



Exposure to Metal Powders in Additive Manufacturing

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There is established evidence from various manufacturing industries that occupational exposure to metals can cause skin and lung diseases. Additive manufacturing (AM) is the general term for a range of techniques used to precisely construct three-dimensional objects layer by layer. Some AM techniques create 3D objects from metal powders. As a relatively recent technology in 2015, there was little published evidence about whether AM workers were at risk of exposure to metals.

Three AM sites were visited in 2015 by HSE scientists. Two of which were examples of early commercial operations and one was a research centre. The various exposure controls in place were noted and a range of techniques were used to examine the potential for metal powder exposure throughout the AM production life cycle. Individual reports summarising the findings were presented to each site for them to learn about the stages of the AM lifecycles where their potential risk for exposure was greatest.

The research suggested that average concentrations of airborne inhalable particles were low but spikes in emissions were measured during some activities e.g. manual cleaning, powder testing and transferring the powder. The highest surface concentrations of metals occurred in areas where powder transfer tasks were carried out. Workers had low levels of metals in their urine at concentrations consistent with levels found in the general population.

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Exposure to Metal Powders in Additive Manufacturing

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Key Messages

Additive manufacturing (AM) is the general term for a range of techniques used to precisely construct three-dimensional (3D) objects layer by layer. Some AM techniques create 3D objects from metal powders. There is peer-reviewed evidence that occupational exposure to some metal dusts and fumes can cause skin and lung disease. When this work was undertaken, there was little published evidence about occupational exposure to metal powders in AM facilities.

Research by HSE scientists, undertaken in 2015, measured occupational exposure to metal powders at three AM sites. Two of which were examples of early commercial operations, and one was a research centre. Whilst it is likely that AM technology will have moved on since 2015, the findings of this research surrounding the importance of effective engineering controls and the need to focus on areas where increased powder emission occurs are still relevant. Individual reports summarising the findings were presented to each volunteer site for them to learn about the stages of the AM lifecycles where their potential risk for exposure was greatest. This report summarises the results from these three site visit studies.

Containment was a key engineering control measure used at each site during key AM stages like printing. Average concentrations of airborne inhalable particles over the AM life cycle were low. The highest surface concentrations of metals occurred in areas where powder transfer tasks were carried out. Real-time aerosol monitoring showed spikes in emissions during some manual tasks where personal protective equipment was the primary control measure. The relevance of these spikes to the risk of adverse health outcomes is unclear without data on accumulative exposure and longitudinal studies following the onset of occupational disease. Workers had low levels of metals in their urine at concentrations consistent with levels found in the general population.

The findings suggest that under the conditions observed at these three sites, it was possible to undertake AM without risk of significant exposure to harmful metals. Consideration should be given to how these findings would apply if operations changed e.g. scaling up operations, decreasing powder sizes or deploying operators to repeat one task each day.

Executive Summary

Background

Additive manufacturing (AM) is the general term for a range of techniques used to precisely construct three-dimensional (3D) objects layer by layer. Some AM techniques create 3D objects from metal powders. There is established evidence from various manufacturing industries that occupational exposure to metals can cause skin and lung diseases. As a relatively recent technology in 2015, there was little published evidence about whether AM workers were at risk of exposure to metals. Whilst it is likely that AM technology will have moved on since 2015, the findings of this research surrounding the importance of effective engineering controls and the need to focus on areas where increased powder emission occurs are still relevant.

Aim

The aim of the research was to examine occupational exposure to metal powders throughout the AM production lifecycle.

Methodology

Three AM sites were visited by HSE scientists. Two of which were examples of early commercial operations, and one was a research centre. Individual reports summarising the findings were presented to each volunteer site for them to learn about the stages of the AM lifecycles where their potential risk for exposure was greatest. This report summarises the results from these three site visit studies.

The metal powders most commonly in use across all three sites visited were aluminium, titanium, copper, nickel, and nickel-chromium-based alloys. The stages of the AM production life cycle varied at each site, but the core activities examined were:

- Powder processing: sieving and mixing metal powders.

- Powder analysis: laboratory quality tests on metal powders.
- Printing processes: printing, cleaning, and maintenance of the 3D printers.
- Recycling: recovery and recycling of metal powders.
- Post processing: applying finishing techniques to printed parts.
- Moving and handling powder stocks between each stage of the AM process.

HSE scientists used personal and static air sampling methods and real-time aerosol monitors to determine airborne concentrations; the metal constituents of which were subsequently determined using Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) and ICP-Mass Spectroscopy (MS).

The surface deposition of metals was investigated using wipe sampling, ICP-AES and ICP-MS.

HSE scientists undertook biological monitoring (BM) to quantify concentrations of different metals in the urine of the workforce. Contextual information was collected about the tasks and procedures carried out at each site and the control strategies implemented including the use of Personal Protective Equipment (PPE).

Findings

- Average airborne concentrations were low but real-time aerosol monitoring demonstrated short duration spikes in concentration for some powder handling activities such as powder testing and transferring powders into transport containers. These tasks were less likely to include engineering controls and more likely to be manual tasks where PPE was the primary control measure. The relevance of these brief emission peaks to the risk of inhalation and adverse health outcomes is not

clear without data on accumulative personal exposure and longitudinal studies following the onset of occupational disease.

- Surface concentrations did not suggest an accumulation of powder on raised surfaces. The highest concentrations occurred in areas where powder transfer tasks were carried out.
- BM data demonstrated no difference between the urine metal levels in the workers handling metal powders with those found in the general population. Neither was there a significant difference between pre-shift and post-shift concentrations of metal in urine.
- Containment was key to minimising worker exposures to metal powders. The design of some of the ancillary powder handling equipment was found to require improvement to further reduce risks for operator exposure. There was an over reliance on respiratory protective equipment at the three sites. Other methods besides PPE can be prioritised to minimise exposure following the hierarchy of control.
- The findings suggest that under the conditions observed at these three sites, it was possible to undertake AM without risk of significant exposure to harmful metals.

Other Considerations

Further development of the technology may include printing with finer powders that could potentially increase the risk of lung exposure and present more challenges for containment. Much of the equipment in use was small-scale for prototyping and was unsuitable for manufacturing with large powder batches. The AM industry was rapidly growing, and consideration would need to be given to how the findings might apply when operations are scaled up.

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Introduction

Background

Additive manufacturing (AM) is the general term for a range of techniques used to precisely construct three-dimensional (3D) objects layer by layer. Some AM techniques create 3D objects from metal powders. Computer aided design software is used to design the object and subsequently instruct the printer to form precisely determined internal and external build topography. The development of equipment for additive printing has advanced significantly in the last decade, particularly for prototyping applications. More recent developments have led to advances in AM products and components which could see AM replace some traditional manufacturing processes.

The use of metal powders in AM holds promise for replacing traditional casting or machining to manufacture lightweight, strong, and complex metal components with less waste material. However, metal powder AM is at an intermediate stage of development. Whether additively manufactured components can be used in safety critical environments depends on demonstrating their reliability and durability to be at least equivalent to those made using casting or machining processes.

There is evidence that occupational exposure to metal particles, fumes, or soluble metals can cause skin disease (Anderson and Meade, 2014), non-malignant and malignant lung disease (Nemery 1990, Blanc P et al, 2019) cardiovascular disease (Fang SC, et al, 2010) and reproductive toxicity (Snijder CA et al, 2012). When this work was undertaken, there was little published evidence about occupational exposure to metal powders in additive manufacturing AM facilities. As a relatively recent technology in 2015, it was not clear whether AM workers were exposed to metal powders and at risk of occupational lung and skin disease.

The Manufacturing Technology Centre (MTC), Coventry, is a government and industry funded technology catapult centre undertaking applied research into advanced

manufacturing technologies. The MTC Core Research Programme (CRP) was set up to examine the safe use of metal powders in the production life cycle of AM. This provided the Health and Safety Executive (HSE), through their 'Advanced Materials and Manufacturing' Strategic Research Programme (SRP), an opportunity to work with the MTC and its members to understand the health and safety implications for AM with metal powders.

The SRP aimed to investigate whether workers using advanced materials and manufacturing techniques could be exposed to hazardous substances and what preventive control measures could be designed into new processes to minimise risks to health. One particular focus of this research became AM. HSE's Science Division (HSE SD), formerly known as 'HSL', joined the MTC as a tier 3 member to collaborate and contribute its expertise on health and safety. The focus of HSE SD's contribution was to organise and undertake three exposure monitoring site visits to centres using metal powders in AM. Individual reports summarising the findings were presented to each volunteer site for them to learn about the stages of the AM lifecycles where their potential risk for exposure was greatest. This report summarises the results from these three site visit studies.

The scope of this research was to investigate the potential for occupational exposure to metal powders used in Selective Laser Melting (SLM) and Electron Beam Melting (EBM) printers. These printers sinter and fuse beads of different metals with diameters typically within a size range from $\sim 15 \mu\text{m}$ to $>100 \mu\text{m}$.

The typical size range of these metal powders contains many particles greater than those defined as inhalable or respirable. Particles have a 50% penetration for the inhalable or respirable fractions with aerodynamic diameters of $100 \mu\text{m}$ and $4.0 \mu\text{m}$ respectively (British Standards Institution, 1993). Thus, pristine metal powder beads used for AM may be unlikely to enter the upper and or lower respiratory tract and may be more likely to rapidly settle out of the air, due to their size and respective weight. However, during AM printing, the intense heat from the laser or electron beam could generate smaller particles that might escape from the printers or be released during the sieving and recycling of used

powders. For these reasons, studies of metal powders in AM need to consider the potential for a wide range of metal particle emissions as well as other hazardous by-products formed during printing.

The metal powders in use across all three sites visited included aluminium, titanium, copper, nickel, and nickel-chromium-based alloys. Other key components of the alloys in use were manganese, silica, and cobalt. Replacing the use of certain hazardous metals in AM is not an easy route for control given the essential properties of these metals and their intended applications. Therefore other methods of control need to be considered in order of priority as outlined in COSHH (Control of Substances Hazardous to Health) (HSE, 2012). COSHH is the law that requires employers to control substances that are hazardous to health.

Aim

The aim of the research was to examine occupational exposure to metal powders in AM.

