HSE

Health and Safety Executive

A survey of occupational exposure to MbOCA in the polyurethane elastomer industry in Great Britain 2005-2006

Foreword

The Disease Reduction Programme (DRP) is part of the Health and Safety Executive's Fit3 programme to deliver a 6% reduction in the incidence rate of cases of work-related ill health by April 2008 and thereby deliver the Public Service Agreement target. The DRP includes the Skin disease, Cancer and Respiratory Disease Projects.

The Cancer Project has two main components – occupational cancer caused by exposure to asbestos and occupational cancer caused by exposure to other chemical carcinogens. The latter component aims at providing a better evidence base from which HSE and various stakeholders can develop recommendations for intervention activity and to identify priorities for intervention to reduce the future risk of occupational cancer.

This survey on exposure to 4,4'-methylene-bis (2-chloroaniline), ie MbOCA, a probable carcinogen in man, in the polyurethane elastomer manufacturing industry in Great Britain, was conducted in 2005 and 2006 as one workstrand of the Cancer Project to review the impact of past and current exposure control interventions. The implementation of HSE's recommendations contained in the report should contribute to a reduction of exposure to MbOCA in the industry and thereby reduce the risks of occupational cancer.

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Contents

Main findings

This study was carried out as part of the Health and Safety Executive's (HSE's) Disease Reduction Programme - Cancer Project to review the impact of past and current workplace interventions, in particular in the polyurethane elastomer industry, and thereby reduce the burden of occupational cancer.

Objectives

The main objective of the survey was to review the effectiveness of past exposure control interventions and the impact of 'live' interventions during the handling of 4,4'-methylene-bis (chloroaniline), ie MbOCA, in the polyurethane elastomer industry.

This was to be achieved by measuring personal inhalation exposure to and fixed place background concentrations of MbOCA, measuring MbOCA concentrations on surfaces, inner and outer gloves, carrying out biological monitoring, ie urinary MbOCA and isocyanates, assessing the measures to prevent and/or control exposure to MbOCA and, where appropriate, providing advice and recommendations to reduce exposure.

A statistical analysis was carried out to assess for consistency of results across comparable companies and comparable jobs and to investigate the relationships between MbOCA in air, surface and glove samples and the relationship between MbOCA and isocyanate metabolites in urine samples.

Twenty polyurethane elastomer manufacturers and two suppliers of the MbOCA were visited during the survey.

Main findings

1 Of 80 personal inhalation exposures to MbOCA, only two exceeded the Workplace Exposure Limit (WEL) of 0.005 mg/m^3 8-hour Time Weighted Average (TWA). The two workers were pouring mixed liquid polyurethane into moulds without the use of extraction.

2 The highest background concentration of MbOCA ie 0.01 mg/m^3 was measured inside an extraction booth and was related to the heating of the MbOCA.

3 A total of 334 surface samples were collected from the MbOCA users and suppliers. There was evidence of sloppy handling of MbOCA throughout the industry, ie poor housekeeping, and spread into areas, for example the canteen, where MbOCA was not directly handled.

4 There was evidence of MbOCA on imported kegs.

5 Contamination on the outergloves was higher than on the inner gloves. There was a relationship between urinary MbOCA and contamination of the outer gloves. This may indicate poor putting on and removal of the gloves.

6 A total of 78 urine samples were collected. The results indicated that exposure to MbOCA by all routes was more likely to occur during casting (pouring liquid polyurethane into moulds only) and during moulding (casting, removal and trimming of the moulds).

7 The 90th percentile figure from the urine results was 8.8 µmol/mol creatinine. The current Biological Monitoring Guidance Value (BMGV) for urinary MbOCA of 15 µmol/mol creatinine is based on the 90th percentile from previous studies.

8 There was evidence of urinary isocyanate (as diamine metabolites) concentrations above the BMGV of 1 µmol/mol creatinine indicating poor exposure control during handling.

9 The concentrations of MbOCA and isocyanate metabolites in urine appeared to be correlated. Urine samples from subjects without direct exposure to MbOCA or isocyanates contained evidence of both substances. This indicates poor exposure control.

10 About 75% of company risk assessments were insufficient and unsuitable. Generally, they contained little information on the MbOCA handling processes and the measures to prevent or control exposure.

11 In most cases the local exhaust ventilation (LEV) systems used to control exposure during MbOCA/resin handling were ineffective, inefficient and poorly maintained.

12 Most firms had not had their LEV systems thoroughly examined and tested at least once every 14 months as required by regulation 9 of the Control of Substances Hazardous to Health Regulations 2002 (as amended) (COSHH).

13 There was no standardisation of the types of inner and outer gloves worn, for example five types of inner glove (mainly cotton) and 12 types of outer gloves (mainly leather) were worn.

