.1080/15459624.2018.1559925.

González, Y., Rodríguez, S., Guerra García, J.C., Trujillo, J.L., García, R., 2011. Ultrafine particles pollution in urban coastal air due to ship emissions. Atmos. Environ. 45 (28), 4907–4914. https://doi.org/10.1016/j.atmosenv.2011.06.002.

Gottschalk, F., Scholz, R.W., Nowack, B., 2010. Probabilistic material flow modeling for assessing the environmental exposure to compounds: methodology and an application to engineered nano-TiO2 particles. Environ. Model. Softw. 25 (3), 320–332. https://doi.org/10.1016/j.envsoft.2009.08.011.

Grousset, F.E., Quetel, C.R., Thomas, B., Donard, O.F.X., Lambert, C.E., Guillard, F., Monaco, A., 1995. Anthropogenic vs. lithogenic origins of trace elements (As, Cd, Pb, Rb, Sb, Sc, Sn, Zn) in water column particles: northwestern Mediterranean Sea. Marine Chemistry 48 (3–4), 291–310. https://doi.org/10.1016/0304-4203(94)00056-J.

Heimbürger, L.-E., Migon, C., Cossa, D., 2011. Impact of atmospheric deposition of anthropogenic and natural trace metals on northwestern Mediterranean surface waters: a box model assessment. Environ. Pollut. 159 (6), 1629–1634. https://doi.org/10.1016/j.envpol.2011.02.046.

Jitar, O., Teodosiu, C., Oros, A., Plavan, G., Nicoara, M., 2015. Bioaccumulation of heavy metals in marine organisms from the Romanian sector of the Black Sea. New Biotechnol. 32 (3), 369–378. https://doi.org/10.1016/j.nbt.2014.11.004.

Karl, M., Jonson, J.E., Uppstu, A., Aulinger, A., Prank, M., Sofiev, M., Jalkanen, J.-P., Johansson, L., Quante, M., Matthias, V., 2019. Effects of ship emissions on air quality in the Baltic Sea region simulated with three different chemistry transport models. Atmos. Chem. Phys. 19 (10), 7019–7053. https://doi.org/10.5194/acp-19-7019-2019.

Keuken, M.P., Henzing, J.S., Zandveld, P., van den Elshout, S., Karl, M., 2012. Dispersion of particle numbers and elemental carbon from road traffic, a harbour and an airstrip in the Netherlands. Atmos. Environ. 54, 320–327. https://doi.org/10.1016/j.atmosenv.2012.01.012.

Khan, I., Saeed, K., Khan, I., 2019. Nanoparticles: properties, applications and toxicities. Arab. J. Chem. 12 (7), 908–931. https://doi.org/10.1016/j.arabjc.2017.05.011.

Kittelson, D.B., Watts, W.F., Johnson, J.P., 2004. Nanoparticle emissions on Minnesota highways. Atmos. Environ. 38 (1), 9–19. https://doi.org/10.1016/j.atmosenv.2003.09.037.

Koehler, K.A., Clark, P., Volckens, J., 2009. Development of a sampler for total aerosol deposition in the human respiratory tract. Ann. Occup. Hyg. 53 (7), 731–738. https://doi.org/10.1093/annhyg/mep053.

Koivisto, A.J., Jensen, A.C.Ø., Kling, K.I., Nørgaard, A., Brinch, A., Christensen, F., Jensen, K.A., 2017. Quantitative material releases from products and articles containing manufactured nanomaterials: Towards a release library. NanoImpact. vol. 5. Elsevier, pp. 119–132. https://doi.org/10.1016/j.impact.2017.02.001.

Koulouri, E., Saarikoski, S., Theodosi, C., Markaki, Z., Gerasopoulos, E., Kouvarakis, G., Mäkelä, T., Hillamo, R., Mihalopoulos, N., 2008. Chemical composition and sources of fine and coarse aerosol particles in the eastern Mediterranean. Atmos. Environ. 42 (26), 6542–6550. https://doi.org/10.1016/j.atmosenv.2008.04.010.