Objectives

- To undertake exposure-monitoring site visit surveys at three different organisations that use metal powders in AM.
- To quantify airborne concentrations, surface contamination, and personal exposure to metal powders used in AM.
- To collect supporting contextual data e.g. hygiene, safety equipment and processes, and control practices designed to minimise exposure to metal powders.

Additive manufacturing production lifecycle

The basic stages of the AM production life cycle are summarised in Figure 1. The points in the cycle where manual tasks were observed or engineering controls were in place were noted.

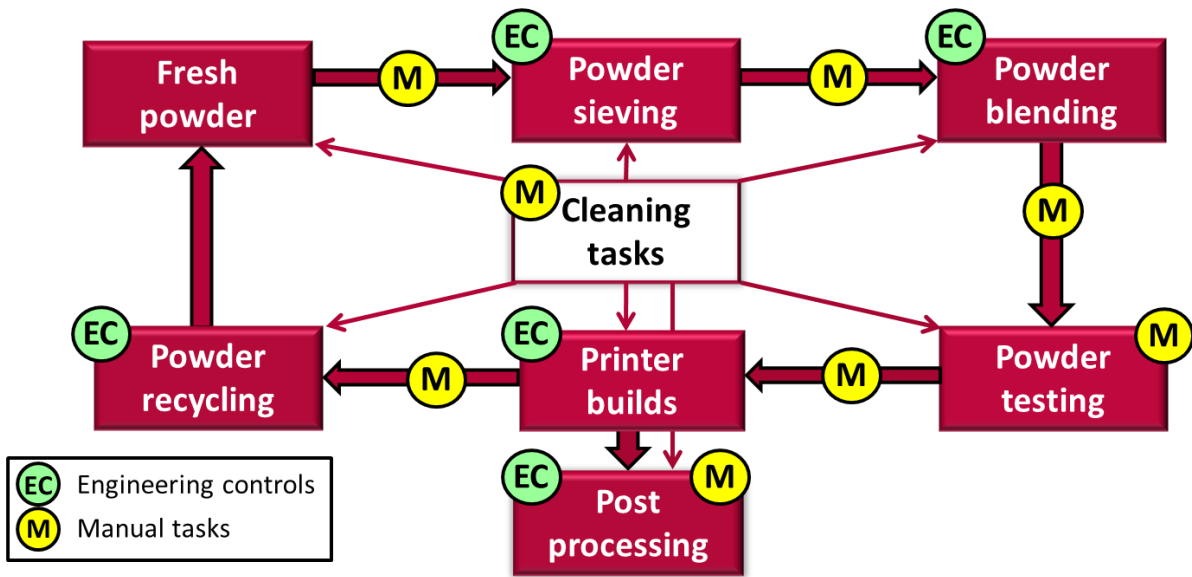


Figure 1 Additive manufacturing production life cycle with the points at which manual tasks were observed distinguished by yellow markers and areas where engineering controls were in place indicated by green markers.

In addition to the safe operation of AM equipment, the potential cross contamination of metal powders is a concern for those involved in manufacturing safety critical components. To minimise this risk, particularly in manufacturing environments, the printing and ancillary equipment used in AM may be dedicated for use with a specific metal powder material. The use of bulk metal powders and high intensity lasers and electron beams also increases the risk of combustion and fire in the build chamber prior to passivation of the powder stock. Consequently, compliance with the Dangerous Substances and Explosive Atmospheres Regulations (DSEAR) and ATEX rating (Appareils destinés à être utilisés en ATmosphères EXplosibles: Directive 99/92/EC and 94/9/EC) for equipment in those areas of manufacturing where there is a risk for fire and explosion is a critical aspect of how these facilities are safely managed.

Each SLM or EBM printer contains the metal powder under either a vacuum or an inert gas atmosphere, for safety and quality during the build operation, which requires tight containment. This reduces the likelihood of operator exposure to the metal powder and any emissions occurring during the build stage. Complete containment doesn't always apply to other AM techniques, such as desktop 3D printers. During operation, temperatures inside the build chambers of the printers are elevated to a temperature just

below the specific melt temperature for the metal or alloy, being used. Additional equipment required throughout the production life cycle of AM includes: sieving equipment to process both new and recycled metal powders; powder recycling systems which are typically based on a modified glove box design; equipment to move bulk samples of the metal powders; and cleaning equipment such as vacuum cleaners. Two of these sites had a powder testing laboratory and two had areas set aside for post processing of printed components involving some manual processes and the use of handheld finishing tools.

An approach to consider the potential for exposure across the entire AM production life cycle (Figure 1) was adopted to investigate risks from the introduction of fresh metal powder stocks, through to printing and recycling of used powders.

Methods

Sites visited

Three different sites volunteered to take part in the study and were subsequently visited by HSE Scientists. The sites were aware of the study through the MTC who were working closely with HSE on the project and simultaneously undertaking their own research on the topic. The three sites can be described as follows:

1. A manufacturing research centre in which AM equipment and methods are evaluated for safety and quality.
2. A large additive prototyping and manufacturing company.
3. A prototyping, manufacturing and testing company which also manufactured AM equipment.

Stages of the AM production lifecycle

The main stages of the AM production life cycle investigated for this research were:

- Powder processing: metal powder sieving and mixing of powder stocks.
- Powder analysis: conducting laboratory quality tests on metal powders.
- Printing processes: operating the 3D printers, cleaning, and maintenance of the printers.
- Recycling: recovery and recycling of metal powder.

- Post processing: finishing techniques applied to printed parts.
- Moving and handling powder stocks between each stage of the AM process.

Sampling and measurement techniques

Task-specific personal air sampling was conducted for workers at different stages of the AM production life cycle. The sampling duration varied by task. Inhalable dust was quantified by gravimetric analysis and the concentration of different metals in this dust was determined using Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP AES) and ICP Mass Spectroscopy (MS). Static air sampling was also undertaken at various locations near to AM operations. A broad screen to quantify many metals was conducted.

Direct reading 'real-time' aerosol monitors were used to detect relative changes in the mass concentration of particles in the respirable size fraction. A photometer (TSI SidePak AM510) was used to provide real-time aerosol mass concentration readings of respirable sized airborne particles (0.1 – 10 µm). Transmission Electron Microscopy (TEM) and Energy Dispersive X-ray Spectroscopy (EDX) were used to identify fine and ultrafine airborne metal particles. A condensation particle counter (CPC) (TSI CPC 3007) was also used to monitor ultrafine particulate emissions (0.01 to ~1.0 µm) from a vent port of one 3D printer and exhaust port of powder recycling equipment. This instrument did not differentiate between different types of particles or specific metals.

The surface deposition of a range of metals was investigated using wipe sampling (sample area 10 x 10 cm) and analysis of the metal content was quantified using ICP AES and ICP MS. Portable X-Ray Fluorescence (PXRF) allowed surface concentrations to be determined in real-time and readings before and after wipe sampling indicated how engrained or dislodge-able metal was.

A voluntary Biological Monitoring (BM) programme was employed to quantify concentrations of different metals in the urine of the workers using ICP-MS. The BM programme was independently reviewed and approved by the University of Sheffield

Medical School Research Ethics Committee. Participants provided signed informed consent and were free to withdraw from the study without explanation. Workers who took part in the BM programme provided pre-shift and post-shift urine samples over a working week including a weekend (Monday to Monday). Individual BM results were anonymised, and the samples were disposed of upon completion of the study.

To assess the risk of exposure to metal powders, an HSE occupational hygienist collected contextual information about the tasks and procedures carried out at each site through observations and conversations with various members of staff including operators, supervisors, and managers. The control strategies that each organisation had implemented prior to this study were also observed in the workplace and included the use of Personal Protective Equipment (PPE).

Data analysis and statistics

Air monitoring was undertaken to survey the range of concentrations found at different stages of the AM production lifecycle. Therefore, the time over which each sample was taken varied. The raw data are presented in this report with graphs generated using GraphPad Prism™ version 6.0 for Windows. The statistical analysis of the data was undertaken with the assistance of the HSE SD statistics team.

The wipe sampling data was analysed using the non-parametric Kruskal-Wallis test to compare results between the sites. Two non-parametric tests were used to assess the samples taken from the raised surfaces versus those from the floor. The Wilcoxon signed rank test and the Mann-Whitney U test were used for comparing two samples. For these tests any 'non-detect' values were replaced by half the limit of detection.

Parametric unpaired t-tests were used to compare pre- and post-shift urine samples across sites using a re-sampling method termed bootstrapping based on 1000 replicates. Bootstrapping is a statistical procedure based on resampling a single dataset to create simulated samples to estimate standard errors and confidence intervals. This method was

used because some of the results were below the level of reliable detection and therefore each was assigned the same value.

Results

Air sampling

Personal and static air sampling

Both personal (worker breathing zone) and static (approximate head height at a fixed position) air sampling results for concentrations of metals in the inhalable fraction are shown in Figures 2, 3 and 4. Emissions and exposure to aluminium, nickel and titanium were measured as those metals were used by all three sites and are also commonly used in other print studies. Some additional metals were also examined to assess the contribution from minor alloy components or contamination from previous work. In addition, calcium was measured as an indication of general background dust concentrations e.g. from building materials.

It should be noted that direct comparisons were not made between these three sites because the type and level of printing activity differed, along with the volume of metal powders used. Instead, the study focussed on the broad types of activities undertaken and identifying circumstances where the likelihood for exposure to metal powders was increased compared to other activities. In addition, this study considered whether certain actions taken to mitigate exposure were effective in reducing background levels of these metals.

Real-time aerosol concentration monitoring

The photometer provided relative real-time aerosol mass concentration readings of respirable sized particles in the air and was used to assess the dust emissions during various powder processing and handling tasks.