14 There was evidence of poor maintenance of the personal protective equipment (PPE) including the respiratory protective equipment (RPE) worn, eg inadequate storage.

15 Welfare facilities at some sites were poor, for example one company had no washing facilities in the MbOCA work area.

16 At several companies the health surveillance provided was inadequate.

17 Most of the companies visited provided little or no information, instruction and training on the hazards associated with the handling of MbOCA and isocyanates or on the measures to control exposure.

Recommendations

Recommendations include, for example, improve housekeeping to reduce surface contamination, wear appropriate PPE during all stages of MbOCA handling to mitigate skin exposure, change gloves frequently to prevent the build-up of glove contamination, ensure that all LEV systems are well maintained, provide appropriate health surveillance etc. More detail is given in the report.

Furthermore, the present BMGV for urinary MbOCA is 15 µmol/mol creatinine. It should be reviewed to reflect good practice in the polyurethane elastomer manufacturing industry today. The data from this study suggests that a conservative estimate of the 90th percentile of urine data would be about 10 µmol/ mol creatinine.

Revise HSE's guidance on the control of MbOCA in the workplace, eg *COSHH essentials*.

Apply 'live' interventions where appropriate to control the exposure of other suspect carcinogens.

Provide Trades Associations eg Polyurethane Elastomers Group and relevant stakeholders with information to update their own guidance material.

Conclusions

Past interventions to prevent or control exposure to MbOCA (and isocyanates) in the polyureththane elastomer industry were successful. However, this survey found that the exposure control measures then implemented by the industry were not sustained.

The implementation of 'live' interventions carried out during the survey to reduce exposure to MbOCA as part of the DRP- Cancer Project have been a success. This should cause a reduction in exposure to MbOCA by all routes and in the long-term reduce the burden of cancer in the industry in particular if the achievements made are sustained.

It will require a continuation of the excellent working relations with the relevant Trade Associations etc and their commitment to improving health and safety in the industry to ensure the likelihood of maintaining exposure control to MbOCA over the coming years.

The risk of exposure to MbOCA via skin absorption, inhalation and ingestion will be high if the control measures used are ineffective. The principles of good practice as outlined in COSHH Schedule 2A should be applied at all times to ensure that exposure to the suspect bladder carcinogen is reduced.

1 Introduction

1.1 The Fit3 strategic programme has been designed to deliver the Public Service Agreement (PSA) target on reducing work-related ill health, injury and days lost. To meet the PSA target which is the Health and Safety Executive's (HSE's) target with government by 2007/2008, HSE needs to deliver against a baseline of 2004/2005 a:

- 3% reduction in the incidence rate of work-related fatal and major injuries;
- 6% reduction in the incidence rate of cases of work-related ill health; and
- 9% reduction in the incidence rate of days lost due to work-related injuries and ill health.

1.2 To meet PSA targets the Fit3 strategic programme comprises a number of component programmes, ie Injury Reduction, Ill Health Reduction and Days Lost Reduction. The Ill Health Reduction Programme includes Stress, Musculoskeletal Disorders, Occupational Health Support, Disease Reduction, Noise and Hand Arm Vibration.

Disease Reduction Programme

1.3 The Disease Reduction Programme (DRP) is focussed on three main areas: cancer, respiratory disease and skin disease. It aims to reduce ill health that results from failures to properly control hazardous substances in the workplace in a diverse range of occupations and sectors. For example, there are 6000 deaths a year from occupational cancer, 3500 of which are related to asbestos exposure.

1.4 In each of the priority areas the DRP will deliver a variety of interventions including inspections, publicity campaigns, stakeholder engagement interventions and supply-chain initiatives. The aim of the interventions is to raise awareness that will lead to a change in behaviour in target industries, thereby reducing exposure to causative agents and ultimately reducing the incidence of ill health.

1.5 There are four workstrands to the Cancer Project:

- cancer epidemiology to develop and update estimates of the burden of occupational cancer in Great Britain (GB);
- chemical carcinogens profiling to determine the use of chemical carcinogens and provide a sound evidence base from which priorites and recommendations can be developed for future intervention activities;
- workplace intervention to determine the effectiveness of past and present HSE interventions (this strand of the Cancer Project includes the present investigation of exposure to MbOCA in Great Britain); and
- a high-level stakeholder workshop to share, discuss and debate the findings of the DRP activity on carcinogens.

Why MbOCA?

Evidence from site visits

1.6 In 2002, a routine HSE inspection at a company using MbOCA in the production of high-quality polyurethane elastomer products revealed evidence of poor exposure control to MbOCA. The inhalation exposure of one worker was

above the WEL of 0.005 mg/m^3 8-hour TWA. In another worker the urinary MbOCA level exceeded the BMGV; it was 16.85 µmol/mol creatinine. Evidence from surface sampling revealed widespread contamination.