Kuhlbusch, T.A.J., Neumann, S., Fissan, H., 2004. Number size distribution, mass concentration, and particle composition of PM1 PM2.5, and PM10 in bag filling areas of carbon black production. J. Occup. Environ. Hyg. 1 (10), 660–671. https://doi.org/10.1080/15459620490502242.

Kuhlbusch, Thomas A.J., Wijnhoven, S.W.P., Haase, A., 2018. Nanomaterial exposures for worker, consumer and the general public. NanoImpact 10 (June 2017), 11–25. https://doi.org/10.1016/j.impact.2017.11.003.

Lack, D.A., Corbett, J.J., 2012. Black carbon from ships: a review of the effects of ship speed, fuel quality and exhaust gas scrubbing. Atmos. Chem. Phys. 12 (9), 3985–4000. https://doi.org/10.5194/acp-12-3985-2012.

Ledoux, F., Roche, C., Cazier, F., Beaugard, C., Courcot, D., 2018. Influence of ship emissions on NOx, SO2, O3 and PM concentrations in a North-Sea harbor in France. J. Environ. Sci. 71, 56–66. https://doi.org/10.1016/j.jes.2018.03.030.

Lee, G.H., Ahn, K.H., Yu, I.J., 2016. Testing of nanoparticle release from a composite containing nanomaterial using a chamber system. J. Vis. Exp. 2016 (117), 54449. https://doi.org/10.3791/54449.

Lee, G., You, S.(Iris), Ritchie, S.G., Saphores, J.-D., Jayakrishnan, R., Ogunseitan, O., 2012. Assessing air quality and health benefits of the Clean Truck Program in the Alameda corridor, CA. Transp. Res. A Policy Pract. 46 (8), 1177–1193. https://doi.org/10.1016/j.tra.2012.05.005.

Lu, S., Zhang, W., Zhang, R., Liu, P., Wang, Q., Shang, Y., Wu, M., Donaldson, K., Wang, Q., 2015. Comparison of cellular toxicity caused by ambient ultrafine particles and engineered metal oxide nanoparticles. Part. Fibre Toxicol. 12.

Maceda-Veiga, A., Monroy, M., Sostoa, A., 2012. Metal bioaccumulation in the Mediterranean barbel (Barbus meridionalis) in a Mediterranean River receiving effluents from urban and industrial wastewater treatment plants. Ecotoxicol. Environ. Saf. 76, 93–101. https://doi.org/10.1016/j.ecoenv.2011.09.013.

Malherbe, L., Mandin, C., 2007. VOC emissions during outdoor ship painting and health-risk assessment. Atmos. Environ. 41 (30), 6322–6330. https://doi.org/10.1016/j.atmosenv.2007.02.018.

Mamoudou, I., Zhang, F., Chen, Q., Wang, P., Chen, Y., 2018. Characteristics of PM2.5from ship emissions and their impacts on the ambient air: a case study in Yangshan Harbor, Shanghai. Sci. Total Environ. 640–641, 207–216. https://doi.org/10.1016/j.scitotenv.2018.05.261.

Manoli, E., Chelioti-Chatzidimitriou, A., Karageorgou, K., Kouras, A., Voutsa, D., Samara, C., Kampanos, I., 2017. Polycyclic aromatic hydrocarbons and trace elements bounded to airborne PM10 in the harbor of Volos, Greece: implications for the impact of harbor activities. Atmos. Environ. 167, 61–72. https://doi.org/10.1016/j.atmosenv.2017.08.001.

Martín, F., Pujadas, M., Artiñano, B., Gómez-Moreno, F., Palomino, I., Moreno, N., Alastuey, A., Querol, X., Basora, J., Luaces, J.A., Guerra, A., 2007. Estimates of atmospheric particle emissions from bulk handling of dusty materials in Spanish Harbours. Atmos. Environ. 41 (30), 6356–6365. https://doi.org/10.1016/j.atmosenv.2006.12.003.