Powder processing

The metal powder processing stage included preparative tasks to filter out larger agglomerated particles in order to maintain the quality of new or reused powder. The average mass concentrations of particles measured at all three sites during powder

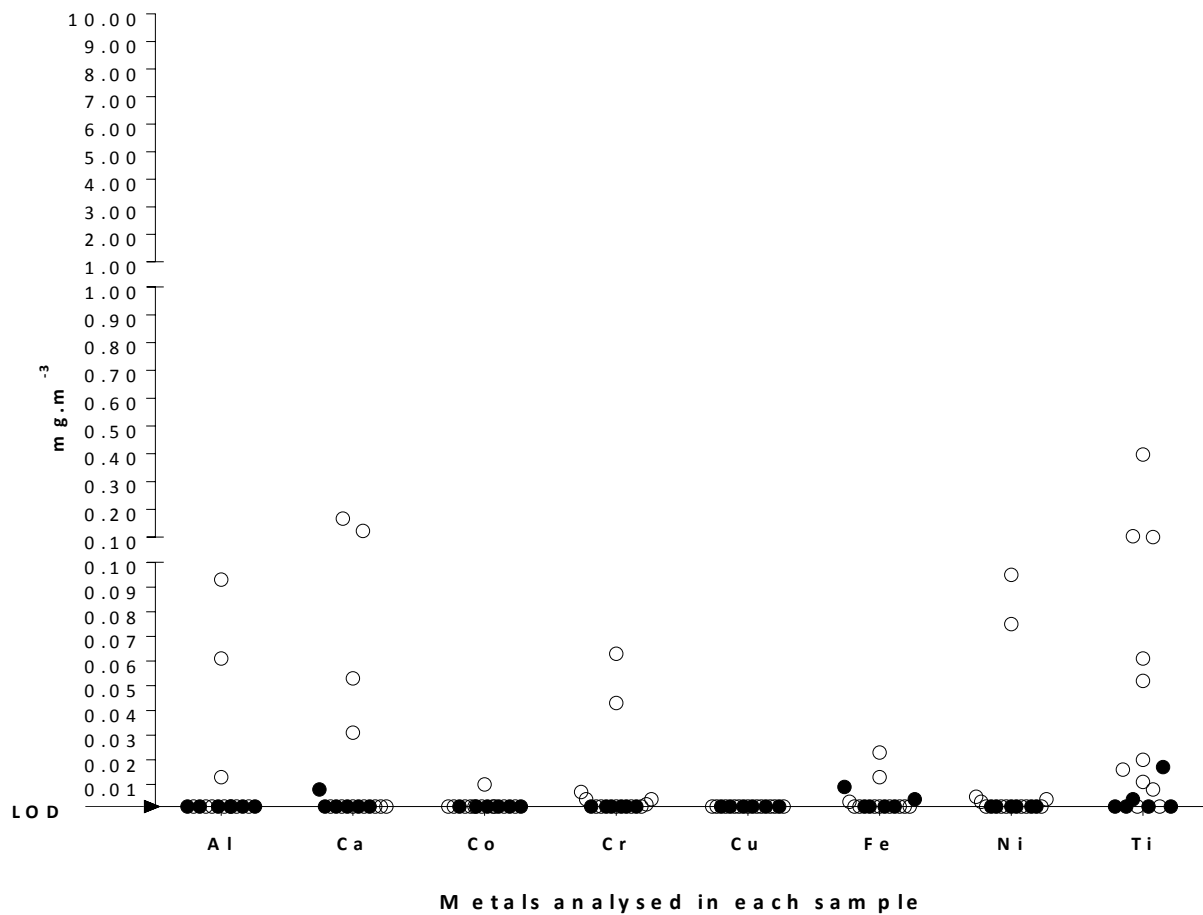


Figure 4 Site 3: Concentrations ($\text{mg}\cdot\text{m}^{-3}$) of different metals in 6 static air samples of inhalable dust (●) and 11 personal air samples of inhalable dust (○); each of these samples was analysed using ICP-AES. Aluminium (Al), calcium (Ca), cobalt (Co), chromium (Cr), copper (Cu), iron (Fe), nickel (Ni), and titanium (Ti). The position of the term LOD marks the lower limit of detection.

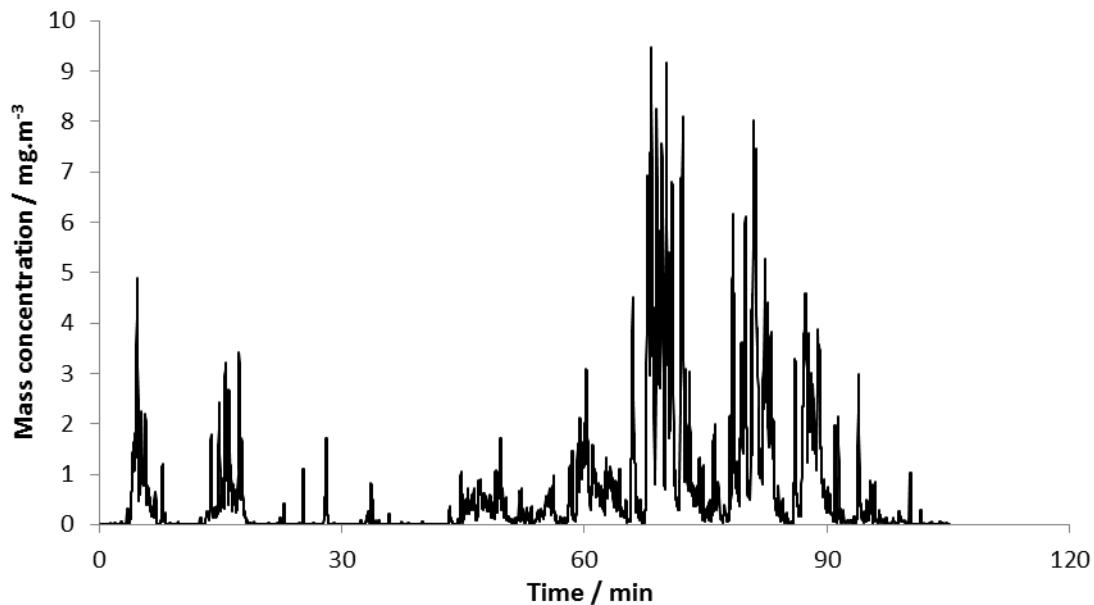


Figure 5 Ten second moving average of the mass concentration of particles between 0.1 - 10 μm , measured using a photometer while the worker undertook 'hand riffing' and sample blending of aluminium powder.

Printing

The mean particle mass concentration for static and personal monitoring throughout both SLM and EBM printing was less than 0.1 mg.m^{-3} .

Spikes in emissions were recorded when loading the printers at all sites but these were usually infrequent and lasted only seconds. Loading the printers manually by pouring from small containers filled with metal powder (Figure 6) produced more sustained raised concentrations compared with the same activity at another site where this task was completed using containers attached to the printer and emptied using a valve system (Figure 7). However, the mean concentration in both cases remained low. A titanium-based powder was used in both instances.

When manually filling a printer with nickel powder at the third site, the mean concentration also remained below 0.1 mg.m^{-3} however, spikes in the data were observed throughout the task (Figure 8).

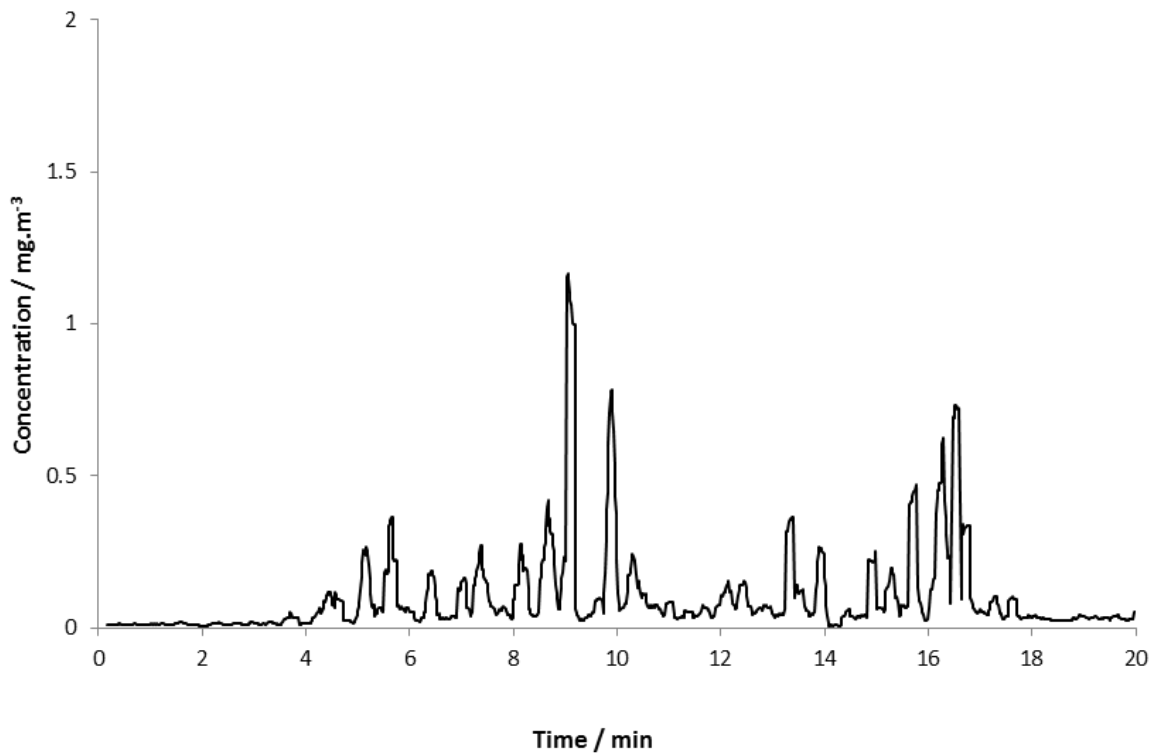


Figure 6 Ten-second moving average of the mass concentration of respirable particles measured using a photometer in the worker's breathing zone as they loaded a printer by manually pouring in a titanium-based powder from smaller containers.