1.7 The local exhaust ventilation (LEV) systems used to control exposure to MbOCA vapour during casting had not been thoroughly examined and tested (COSHH regulation 9 – Maintenance, examination and testing of control measures). An Improvement Notice (IN) was served to remedy this situation. Two other INs were issued, one to improve overall MbOCA exposure control and the other to provide adequate health surveillance.

1.8 A subsequent review of reports of past HSE site visits to MbOCA users provided evidence of poor exposure control with the increased risks of ill health.

1.9 As part of a pilot study by the Northern Specialist Group, Leeds (HSL JS500/9600) an investigation was carried out in 2004 at four sites to assess MbOCA exposure control. There was evidence that exposure control was ineffective for example, the WEL was exceeded at one site (0.022 mg/m^3 8-hour TWA) and the levels of urinary MbOCA for five workers were around or exceeded the BMGV. Heavy surface contamination was found at all sites.

1.10 Furthermore, evidence was obtained from the site visits that recently purchased kegs were contaminated with MbOCA on the outside. The kegs were tested for MbOCA contamination at the point of delivery and before they were transferred inside the premises for use.

1.11 Subsequent sampling of kegs containing MbOCA at the three main suppliers all indicated surface contamination. Action was taken to identify the supply chain. There were six main manufacturers of the substance all located in the Far East, eg China, Taiwan, Japan. All supplied MbOCA to the United Kingdom.

1.12 The above evidence (past interventions) indicated that the measures to control exposure to MbOCA in the polyurethane elastomer industry were mainly ineffective in particular during the pouring of mixed liquid polyurethane.

1.13 HSE concluded that a study should be conducted nationally to provide a sound evidence base of the handling of MbOCA in the polyurethane elastomer industry (current 'live' interventions). This would establish the extent of poor exposure control during the use of the substance and determine the appropriate interventions to use to reduce exposure to the suspect carcinogen. The study was part of the DRP – Cancer Project. This report is the result of that study.

Evidence from exposure

1.14 MbOCA is defined as a carcinogen under the Control of Substances Hazardous to Health Regulations 2002 (as amended) (COSHH). It has been assigned the risk phrase R45 'May cause cancer' and hence a 'Carc' annotation in HSE's EH 40/2005 *Workplace exposure limits*. It is also classified as a Category 2A carcinogen - 'probably causes cancer in man' by the International Agency for Research on Cancer (IARC).

1.15 Workplace exposure to MbOCA can occur through inhalation, skin absorption and ingestion. The chemical is rapidly absorbed through the skin and has been assigned a 'Sk' annotation – 'Can be absorbed through the skin'. It has also been assigned a Workplace Exposure Limit (WEL) of 0.005 mg/m^3 8-hour Time Weighted Average (TWA); there is no short-term exposure limit.

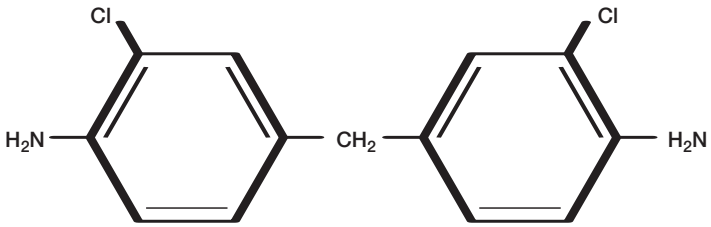
1.16 Exposure to airborne MbOCA should be reduced as far below the WEL as is reasonably practicable using the princples of good practice as set out in COSHH Schedule 2A regulation 7(7).

1.17 Biological monitoring for urinary MbOCA can be used to monitor exposure to the substance by the various routes in particular skin absorption and thereby assess the effectiveness of the control measures used. The Biological Monitoring Benchmark Guidance Value (BMGV) is 15 µmol/mol creatinine (urine post-shift sample).

Chemistry and health effects

1.18 MbOCA – 4,4'methylene-bis (2-chloroaniline) or 2,2'– dichloro-4,4'-methylene dianiline as named in HSE's EH40/2005 *Workplace exposure limits*) is supplied as yellow to light grey-tan pellets, beads or granules (generally dust free). It is supplied with the trade name Curalon, Curalin, Curene etc. The CAS No is 101-14-4. The chemical has a molecular formula of $C_{13}H_{12}Cl_2N_2$ and a molecular weight of 267.16.