Martínez-Laserna, Yolanda, Expósito-Rossell, J.F., Deyá-Serra, P.M., Piña-Capó, M.de las N., Fonseca, A.S., Viana, M., 2016. OCCUPATIONAL EXPOSURE OF PARTICULATE MATTER DURING SANDING OPERATIONS OF VESSEL SURFACE. Workplace and Indoor Aerosols Conference 2016, Barcelona.

Mayet, R., 2017. The EU port policy and green ports. European Energy Inovation. http://www.europeanenergyinnovation.eu/Articles/Autumn-2017/The-EU-port-policy-and-green-ports.

Merico, E., Donateo, A., Gambaro, A., Cesari, D., Gregoris, E., Barbaro, E., Dinoi, A., Giovanelli, G., Masieri, S., Contini, D., 2016. Influence of in-port ships emissions to gaseous atmospheric pollutants and to particulate matter of different sizes in a Mediterranean harbour in Italy. Atmos. Environ. 139, 1–10. https://doi.org/10.1016/j.atmosenv.2016.05.024.

Miller, R.J., Adeleye, A.S., Page, H.M., Kui, L., Lenihan, H.S., Keller, A.A., 2020. Nano and traditional copper and zinc antifouling coatings: metal release and impact on marine sessile invertebrate communities. J. Nanopart. Res. 22 (5). https://doi.org/10.1007/s11051-020-04875-x.

Minguillón, M.C., Arhami, M., Schauer, J.J., Sioutas, C., 2008. Seasonal and spatial variations of sources of fine and quasi-ultrafine particulate matter in neighborhoods near the Los Angeles-Long Beach harbor. Atmos. Environ. 42 (32), 7317–7328. https://doi.org/10.1016/j.atmosenv.2008.07.036.

Moore, K., Krudysz, M., Pakbin, P., Hudda, N., Sioutas, C., 2009. Intra-community variability in total particle number concentrations in the San Pedro harbor area (Los Angeles, California). Aerosol Sci. Technol. 43 (6), 587–603. https://doi.org/10.1080/02786820902800900.

Morgeneyer, M., Aguerre-Chariol, O., Bressot, C., 2018. STEM imaging to characterize nanoparticle emissions and help to design nanosafer paints. Chem. Eng. Res. Des. 136, 663–674. https://doi.org/10.1016/j.cherd.2018.06.013.

Morgeneyer, M., Ramírez-Gómez, A., Poletto, M., Ward-Smith, S., Tweedie, R.J., Heng, J.Y.Y., Maass, S., Bressot, C., 2019. Particle technology as a uniform discipline? Towards a holistic approach to particles, their creation, characterisation, handling and processing! Chem. Eng. Res. Des. 146, 162–165. https://doi.org/10.1016/j.cherd.2018.11.029.

Morgeneyer, M., Shandilya, N., Chen, Y.M., Le Bihan, O., 2015. Use of a modified taber abrasion apparatus for investigating the complete stress state during abrasion and in-process wear particle aerosol generation. Chem. Eng. Res. Des. 93 (April), 251–256. https://doi.org/10.1016/j.cherd.2014.04.029.

Newton, A., Serdar, B., Adams, K., Dickinson, L.M., Koehler, K., 2021. Lung deposition versus inhalable sampling to estimate body burden of welding fume exposure: a pilot sampler study in stainless steel welders. J. Aerosol Sci. 153, 105721. https://doi.org/10.1016/j.jaerosci.2020.105721.

Oberdörster, G., 2001. Pulmonary effects of inhaled ultrafine particles. Int. Arch. Occup. Environ. Health 74, 1–8.