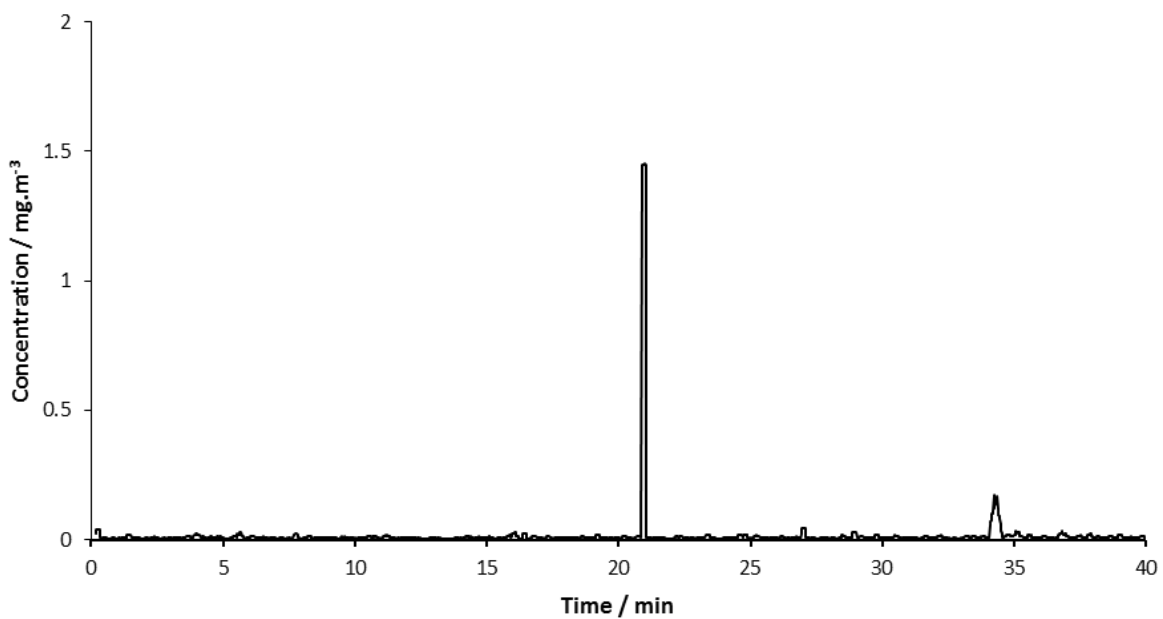


Figure 7 Ten-second moving average of the mass concentration of respirable particles measured using a photometer in the worker's breathing zone as they loaded a printer with titanium-based powder using containers attached by valves.

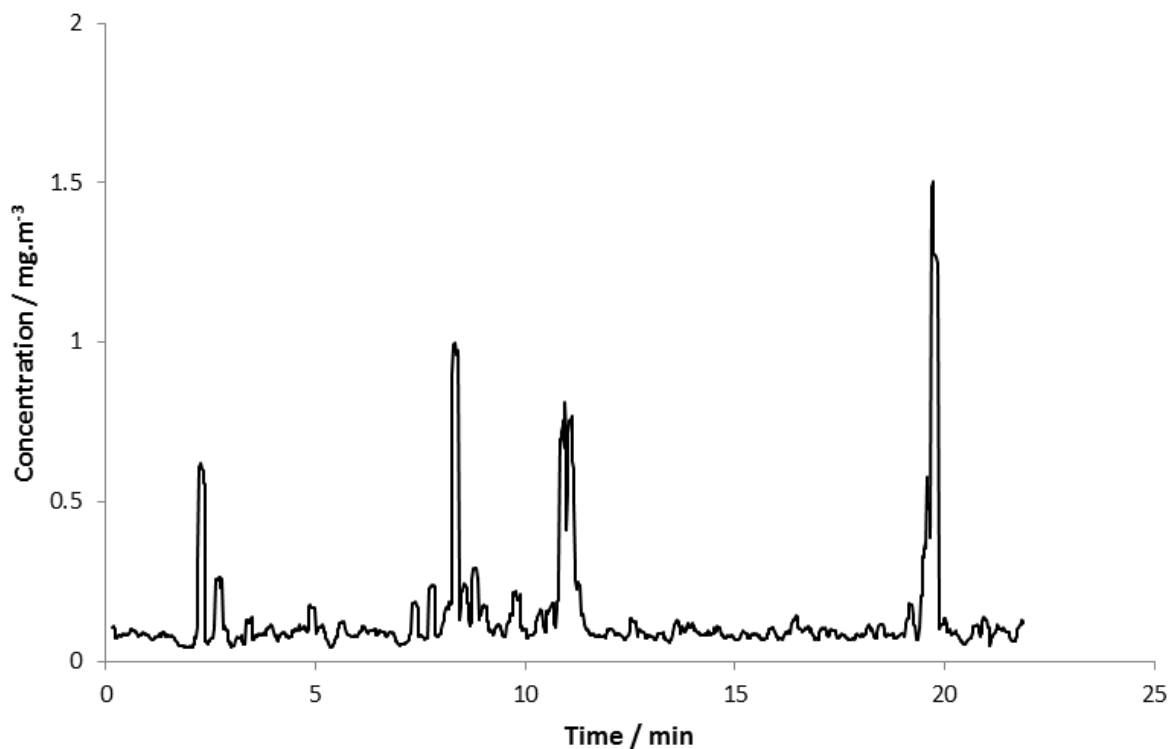


Figure 8 Ten-second moving average of the mass concentration of respirable particles measured using a photometer in the worker's breathing zone as they loaded a printer by manually pouring in nickel-based powder from smaller containers.

Powder recovery and recycling

Although mean concentrations remained low, frequent emissions spikes were measured using personal real-time direct-reading aerosol monitors during some powder recovery and recycling tasks e.g. the removal and manual sieving of copper powder using a scoop inside a printer (Figure 9). These peaks of particulate mass were typically of very short duration (less than a minute) and related to activities that briefly displaced the powder bed. Whilst the particulate mass sometimes peaked above 1.0 mg.m^{-3} , these events represented a small segment of the elapsed task time (from 20-100 minutes).

At one of the sites, the exhaust air from a dedicated powder-recycling machine was passed through filters before being vented back into the workspace. The exhaust air was monitored using the CPC and no significant increase in the particle number was found when compared to the background particle levels recorded when the equipment was not in use.

Post processing

The average mass concentration of respirable particles was less than 0.1 mg.m^{-3} measured by both the static and personal monitors when blasting a stainless steel part in a glove box. However, when using a range of hand tools to finish these printed parts, particle concentrations in the worker's breathing zone measured using the photometer logged high and frequent spikes in particle emissions in the data (Figure 10).

Maintenance and cleaning

The real-time respirable particle mass concentration was measured when used printer filters were cleaned and replaced, when engineering maintenance was carried out on a printer and when the print chamber was cleaned. The mean values for all cleaning and maintenance activities were below 0.1 mg.m^{-3} .

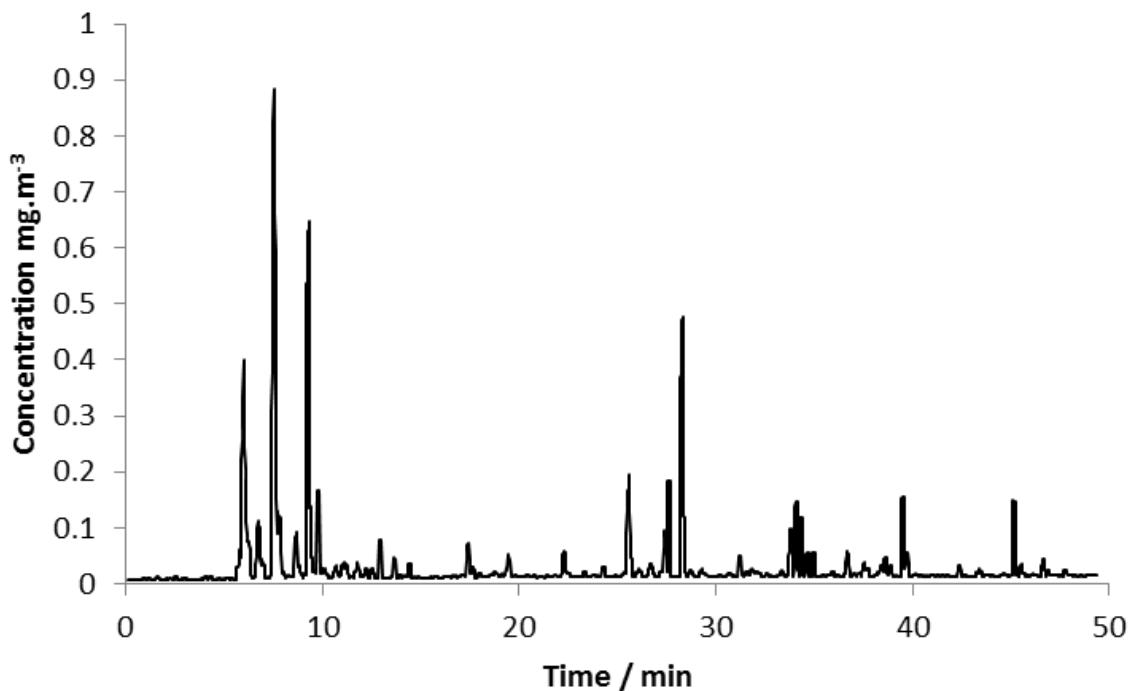


Figure 9 Ten-second moving average of the mass concentration of particles measured in the worker's breathing zone using a photometer whilst they removed copper powder from inside the printer using a scoop to that it could be recovered and sieved.