MbOCA chemical structure



1.19 The melting point of MbOCA is between 100 to 110°C. At 200°C it decomposes to generate an irritant and toxic fume which contains orthochloroaniline and 2-chloro-p-toluidine. The chemical has a low vapour pressure and hence a low volatility ie at 25°C 1.0 x 10-5 mmHg and at 100°C 3.5 x 10-5 mmHg. It is soluble in most organic solvents such as acetone and toluene but only slightly so in water.

1.20 There are no major acute health effects if MbOCA is absorbed dermally or is inhaled. However, it may cause irritation to the eyes and skin following exposure.

1.21 MbOCA is a suspected bladder carcinogen, ie classified by IARC as a Category 2A carcinogen (probably causes cancer in humans). The human evidence relates to work in the manufacture of MbOCA and not its use in the polyurethane elastomer industry.

1.22 HSE has assigned MbOCA a provisional potency estimate of level B. Although assigned to this level, the chemical appears on animal evidence (relatively low doses and short exposure periods) to be more potent than many other carcinogenic aromatic amines.

2 Survey strategy

Site selection

2.1 HSE identified that there were 25 companies ranging in size from micro firms (almost half and employing less than 10) to small to medium enterprises (SMEs), ie employing from between 10 and 250 staff, using MbOCA in the production of polyurethane elastomers. A cross-section of 20 firms were chosen for the survey in terms of company size, quantity of MbOCA used, products manufactured, processes used etc. Four suppliers of MbOCA were identified but only two were still supplying the chemical when the survey started. These two suppliers were included in the survey.

2.2 A HM Specialist Inspector (Occupational Hygiene) and a Scientist (Health and Safety Laboratory – HSL) visited each MbOCA polyurethane elastomer manufacturer and MbOCA supplier sites. A HM Inspector of Health and Safety and a HM Inspector of Occupational Health attended several of the visits.

2.3 Each site was visited to gather the following information:

- a description of the workplace, the processes used;
- an assessment of the types of exposure control used for example, local exhaust ventilation (LEV), personal protective equipment (PPE)/respiratory protective equipment (RPE) etc;
- details of work activities including range and timing of employee's work, worker behaviour;
- an assessment of the suitability of company risk assessments, level of control maintenance, degree of health surveillance, training etc;
- measurement of personal inhalation exposure to and background concentrations of MbOCA, surface and glove contamination levels and urinary MbOCA and isocyanate levels.

Sample collection strategy

Personal inhalation and background samples

2.4 The personal inhalation samples were collected in the breathing zones of workers during their working day shift and when handling the MbOCA during scooping, weighing, melting, mixing etc. Samples were also collected from workers not directly involved with the handling of MbOCA, eg working in the vicinity of the work area.

2.5 The time periods for the manual handling of MbOCA and also its use in automatic processes during plastic production were approximately 3 hours and 8 hours respectively. Where appropriate the sampling time was 100 minutes with 200 litres of air sampled. All the results were reported as 8-hour Time Weighted Averages (TWAs) to represent a full working shift and checked for compliance with the WEL.

2.6 Background samples were collected in areas to check the effectiveness of the controls (eg adjacent a booth) and to determine workplace contaminant concentrations. Several were placed inside a booth to measure MbOCA vapour concentrations during heating.

Surface sampling and gloves

2.7 Surface samples were collected in those areas where contamination was likely for example, in and around extraction booths and in areas where little or no contamination was expected such as in the canteen area or office.

2.8 At most companies visited, samples were taken from the tops and sides of unopened MbOCA kegs or drums kept in storage facilites. Similar samples were also collected from kegs in storage facilities at the two suppliers.

2.9 The inner and outergloves worn by workers handling the MbOCA were collected when they finished a task or when a shift was completed depending on their use and disposal during a normal working day.

2.10 No samples were directly collected from workers' hands to measure skin contamination. Methanol has been used to wash MbOCA from the skin but this has been shown to aid skin absorption. For ethical reasons measurement of MbOCA directly on the skin was therefore not carried out.

Urines

2.11 At each company, urine samples were collected at the end of the shift from those employees handling MbOCA and from those not handling the substance to use as controls. The urine samples were also collected for the measurement of urinary isocyanate metabolites. Ideally, urine samples for isocyanates should be collected at the end of exposure. In many industries this is generally 2–4 hours. But in the polyurethane elastomer industry exposure to isocyanates (from handling pre-polymer resins) may be over a full 8-hour shift.

Objectives of survey

2.12 The objectives of the survey were to review the impact of past exposure control interventions in the manufacture of polyurethane elastomers and assess whether 'live' interventions during the site visits by HSE could mitigate MbOCA exposure. This was to be achieved by:

- measuring personal inhalation exposure to and background concentrations of MbOCA;
- measuring surface MbOCA contamination levels and that on inner and outer gloves worn during handling;
- assessing the measures to prevent or control exposure and whether they complied with good practice as outlined in COSHH Schedule 2A;
- carrying out biological monitoring for urinary MbOCA and isocyanate metabolites to assess the efficacy of control of exposure by all routes and for comparison with the current BMGVs;
- providing advice and recommendations where appropriate; and
- carrying out a full statistical analysis of the results.