Ribalta, C., López-Lilao, A., Estupiñá, S., Fonseca, A.S., Tobías, A., García-Cobos, A., Minguillón, M.C., Monfort, E., Viana, M., 2019. Health risk assessment from exposure to particles during packing in working environments. Sci. Total Environ. 671, 474–487. https://doi.org/10.1016/j.scitotenv.2019.03.347.

Ribalta, Carla, Koivisto, A.J., Salmatonidis, A., López-Lilao, A., Monfort, E., Viana, M., 2019. Modeling of high nanoparticle exposure in an indoor industrial scenario with a one-box model. Int. J. Environ. Res. Public Health 16 (10), 1695. https://doi.org/10.3390/ijerph16101695.

Salmatonidis, A., Ribalta, C., Sanfélix, V., Bezantakos, S., Biskos, G., Vulpoi, A., Simion, S., Monfort, E., Viana, M., 2019. Workplace exposure to nanoparticles during thermal spraying of ceramic coatings. Ann. Work Expo. Health 63 (1). https://doi.org/10.1093/annweh/wxy094.

Sanfélix, V., Escrig, A., López-Lilao, A., Celades, I., Monfort, E., 2015. On the source inversion of fugitive surface layer releases. Part I. Model formulation and application to simple sources. Atmos. Environ. 109, 171–177. https://doi.org/10.1016/j.atmosenv.2015.03.024.

Shandilya, N., Le Bihan, O., Morgeneyer, M., 2014. A review on the study of the generation of (nano)particles aerosols during the mechanical solicitation of materials. J. Nanomater. 2014. https://doi.org/10.1155/2014/289108.

Shandilya, N., Morgeneyer, M., Bihan, O.Le., 2015. First development to model aerosol emission from solid surfaces subjected to mechanical stresses: II. Experiment-theory comparison, simulation and sensibility analysis. J. Aerosol Sci. 89, 1–17. https://doi.org/10.1016/j.jaerosci.2015.06.004.

Shandilya, N., Morgeneyer, M., Le Bihan, O., 2015. First development to model aerosol emission from solid surfaces subjected to mechanical stresses: I. Development and results. J. Aerosol Sci. 89, 43–57. https://doi.org/10.1016/j.jaerosci.2015.06.010.

Smulders, S., Luyts, K., Brabants, G., Landuyt, K.Van, Kirschhock, C., Smolders, E., Golanski, L., Vanoirbeek, J., Hoet, P.H.M., 2014. Toxicity of nanoparticles embedded in paints compared with pristine nanoparticles in mice. Toxicol. Sci. 141 (1), 132–140. https://doi.org/10.1093/toxsci/kfu112.

Soroldoni, S., Castro, Í.B., Abreu, F., Duarte, F.A., Choueri, R.B., Möller, O.O., Fillmann, G., Pinho, G.L.L., 2018. Antifouling paint particles: sources, occurrence, composition and dynamics. Water Res. 137, 47–56. https://doi.org/10.1016/j.watres.2018.02.064.

STG, 2021. Ship Technology Global.

Tsai, S.J., Ada, E., Isaacs, A., J. M., &. J.Ellenbecker, 2008. Airborne nanoparticle exposures associated with the manual handling of nanoalumina and nanosilver in fume hoods. J. Nanopart. Res. 11 (1), 147–161. https://doi.org/10.1007/s11051-008-9459-z.

Viana, M., Amato, F., Alastuey, A., Querol, X., Moreno, T., Dos Santos, S.G., Herce, M.D., Fernández-Patier, R., 2009. Chemical tracers of particulate emissions from commercial shipping. Environ. Sci. Technol. 43 (19). https://doi.org/10.1021/es901558t.

Viana, M., Fonseca, A.S., Querol, X., López-Lilao, A., Carpio, P., Salmatonidis, A., Monfort, E., 2017. Workplace exposure and release of ultrafine particles during atmospheric plasma spraying in the ceramic industry. Sci. Total Environ. 599–600, 2065–2073. https://doi.org/10.1016/j.scitotenv.2017.05.132.