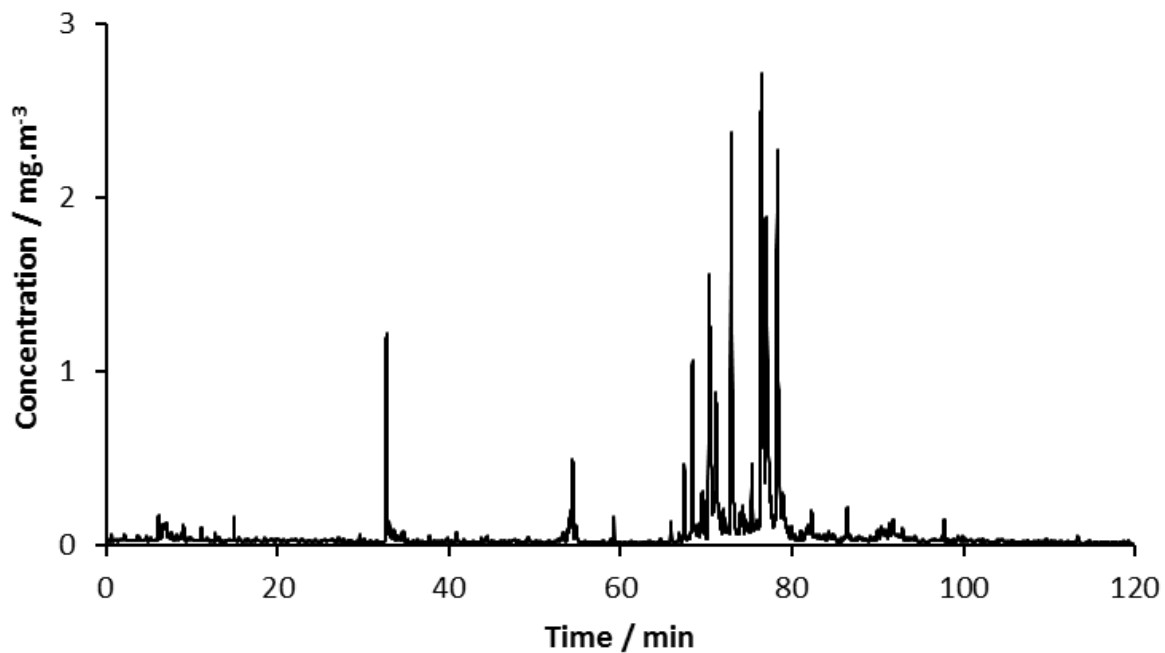


Figure 10 Ten-second moving average of the real-time mass concentration of respirable particles measured in the worker's breathing zone using a photometer while they hand finished stainless steel printed parts.

Surface sampling

General

Wipe sampling results for surface metal contamination at the three sites are shown in Figures 11, 12 and 13. Specific results for aluminium, titanium and nickel are presented as the three most common metals used across the sites. There are no 'reference' standards against which surface concentrations of metals can be judged to determine good control practice. The measurements obtained are indicative of differences in surface contamination between samples taken from the floors and on raised surfaces. However, there are insufficient number replicates of each type of sample number to draw firm conclusions based on statistical analysis.

Aluminium

At two of the centres, the highest levels of aluminium powder measured on the floor were $\sim 17.0 \mu\text{g.cm}^{-2}$ in an SLM recycling area and on a table at the centre of an AM workshop. At one site similar levels were also found on a 'sticky mat' located at the entrance to the

room. This mat was used to reduce the spread of powder through the facility from the powder-testing laboratory.

Concentrations of aluminium as high as $65.0 \mu\text{g}\cdot\text{cm}^{-2}$ were measured on the surface of a wooden trolley used to move equipment and parts around the facility.

At one of the sites near to an EBM machine, the highest floor surface concentration of aluminium was $0.92 \mu\text{g}\cdot\text{cm}^{-2}$ with concentrations at other wipe positions ranging from 0.07 to $15.0 \mu\text{g}\cdot\text{cm}^{-2}$.

The mean concentrations of aluminium measured at the 'floor' level at sites 1, 2 and 3 were 4.82 , 7.81 and $1.12 \mu\text{g}\cdot\text{cm}^{-2}$ respectively, compared with concentrations of 0.71 , 9.26 and $11.5 \mu\text{g}\cdot\text{cm}^{-2}$ on raised surfaces.

Titanium

Surface contamination of titanium was found in most of the samples collected with the higher concentrations of $\sim 2.0 \mu\text{g}\cdot\text{cm}^{-2}$ measured on the floor of a powder testing laboratory, foot mats in front of SLM printers, and on a trolley surface. At another site the highest surface concentration was $\sim 5.0 \mu\text{g}\cdot\text{cm}^{-2}$ on the floor in front of a workbench in a post-processing workshop.

The mean concentrations of titanium measured at the 'floor' level at sites 1, 2 and 3 were 0.56 , 1.17 and $0.05 \mu\text{g}\cdot\text{cm}^{-2}$ respectively, compared with concentrations of 0.09 , 1.15 and $0.46 \mu\text{g}\cdot\text{cm}^{-2}$ on raised surfaces.

Nickel

Contamination was detected on most of the samples across all three sites; the highest concentrations up to $170 \mu\text{g}\cdot\text{cm}^{-2}$ being found on the floor of a powder testing laboratory, the 'visual inspection bench' in an AM workshop, and the floor in front of a workbench in the post processing workshop. Other areas with high contamination were found on the floor of an SLM printer room, a sieving room, a mat in front a printer and the surface of a

trolley used for moving filters and powder stocks. In other areas, the levels of surface nickel were beneath $\sim 15.0 \mu\text{g}\cdot\text{cm}^{-2}$.

The mean concentrations of nickel measured at the 'floor' level at sites 1, 2 and 3 were 24.0, 51.0, and $0.78 \mu\text{g}\cdot\text{cm}^{-2}$ respectively, compared with concentrations of 3.18, 58.6 and $18.8 \mu\text{g}\cdot\text{cm}^{-2}$ on raised surfaces.

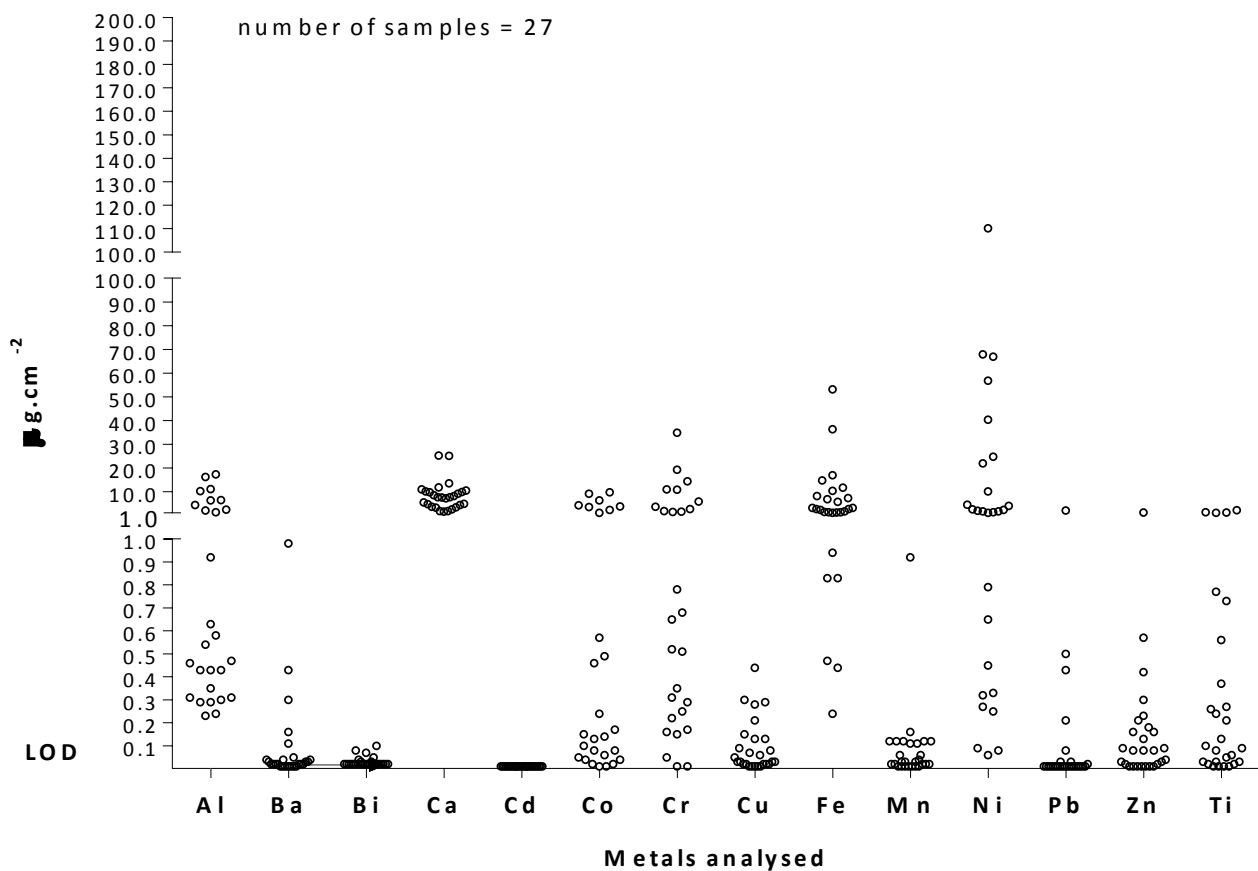


Figure 11 Concentrations ($\mu\text{g}\cdot\text{cm}^{-2}$) of aluminium (Al), barium (Ba), calcium (Ca), cadmium (Cd), Cobalt (Co), chromium (Cr), copper (Cu), iron (Fe), manganese (Mn), nickel (Ni), lead (Pb), zinc (Zn) and titanium (Ti) in wipe samples taken from the floor and raised surfaces at site 1.