2.13 It is expected that the outcome of the study will be to revise HSE guidance on the control of MbOCA, eg *COSHH essentials*, to reflect good working practices in the industry as outlined in Schedule 2A (COSHH). The results of the survey will also be used to provide the trade associations with relevant data on exposure control to provide to their members and to update their own guidance on the topic.

2.14 Furthermore, it is also expected that the approaches used in this study to control overall exposure to a suspect carcinogen, ie using 'live' intervention strategies can be applied to other occupational carcinogens.

3 Sampling and analytical methodologies

3.1 Four types of sample were collected, ie air samples (personal inhalation exposures and background concentrations), surface samples, glove samples (inner and outer where appropriate) and urine samples. All samples were subsequently analysed to determine the quantity of MbOCA present. The sampling and analytical methodologies for the air sampling and surface sampling used are described below.

Air sampling

3.2 The sampling protocol is given in MDHS 75 (HSE, 1993). A measured volume of air was drawn through an acid-coated GF/A filter contained in a seven-holed inhalable sampler head. The filter was acid impregnated.

3.3 The flow rate of the sampling head was set to 2 litres/minute and it was checked periodically during the sampling time period of 100 minutes. To ensure that the sampling time period was achieved the maximum amount of air sampled was set to 200 litres.

3.4 After the samples were collected, the filters were removed with tweezers to prevent contamination and placed into filter tins. They were then placed into a cool box before being transported to the laboratory and fridged.

3.5 Each filter was desorbed in the desorbing solution (sodium hydroxide and methanol) and then analysed using high-performance liquid chromatography (HPLC).

Surface sampling

3.6 Surface contamination was measured by sampling various surfaces. The samples were collected using Regal filamented wipes impregnated with 1 ml of methanol. To collect a sample from a flat area (eg floor) a 10 x 10 cm template was placed onto the surface. To collect samples from uneven surfaces (eg barrel rim) a specific area was measured.

3.7 A wipe sample was collected inside the demarcated area by wiping with a circular motion and going over the area three times.

3.8 After the samples were collected, the wipes were placed into glass jars and then into a cool box before being taken to the laboratory and fridged.

3.9 Each wipe was completely covered with methanol and left to desorb for 3 hours. An HPLC was used to analyse each desorbed solution and hence determine the quantity of MbOCA present.

Glove sampling

3.10 Inner and outer gloves of various materials for example, cotton, leather, nitrile, polythene and vinyl were collected and placed into plastic bags. They were then fridged prior to desorption and analysis.

3.11 There is as yet no recognised HSL method for the recovery of MbOCA and the subsequent analysis from all the gloves used. But methanol was successfully used to extract the chemical from polythene, vinyl and cotton gloves. HPLC was used to measure the quantity of MbOCA present.

3.12 MbOCA from disposable nitrile and leather rigger gloves couldn't be successfully extracted using methanol. These glove types were submitted from many of the sites visited. However, HSL have subsequently developed a method for the extraction and analysis of MbOCA from these types of gloves (Method validation for MbOCA analysis on nitrile and leather rigger gloves – OMS/2006/03).

Urine sampling

3.13 Urine samples (about 25 ml) from workers at each site were collected in a polystyrene universal container towards the end of their shifts. The samples collected were obtained from those workers handling the MbOCA directly and from those workers not directly handling the substance, eg office staff.

3.14 The urine samples were analysed using high-performance liquid chromatography.

3.15 It is recommended by HSL that the polystyrene container for the collection of urine for isocyanates should contain 0.5 g of citric acid. This was not always the case.

4 Processes

4.1 MbOCA is no longer manufactured in the United Kingdom. Most manufacturing of the substance is in the Far East, eg China and Taiwan, by the reaction of orthochloroaniline with formaldehyde. In 2005 over 200 tonnes of MbOCA and over 2000 tonnes of pre-polymer resin containing isocyanate (mainly toluene diisocyanate) was sold in the UK to about 25 polyurethane elastomer producers. In 1984 there were about 36 users but only 100 tonnes was consumed.

4.2 MbOCA is used as a crosslinking agent for curing epoxy resins or more commonly diisocyanate based pre-polymer resins to produce tough, resistant products. The commercial importance of the chemical therefore lies in its reactions with epoxides and isocyanates.