Viana, M., Hammingh, P., Colette, A., Querol, X., Degraeuwe, B., Vlieger, I.D., van Aardenne, J., 2014. Impact of maritime transport emissions on coastal air quality in Europe. Atmos. Environ. 90. https://doi.org/10.1016/j.atmosenv.2014.03.046.

Viana, M., Rizza, V., Tobías, A., Carr, E., Corbett, J., Sofiev, M., Karanasiou, A., Buonanno, G., Fann, N., 2020. Estimated health impacts from maritime transport in the Mediterranean region and benefits from the use of cleaner fuels. Environ. Int. 138, 105670.

Viitanen, A.K., Uuksulainen, S., Koivisto, A.J., Hämeri, K., Kauppinen, T., 2017. Workplace measurements of ultrafine particles-a literature review. Ann. Work Expo. Health 61 (7), 749–758. https://doi.org/10.1093/annweh/wxx049.

Wang, Z., Han, E., Liu, F., Shi, H., Qiu, Z., Hao, Q., 2014. Application research of marine composite nano-coatings in corrosion protection of ship. Mater. China 33, 14–19. https://doi.org/10.7502/j.issn.1674-3962.2014.01.03.

Weitkamp, E.A., Lipsky, E.M., Pancras, P.J., Ondov, J.M., Polidori, A., Turpin, B.J., Robinson, A.L., 2005. Fine particle emission profile for a large coke production facility based on highly time-resolved fence line measurements. Atmos. Environ. 39 (36), 6719–6733. https://doi.org/10.1016/j.atmosenv.2005.06.028.

Westerlund, J., Hallquist, M., Hallquist, Å.M., 2015. Characterization of fleet emissions from ships through multi-individual determination of size-resolved particle emissions in a coastal area. Atmos. Environ. 112, 159–166. https://doi.org/10.1016/j.atmosenv.2015.04.018.

Wu, G., Yang, Y., Lei, Y., Fu, D., Li, Y., Zhan, Y., Zhen, J., Teng, M., 2020. Hydrophilic nano-SiO2/PVA-based coating with durable antifogging properties. J. Coat. Technol. Res. 17 (5), 1145–1155. https://doi.org/10.1007/s11998-020-00338-z.

Yigit, M., Celikkol, B., Yilmaz, S., Bulut, M., Ozalp, B., Dwyer, R.L., Maita, M., Kizilkaya, B., Yigit, Ü., Ergün, S., Gürses, K., Buyukates, Y., 2018. Bioaccumulation of trace metals in Mediterranean mussels (Mytilus galloprovincialis) from a fish farm with copper-alloy mesh pens and potential risk assessment. Hum. Ecol. Risk Assess. Int. J. 24 (2), 465–481. https://doi.org/10.1080/10807039.2017.1387476.

Zhang, X., Wang, M., Guo, S., Zhang, Z., Li, H., 2017. Effects of weathering and rainfall conditions on the release of SiO2, Ag, and TiO2 engineered nanoparticles from paints. J. Nanopart. Res. 19 (10), 5–10. https://doi.org/10.1007/s11051-017-4022-4.

Zhao, P., Zhang, Y., 2019. The overview of methods of nanoparticle exposure assessment. Methods Mol. Biol.ogy 1894, 353–367. https://doi.org/10.1007/978-1-4939-8916-4_22.

Zheng, Y., Zhou, J., Fu, S.Z., Fan, J., Wu, J.B., 2016. In vitro and in vivo studies on the inhibitory effects of myocardial cell culture medium on growth of a human lung adenocarcinoma cell line, A549. Curr. Oncol. 23 (1), e35–e40. https://doi.org/10.3747/co.23.2844.

Zheng, Yunhao, Yao, M., 2017. Liquid impinger BioSampler's performance for size-resolved viable bioaerosol particles. J. Aerosol Sci. 106, 34–42. https://doi.org/10.1016/j.jaerosci.2017.01.003.