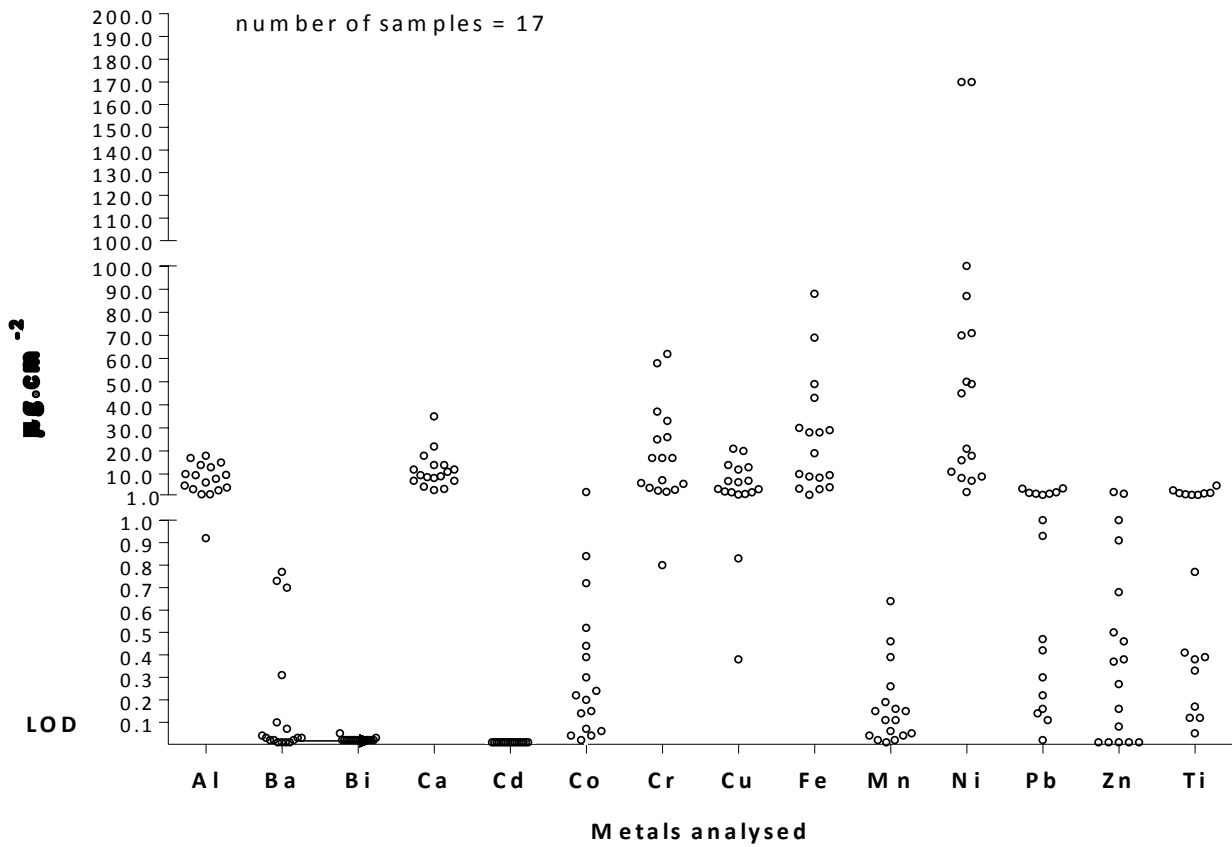


Figure 12 Concentrations ($\mu\text{g}\cdot\text{cm}^{-2}$) of aluminium (Al), barium (Ba), calcium (Ca), cadmium (Cd), cobalt (Co), chromium (Cr), copper (Cu), iron (Fe), manganese (Mn), nickel (Ni), lead (Pb), zinc (Zn) and titanium (Ti) in wipe samples taken from the floor and raised surfaces at site 2.

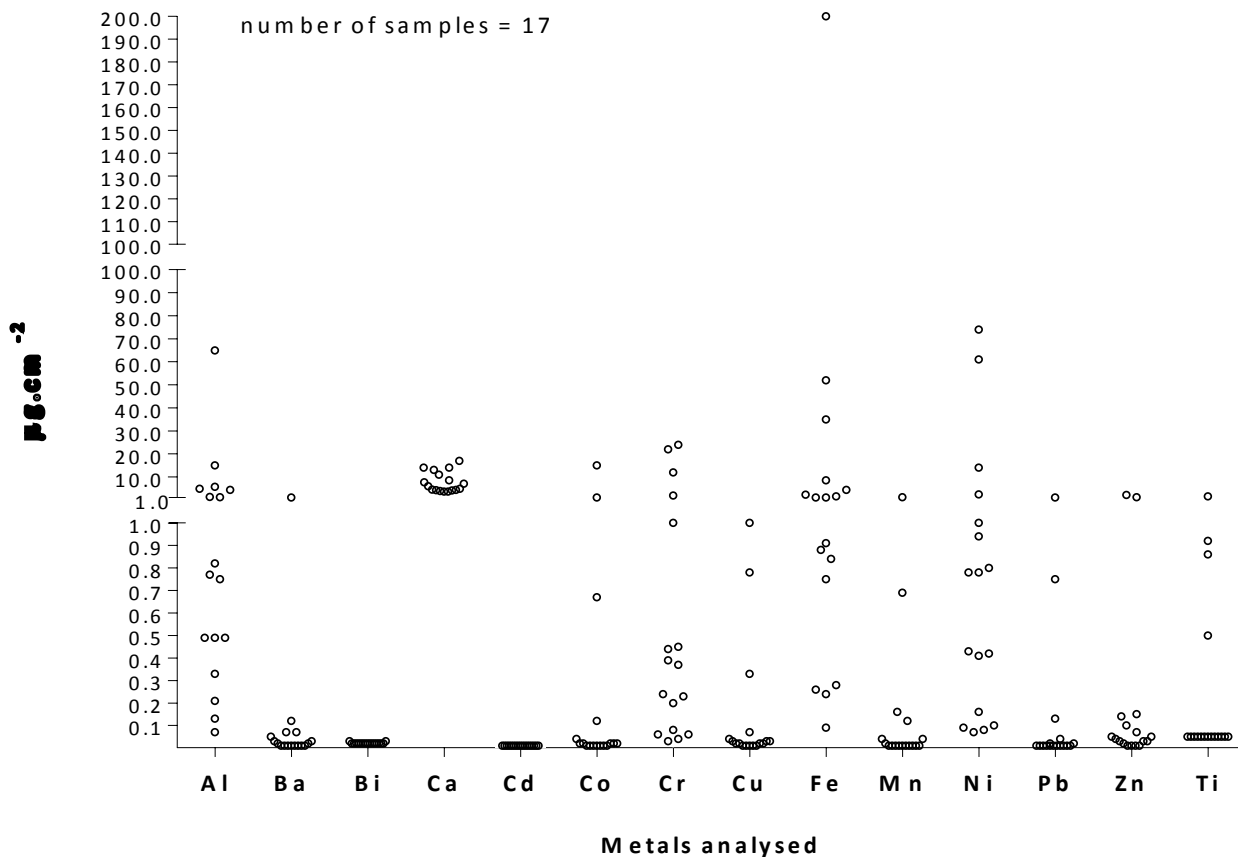


Figure 13 Concentrations ($\mu\text{g}\cdot\text{cm}^{-2}$) of aluminium (Al), barium (Ba), calcium (Ca), cadmium (Cd), cobalt (Co), chromium (Cr), copper (Cu), iron (Fe), manganese (Mn), nickel (Ni), lead (Pb), zinc (Zn) and titanium (Ti) in wipe samples taken from the floor and raised surfaces at site 3.

Other metals

The ICP-MS analysis provided measurements on a wide range of metals including those which may not have been in use at the time of sampling (Figures 11, 12 and 13) or which represented other minor alloy components. These results demonstrated the value of a monitoring strategy and showed the potential for contamination of new builds as well as the potential exposure risks.

PXRF analysis

PXRF analysis was undertaken at two of the three sites and provided an indicative measure of whether surface metal contamination was removed after the wipe sampling of a specific area. The results are not directly comparable to those obtained by wipe sampling. Generally the surface levels of metals were too low for reliable detection by

PXRF. However, the results showed that the surface concentrations of nickel were reduced 2-3 fold after the wiping, demonstrating the value of regular surface cleaning and the need to consider the potential for surface exposure to metals.

Exposure controls

Replacing hazardous materials at source

Replacing the use of certain hazardous metals in AM is not an easy route for control given the essential properties of these metals and their intended applications. Therefore, it is anticipated that the focus of a control strategy might include containment, minimising emissions, and effective Local Exhaust Ventilation (LEV) as the primary measures to reduce the risk of operator exposure. As the technology develops the use of alternative and safer source materials may be possible if they can provide the required properties.

Engineering controls

An important part of the control strategy for minimising exposure to metal powders was the use of containment. Due to the technical requirements of the AM technology and corresponding hazards such as lasers; the printing equipment was fully enclosed and during operation was unlikely to result in workers becoming exposed. However, there were inconsistencies in the advice provided by different manufacturers of printers about the necessity to extract emissions from the vent outlet ports of the printers with some being exhausted into the workplace and others being extracted from the building. One type of printer examined in this study produced measurable fine particle emissions but only during the pre-build purge stage. To minimise oxidation of some metal powders the build chambers are filled with an 'inert' gas such as Argon and in some applications, this may be added at pressure to ensure that air leaks into the chamber are prevented. The addition of these inert gases could also reduce the risk for powder bed combustion.

The Powder Recovery Systems (PRS) were used to recycle used powder and were usually found in separate areas to where the printers were located. These machines were based on a glove box design which, during use, minimised operator exposure. However, the operators were potentially at greater risk of exposure during the transfer of loose

powder when the build was moved into the PRS; from failures to the integrity of PRS door seals when the machine was in use; during cleaning out of the PRS and emptying and recovering waste powder. Some powder handling machines and powder sieves were fitted with poorly designed connections that were used to remove waste or recycled powder from the machines, and these fittings often resulted in powder spills during operator handling. Cleaning the inside of one type of PRS was observed and this task was made complicated by the interior design with limited access for the operator to easily remove powder residues.

Overall the operators at these three sites had good controls in place for the use of the PRS machines and at one site an additional precautionary control step had been taken where other workers were not allowed to enter the room whilst an operator was working at the PRS machine. Further improvement to the design of the powder handling systems and sieves will help to control and minimise these risks for exposure. The exposure monitoring and BM results from this study support the conclusion that at these three sites operators were not exposed to unsafe levels of harmful metals.

Operators are required, during certain points in the build lifecycle, to reach inside the build chamber of the printer, e.g. for loading, unloading, and cleaning. At one of these sites an additional door containing a glove port had been added to further separate the operator and the contents within the chamber. During the observation of this task it was noted that this control was not used.

Not all AM production tasks can be contained, for example, the movement of metal powder stocks between machines. At all three sites, brief emissions of respirable particles were recorded when powder was decanted, and spillages were found on floors below where bulk powder and print builds had been handled during operations.

Administrative controls

Two of the three sites had implemented procedures which separated individuals from potential emission sources. For example, one site had located sieving equipment in separate sealed rooms with the switches for operating the equipment installed on the

outside. This ensured that workers stood outside of the room during sieving operations. The other sites used exclusion zones around powder recovery equipment and where powder was being handled. Activities were also limited to trained operators.