4.3 The use of MbOCA in the production of high-performance polyurethane elastomer products, for example shaft bearings for boats and underground cables, is carried out manually, automatically or by a combination of these methods. During the survey MbOCA wasn't used to produce items using centrifuges mounted on horizontal ovens, though some companies did indicate that such material could be produced if a customer demanded.

4.4 The smaller companies tend to specialise in the manufacture of moulded batches of polyurethane elastomer products where extremely high abasion resistance and lightness is required, eg wheels, tyres etc. In some of the larger factories the use of MbOCA may be intermittent depending on the needs of the motor or aerospace industries.

4.5 It is estimated by HSE that up to 300 workers are directly exposed to MbOCA during polyurethane elastomer production and over 1000 workers indirectly, for example office staff. Workers will handle MbOCA for the whole of their working day shift. This may range from 8 to 12 hours a day. For example, at company N employees will work from 06.00 to 18.00 Monday to Thursday and to 12.00 on Friday. At most plants there will usually be a half-hour lunch break and two 15-minute breaks, one in the morning and one in the afternoon. However, at some firms MbOCA may only be handled for a morning or afternoon depending on customer demand, eg company C.

Production of individual batches

4.6 The manual methods used for handling MbOCA during polyurethane elastomer production are essentially the same at all firms. They consist of seven process stages - scooping, weighing, melting, mixing, casting, curing and finishing. Details of the processes are given below.

4.7 For many years MbOCA could be obtained pre-dissolved in polyol for mixing with isocyanate based pre-polymers. Now all MbOCA is supplied as pellets or granules inside a polyurethane bag within a fibreboard keg, usually in 50, 60 or 70 kg

net weights (50 kg is mainly used). Each company tends to store the kegs in a dedicated store area. When a keg is in use it is either stored under a bench in the work area or in another easily accessible location.

4.8 At almost all firms most of the handling of MbOCA is carried out under local exhaust ventilation (LEV) (see Photo 1). To start the production process a required quantity of MbOCA is manually scooped from a keg and placed into a container (eg pan, beaker). At most companies this initial process stage may not be carried out under extraction.

Photograph 1 Partially enclosed extracted booth with canopy hood

4.9 Within an LEV system the MbOCA in the container is weighed to a specified amount, the container is placed on a hot plate and the MbOCA heated to between 98°C – 105°C. The pellets melt at about 100°C. The melted MbOCA is stored at between 90°C to 100°C in the container. There will be evolution of vapour at this temperature. Some decomposition will occur if the MbOCA is heated above 140°C.

4.10 A liquid pre-polymer resin containing toluene diisocyanate (TDI) or occasionally hexamethylene diisocyanate (HDI) is heated to about 60°C to 80°C in a heated oven and stored until use. When required, the resin is decanted into a container, it is carried lidded to the mixing area and the appropriate quantity of melted MbOCA is added.

4.11 Colourants and other substances may be added at this stage. The mixture is stirred either manually or automatically with a stirrer. The ratio of MbOCA to resin is generally about 1:10. For some high-grade products the MbOCA content can be up to 30%. The MbOCA/resin is mixed for several minutes to form a homogenous polyurethane solution.

4.12 The homogenous, mixed liquid polyurethane is de-gassed (or double de-gassed) under vacuum in a bell jar to remove any air bubbles. The resin may also have been degassed prior to adding to the melted MbOCA.

4.13 The moulds are pre-heated to around 90°C to 95°C in an oven(s) overnight. The mixed liquid polyurethane is carried to the moulds and poured into the open

cavities in an oven or on a bench with or without extraction. Most ovens have extraction to remove MbOCA vapours during pouring.

4.14 Following casting the moulds are cured in the ovens at 100°C to 120°C for between 4 and 24 hours. For most firms the moulds are cured overnight at 90°C but it depends on the type of polyurethane product being produced.

4.15 During curing the polyurethane will set in the moulds as the chemicals react to produce the solid polyurethane product. Some types of product may have a post or secondary curing at 100°C for several hours to ensure full chemical reaction.

4.16 The moulds are removed once cured. A silicone-based releasing agent is sprayed onto the moulds to ease removal. They are removed using compressed air and/or a knife or other tool. Excess flash and sprues are removed by trimming and cutting with scissors or a knife and the edges smoothed using an appropriate abrasive.

Automatic casting (continuous supply and larger batches)

4.17 Prior to automatic casting, a MbOCA keg is either placed onto a feeder hopper (see Photo 2) or into a glove box (under negative pressure). Once on the hopper the keg is open and the pellets are released. To release the pellets using a glove box the operative's hands are placed into two rubber gloves attached to the portal openings. The glove box is open from the inside and the MbOCA pellets are released from the keg.

Photograph 2 MbOCA keg feeding into a reactor vessel

4.18 The released MbOCA pellets from the hopper and glove box (see Photo 3) are fed into the reactor vessel/dispensing machine by vacuum transfer or by gravity feed and mixed with resin, various colour pigments and catalysts. The quantity of material entering the reactor vessel is pre-set to produce the correct formulation for the required polymer.

Photograph 3 A glove box

4.19 In general the empty bags are removed from the keg, placed into a large polythene bag and crushed in a dedicated crushing machine under local exhaust ventilation to capture any dust released when residual pellets are crushed. The kegs are treated likewise.

4.20 Once reaction of the substances in the reactor vessel is complete, the mixed liquid polyurethane may be stored at about 95°C or automatically dispensed via a dispensing nozzle directly into the moulds, eg company S. Alternatively, the mixture can be dispensed into a container, taken to a casting area and then poured into the moulds prior to curing in an oven(s).

Suppliers

4.21 There are four UK suppliers of MbOCA. One of these companies supplies directly to their UK customers from their base in France. The other companies buy direct from their suppliers in the Far East. In 2005, over 200 tonnes of MbOCA and over 2000 tonnes of pre-polymer resin were sold by the three UK companies.

4.22 The MbOCA is packed in polyethylene bags within a fibreboard keg. The kegs are shipped double stacked on pallets to the UK. Most of the kegs supplied are 50 kg net weight. Each pallet holds eight 50 kg kegs.

4.23 Once they reach the suppliers the kegs are stored in dedicated storage areas. One of the distributers (T) stores the MbOCA in two metal sheds away from the main chemical storage facilities. Occasionally a keg may be imported that is damaged and the outside may be contaminated with MbOCA.

4.24 One of the suppliers (R) will daily test the MbOCA and resin manually for quality, ie tensile strength, in a dedicated laboratory on the site. The other supplier will occasionally test the quality of the MbOCA supplied only if a customer requests this service.

4.25 There are no substitutes for MbOCA because its chemical properties are not reproducible, for example when mixed with a pre-polymer resin it produces a hard, resistant polyurethane product. Liquid diamines have been used as potential substitutes for MbOCA but the manufactured products have been of an inferior quality.

MbOCA exposure risks

4.26 There is a risk of inhalation and skin exposure to MbOCA during all stages of polyurethane elastomer production. There is also a risk of MbOCA ingestion. The exposure risks will be highest during the direct handling of the substance. There will also be the potential for burning of the skin with melted MbOCA and liquid polyurethane.

4.27 However, the risks of inhalation exposure, skin exposure and ingestion will be significantly reduced if the appropriate control measures are used during all stages of elastomer production, for example the use of LEV during weighing, mixing etc. The risk of burning from handling melted MbOCA will be decreased significantly if appropriate gloves are worn.

4.28 During the manual scooping of MbOCA from a keg and during the loading of a hopper or glove box there is the potential for dust inhalation and skin contact. The risks should be small because the MbOCA pellets release little dust during handling. However, there is some evidence that the MbOCA pellets manufactured in China may release more airborne dust when handled.

4.29 During the transfer of the scooped MbOCA to a container for weighing or from a keg into a hopper there may be spillage and the subsequent contamination of surfaces with the chemical. Skin contact with these contaminated surfaces may lead to skin absorption.

4.30 When the MbOCA is heated to 90°C or above vapour will be released with the potential for inhalation exposure. The concentrations of released vapour will be highest at temperatures above 100°C. Any molten MbOCA that spills may contaminate for example, the inside of a booth. When it cools it will harden and accumulate on the surface unless it is removed regularly. Until the waste is cleaned there is a high risk of skin contact and absorption.

4.31 There is the potential for inhalation exposure to MbOCA vapours when the molten substance is added to the pre-polymer resin and when it is stirred manually or automatically with a stirrer. There is also the potental for skin contact and subsequent dermal absorption if the liquid polyurethane is spilled onto the skin. There will be the potential for skin contact if the spillage hardens and is allowed to build up in the mixing areas.

4.32 The risks of inhalation exposure to MbOCA vapour may occur when the mixed liquid polyurethane inside a container is carried to and placed inside the Bell jar and when it is lifted out. Skin contact with the liquid may also occur following spillage. There is also the potential for skin contact with contaminated surfaces around the Bell jar.

4.33 MbOCA vapour will be released when the mixed liquid polyurethane is carried in an unlidded container and poured into a heated mould(s), ie casting. During these tasks there will be the potential for inhalation exposure. Skin exposure and subsequent dermal absorption may occur if the mixture is spilled onto the skin and/or has been allowed to build up on surfaces in the mould pouring area(s).