Personal protective equipment

At all three sites, the type of PPE used was by necessity informed by the risks of powder combustion and powder inhalation. The PPE provided to workers at each site included protective coats and flame-retardant overalls, single-use nitrile gloves, and anti-static safety shoes. Each site also provided staff with loose fitting powered Respiratory Protective Equipment (RPE) fitted with high efficiency P3 filters. At two of the three sites, face fitting of RPE was used for specific tasks where there was a residual risk for airborne exposure to metal powders, as informed by the risk assessment.

Cleaning

At all three sites, AM workers were required to clean the printers and other associated equipment. This cleaning is critical to maintain the integrity of new builds particularly when powder stocks and metal powders are changed. It is also important to minimise the risk for combustion events.

Any heavily contaminated work areas including spillages were also cleaned by the production staff. Most of the cleaning work undertaken at these sites involved the use of H-type ATEX rated vacuum cleaners fitted with high efficiency particulate air filters. At one site dry/wet vacuum cleaners were also employed.

At one site manual cleaning by brushing was undertaken for some areas. For another site, general cleaning of the facility was undertaken by a contractor, and they cleaned throughout the day to ensure that surfaces were kept clean.

Biological Monitoring

From two of the three sites, thirteen workers consented to provide pre-shift and post-shift urine samples from the start of one working week to the start of the next. The BM data demonstrated urinary levels of metal were not above general population levels. In total, urine levels of 21 different metals were examined. Of 1,428 separate analyses undertaken, only 17 urine samples contained concentrations of certain metals above the 95th percentile range for non-occupationally-exposed adults (Figures 14 and 15) i.e. concentrations attributable to exposure from diet and the general environment.

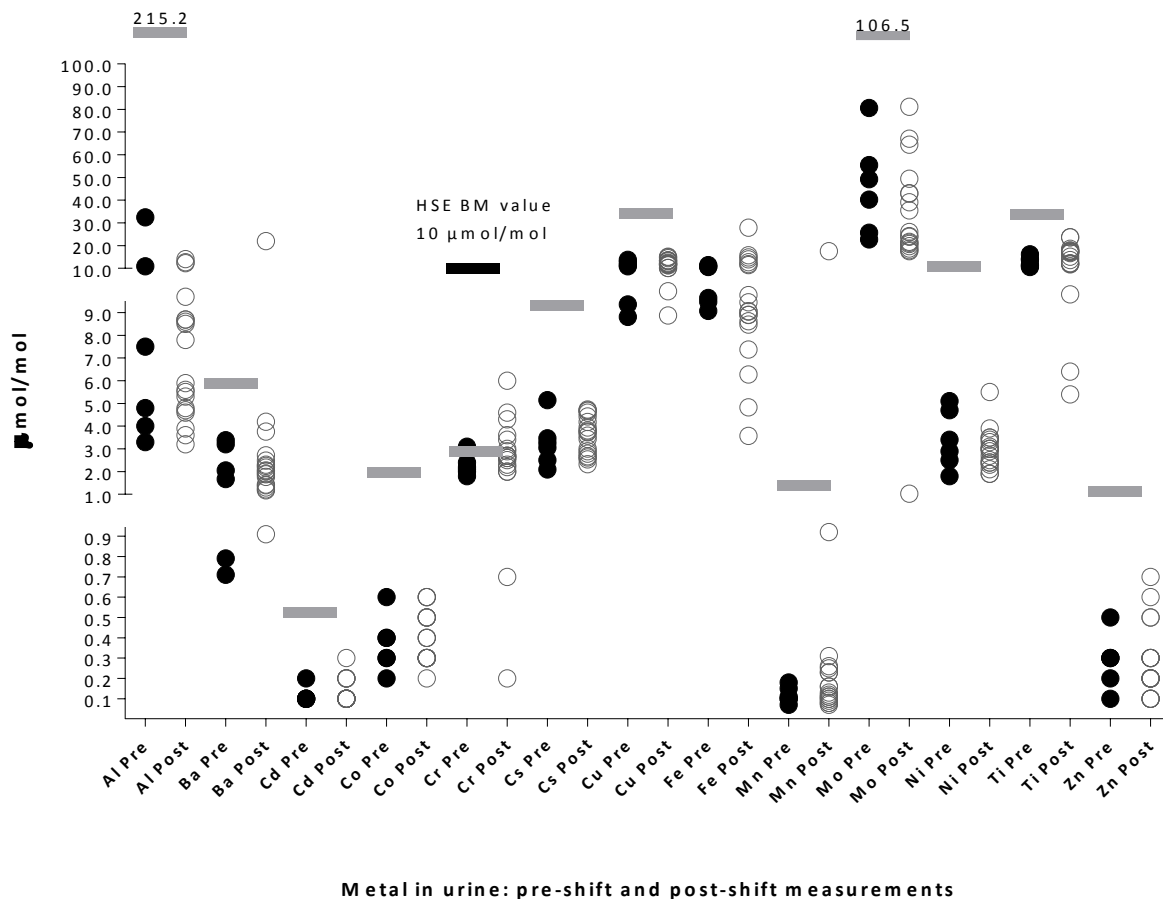


Figure 14 Concentrations of aluminium (Al), barium (Ba), cadmium (Cd), cobalt (Co), chromium (Cr), caesium (Cs), copper (Cu), iron (Fe), manganese (Mn), molybdenum (Mo), nickel (Ni), titanium (Ti) and zinc (Zn) in urine samples pre-shift and post-shift over a working week at site 1. The grey horizontal lines are the upper 95th percentile variation in non-occupationally-exposed controls (there is no 95th percentile value for iron). The horizontal black line is the HSE BM 10

$\mu\text{mol}\cdot\text{mol}^{-1}$ value for chromium. Two of the 95 percentile values for the non-occupational samples are greater than the maximal Y-axis value and are $215.2 \mu\text{mol}\cdot\text{mol}^{-1}$ for aluminium and $106.5 \mu\text{mol}\cdot\text{mol}^{-1}$ for molybdenum.

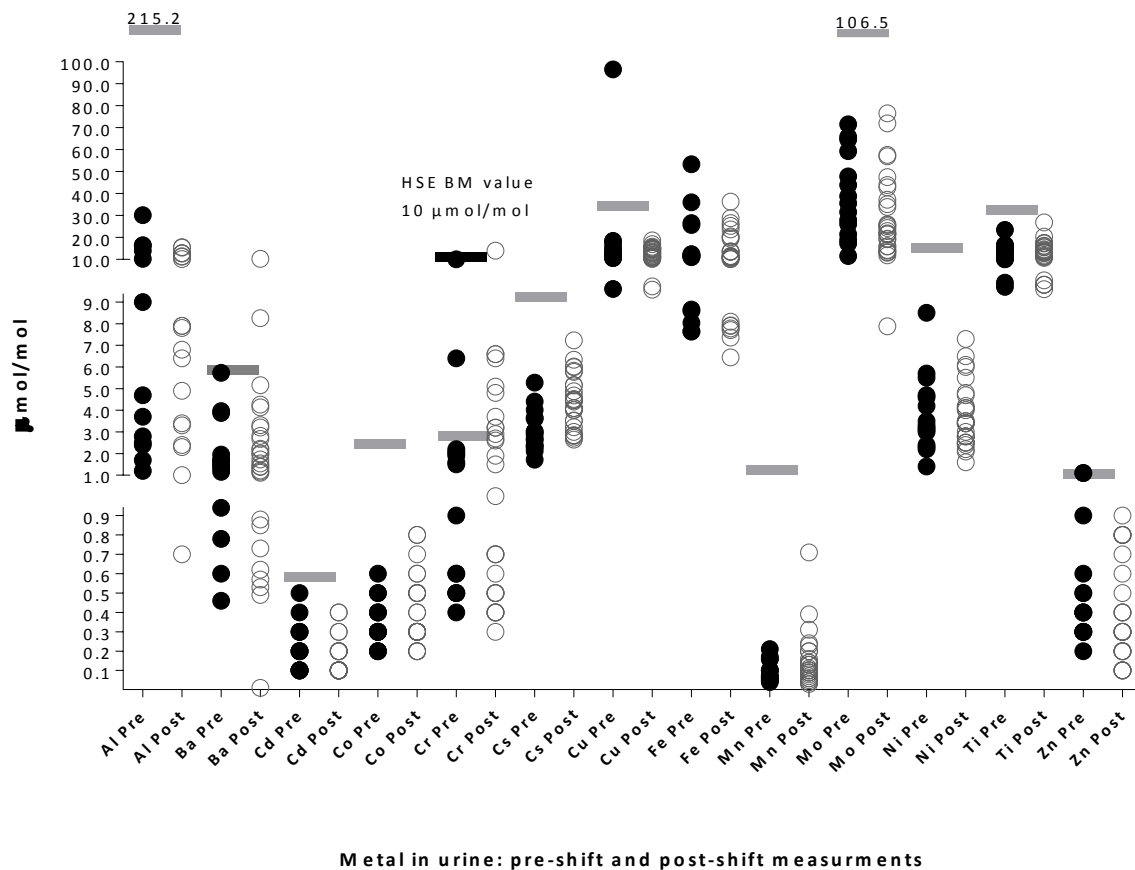


Figure 15 Concentrations of aluminium (Al), barium (Ba), cadmium (Cd), cobalt (Co), chromium (Cr), caesium (Cs), copper (Cu), iron (Fe), manganese (Mn), molybdenum (Mo), nickel (Ni), titanium (Ti) and zinc (Zn) in urine samples pre-shift and post-shift over a working week at site 3. The grey horizontal lines are the upper 95th percentile variation in non-occupationally-exposed controls (there is no 95th percentile value for iron). The horizontal black line marks the HSE BM value for chromium. Two of the 95 percentile values for the non-occupational samples are greater than the maximal Y-axis value and are $215.2 \mu\text{mol}\cdot\text{mol}^{-1}$ for aluminium and $106.5 \mu\text{mol}\cdot\text{mol}^{-1}$ for molybdenum.

Discussion

General

A life cycle approach to monitoring exposure to metal powder in AM was undertaken. This approach was taken to ensure that the risk of exposure to metal powders was considered for all stages and not only those aspects which have attracted most attention i.e. operating the 3D printers.

Based on the work carried out at these three AM sites, the findings suggest that operators can undertake this work without risk of significant exposure to harmful metals based on the size of the metal powders beads being used, and the exposure control and safety procedures being used by these three sites. However, the operators were potentially at greater risk of exposure during the transfer of loose powder such as when the build was moved into the PRS, from the transfer of powder stock to transport vessels, or from emptying and recovering waste powder.

The focus of improvement needs to be not only on the new aspects of AM printing equipment but include manual tasks such as movement of bulk powder, or cleaning tasks, for which emissions were more likely, and about which there is a good understanding about what is good and safe practice. Whilst it is likely that AM technology will have moved on since 2015, the findings of this research surrounding the importance of effective engineering controls and the need to focus on areas where increased powder emission occurs are still relevant.

Exposure to metal powders

When this work was undertaken, there was little published evidence about occupational exposure to metal powders in AM facilities. This study set out to identify where risks for operator exposure to metal powders occur across the AM lifecycle. The three sites visited were different in terms of the type and quantity of metals used; their focus on AM

(manufacturing, machine and process development, technology assurance) which also influenced the procedures they used to work safely with this new technology. Due to this, it was not possible to make a direct comparison between each site, and so this study has considered some of the general principles of operation that were used to prevent or minimise risk to the health of the operators.

The fresh powder beads in use were large enough in diameter (typically $>10\ \mu\text{m}$ diameter) to settle out of the air quite quickly when released from various processes. However, smaller particles could have been produced when the powder was heated under lasers, or electron beams, and may therefore have remained airborne for longer. This would increase the risk of inhalation of these particles including deposition in the lung for smaller particles $<4.0\ \mu\text{m}$ aerodynamic diameter.

In general the highest levels of airborne metals were associated with manual tasks that involved the transfer and movement of powders between equipment. For economic and environmental reasons, unfused powder is recycled where possible. Powder recycling machines and filters were used to ensure consistency of the metal beads either before they were used for the first time in the printers, or when they were recycled. Higher emissions were also observed when the powders were transferred between containers; when powder and 3D printed parts removed from the printers were dropped into powder recycling machines; during post processing activities; sampling of powders; and during sieving activities. Metal levels associated with operation of the printers were low in contrast. The measured concentrations of specific metals in the inhalable dust (Figures 2, 3 and 4) cannot be compared with workplace exposure limits as the samples were collected for short and varying task durations.

Real-time particle monitoring

Real-time aerosol monitoring allowed the capture of data to demonstrate how respirable particle concentrations varied during different activities. This technique did not distinguish between general dust and any metal particles in the aerosol. However, it enabled short spikes in emissions associated with particular tasks to be identified. The clearest example

of this was observed in a powder-testing laboratory where only small samples of powder were handled but this resulted in increased emission of small particles when the operator handled the powder or undertook energetic tests (Figure 5).

Surface deposition monitoring

Analysis of the surface wipe samples using the Wilcoxon rank-sum test demonstrated that metal powders accumulated mostly on the floor and not on bench or machine top raised surfaces (p value = 0.003), although this outcome was largely driven by one of the three sites visited. The floor contamination was patchy and occurred in places where metal powders were mixed or transferred between vessels. Contamination was also noted on a trolley surface used to move around powder stocks, filters, tools, and builds; powder was also found on rough absorbent surfaces such as wooden trolleys and benches that were less easy to clean.

In sites one and two, not all areas of the facilities were cleaned as regularly than at site 3, only those areas adjacent to the equipment to prevent a build-up of surface contamination. At two of the AM centres the concentrations of surface metal powders were higher (Figures 11 and 12) compared to the third site (Figure 13) where the floors and surfaces were cleaned throughout the day.

It is important to note that the results of the wipe sampling are indicative of the contamination in a particular area, and it cannot be assumed that the concentration of metal detected in the 10 x 10 cm sample area is uniform across a surface. Furthermore, a different number of samples were taken from a range of positions across each facility, and the sites undertook different processes. This study was undertaken as a pilot exercise. A more systematic sampling technique would increase the confidence in the surface concentration values and offer further opportunity for direct comparisons to be made.

Equipment and containment as a control

Equipment manufacturers are working towards containing more of the AM manufacturing process, for example, having a powder filter and recycling unit within the printer. To print

with some metal powders the build chamber is filled with inert gases, and it is critical that doors are well sealed so that emissions do not escape but can be cleared and exhausted after passing through particulate filters. These considerations also apply to the design and seals on doors and windows of PRS systems where there is a higher risk for combustion and direct exposure to the powder through contact or inhalation. The transfer of powder beds to a PRS or draining the treated powder from the PRS to a transport container is an area where risk of spillage can occur. However, some of the prototype and small-scale equipment observed in this study was not compatible with the requirements for high throughput large-scale AM with metal powders.

Manual tasks

More consideration is needed about how to perform tasks in the production life cycle stages where manual activities are undertaken in order to minimise personal exposure to metal powders. Dedicated areas and equipment were used for tasks such as sieving or printing but transferring powder from one container to another was carried out on the floor of the workshop with only RPE as the control strategy. Engineering controls such as downdraught benches and doors fitted with glove ports were installed at some sites, but some of this equipment was not properly commissioned and/or staff were not trained in their use.

Personal protective equipment

All three AM sites had adopted a precautionary approach by using RPE as an additional control measure to protect their workers. This decision has been based on the employers' concern that some of the metals in use may cause lung disease. Furthermore, when this work was undertaken, there was little published evidence about the level of airborne exposure to respirable metal powders particles across the AM lifecycle.

This study found that concentrations of inhalable metal particles were generally low but could be further reduced if the manual tasks were better controlled. For sensitising metals such as nickel, it is a legal requirement to reduce exposure to “a level as low as is reasonably practicable” (ALARP), which will help to reduce this over dependency on RPE.

The results of this study demonstrate that it is possible to minimise operator exposure to these metals based on containment and good working practices. For some of the tasks the use of RPE may be essential in which case it is crucial that managers are made aware of the importance that operators undergo 'face fit' (and face-fit testing) to obtain effective protection when using filtering face pieces. Maintenance and training records also need to be kept on RPE to provide evidence that operators have been using RPE safely.

Biological monitoring

For the thirteen workers that participated in BM there was no clear evidence of increased metal in urine. Statistical analysis found no statistical difference between pre-shift and post-shift samples for specific metals (p-value = 0.051); on average the pre-shift samples were slightly higher, but this was not a statistically significant finding. Generally, the urine metal concentrations in the workers handling metal powders were not different from the levels found in the general population.

In a small number of individuals at both sites, levels of chromium were raised slightly above the 95% upper range for those non-occupationally exposed, however these results were not consistent with shift-related occupational exposure where levels would be high post-shift compared with pre-shift. All but one of these raised urine chromium levels were beneath the HSE BM guidance value for hexavalent chromium of $10.0 \mu\text{mol}\cdot\text{mol}^{-1}$ (creatinine).

Skin contact leading to ingestion as a route of exposure should also be considered but the BM results obtained in this study do not indicate that these individuals were significantly exposed by other routes.

Conclusions

Main findings

- The lifecycle approach was an effective strategy to investigate occupational exposure to metal powders in AM.
- Based on the work carried out at these three AM sites, the findings suggest that operators can undertake this work without risk of significant exposure to harmful metals based on the size of the metal powders beads being used, and the exposure control and safety procedures being used by these three sites.
- Average airborne concentrations were low but real time aerosol monitoring demonstrated short duration spikes in emission for some powder handling activities. The relevance of these brief emission peaks to the risk of inhalation and adverse health outcomes is not clear without data on accumulative personal exposure and longitudinal studies following the onset of occupational disease.
- In relation to the exposure risk, the BM data demonstrated no difference between the urine metal levels in the workers handling metal powders with those found in the general population. Neither was there a significant difference between pre-shift and post-shift concentrations of metal in urine.
- Surface concentrations did not suggest an accumulation of powder on raised surfaces. The highest concentrations occurred beneath areas where powder transfer tasks were carried out.
- Containment was a key strategy implemented to minimise worker exposures to metal powders. Whilst the design of the printers and powder handling equipment is based on containment, this study suggested that further consideration may need to

be given to design of the equipment to facilitate cleaning and transfer of the powder stocks.

- As a precautionary method, RPE was worn for a range of tasks where exposure to metal powders may have occurred. The use of RPE should be informed by COSHH principles requiring evidence that exposure cannot be minimized by other control measures (e.g., containment and extraction) before RPE is used.
- This study did not consider all lifecycle stages of metal powder use in AM. Some knowledge gaps were identified e.g. managing metal powder waste, contamination of PPE with metal powder with the risk for transfer to personal clothing or elsewhere.

Other considerations

- If there is a trend towards printing with finer powders of a smaller diameter, this could increase the risk for inhalation exposure and require improved methods for containment of the powder.
- The AM industry is rapidly growing and consideration should be given to how current findings and concerns will apply when operations are scaled up. For example, operators may be more likely to be deployed to repeat one task each day rather than undertake a range of different AM tasks.

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There is established evidence from various manufacturing industries that occupational exposure to metals can cause skin and lung diseases. Additive manufacturing (AM) is the general term for a range of techniques used to precisely construct three-dimensional objects layer by layer. Some AM techniques create 3D objects from metal powders. As a relatively recent technology in 2015, there was little published evidence about whether AM workers were at risk of exposure to metals.

Three AM sites were visited in 2015 by HSE scientists. Two of which were examples of early commercial operations and one was a research centre. The various exposure controls in place were noted and a range of techniques were used to examine the potential for metal powder exposure throughout the AM production life cycle. Individual reports summarising the findings were presented to each site for them to learn about the stages of the AM lifecycles where their potential risk for exposure was greatest.

The research suggested that average concentrations of airborne inhalable particles were low but spikes in emissions were measured during some activities e.g. manual cleaning, powder testing and transferring the powder. The highest surface concentrations of metals occurred in areas where powder transfer tasks were carried out. Workers had low levels of metals in their urine at concentrations consistent with levels found in the general population.