4.34 When the liquid polyurethane is dispensed automatically through a dispensing nozzle into a heated mould or into a container for transfer to a pouring bench, there will be the potential for inhalation exposure to MbOCA vapour. There will also be the potential for dermal exposure if the mixture is spilled during dispensing.

4.35 During the curing of the moulds, MbOCA vapour will be evolved. Airborne concentrations of the chemical will be related to the curing temperature, ie the higher the temperature the more vapour released. When the hot moulds are removed from an oven there is still a small risk of inhalation exposure. There may be the potential for skin exposure if the moulds are directly touched at this stage.

4.36 However, when the mixed liquid polyurethane has reacted, hardened to produce the solid polyurethane product and subsequently cooled it should be completely cured. There should be no free MbOCA present on the cured product to contaminate the skin when the mould is removed and handled to remove excess polyurethane by hand or using scissors.

4.37 If the outside of a keg is contaminated with MbOCA following damage there is the potential for inhalation exposure to dust and skin contact with the substance. Such accidental damage may occur at both user and supplier sites. Appropriate measures, eg isolating and cleaning the area, should be taken to deal with the damaged keg and thereby reduce the risks of exposure.

4.38 There is evidence that the outside of imported kegs may be contaminated with MbOCA, for example on the lid surface. There is therefore the potential for inhalation exposure to and skin contact with MbOCA dust when a contaminated keg is removed from the pallet. Dockworkers, transport staff, supply staff, users and others handling contaminated MbOCA kegs will be at risk of exposure to the substance.

4.39 Skin contact with any MbOCA contaminated surfaces will result in skin absorption. Contaminated surfaces may not necessarily be restricted to the MbOCA work area but could be located in toilets, the staff room, the office etc. The level of surface contamination and the risk of dermal exposure will be related to the effectiveness of the controls measures used at a site in particular good housekeeping.

4.40 All workers handling the MbOCA directly during the various stages of polyurethane elastomer production (manual and automatic) and those working in the vicinity of the production area are at a high risk of exposure to the substance. Maintenance personnel may be at a particular high risk of MbOCA exposure, especially when they are servicing the local exhaust ventilation systems used for controlling exposure.

4.41 But there are others who may be at risk of exposure albeit at a lower level, for example office staff and contract workers who may enter the MbOCA work area but do not come into direct contact with the substance. Exposure is more likely to be via skin contact with contaminated surfaces rather than inhalation of the dust or vapour.

4.42 Employees working at a distance from the main MBOCA processing area or those working in a different part of the building may be exposed to the substance via skin contact with contaminated surfaces, eg in the canteen, smoking areas etc.

Isocyanate exposure

4.43 The suppliers of pre-polymer resins indicate that they should contain little or no free TDI or MDI monomer; they are marketed as a low-hazard/low-risk products. This may be the case. However, the resins supplied still contain isocyanate and therefore inhalation exposure to and skin contact with the heated resin will need to be effectively controlled to reduce the exposure health risks.

4.44 Potential inhalation exposure to isocyanate vapour will occur when a drum of heated resin (to about 60°C) is opened. There will be a further risk of inhalation exposure to vapour/aerosols when the resin is decanted into a container and transported to the MbOCA weighing/mixing area. There is also the risk of skin exposure if the resin is spilled during transfer.

4.45 Furthermore, there will be the potential for inhalation exposure to and skin contact with isocyanate when the melted MbOCA is mixed with the resin and stirred to form a homogenous mixture, when the liquid polyurethane mixture is poured into a mould (manually and automatically) and during mould curing in an oven.

4.46 There is also the potential for skin contact with surfaces contaminated with the resin during all stages of its use. Though the risks are small, skin contact may result in skin irritation and dermatitis.

5 Comments and observations

Risk assessments

5.1 A suitable and sufficient risk assessment is required to assess the risks to health created by the work with MbOCA and other hazardous substances during the manufacture of polyurethane elastomers. The assessment should include details on the nature of MbOCA (and other hazardous substances), the routes of exposure, the processes in which the substance is handled, the exposure controls used etc.

5.2 To comply with COSHH regulation 6 (4) those companies employing five or more employees must record any significant findings, for example details on the means to control exposure. During the survey only three manufacturers were found to employ less than five workers (D, F and G) but they recorded their risk assessments. The manager/owners of the companies compiled their own risk assessments.

5.3 Most polyurethane elastomer producers risk assessments were classified as poor, ie 15 (75%). But 5 (25%) company risk assessments were satisfactory (F, I, K, M and O); three of these firms use manual methods for handling the MbOCA and two use automated methods. Interestingly, one of these companies is a micro-firm and employs four workers (F). Both the MbOCA/resin suppliers risk assessments were satisfactory.

5.4 Almost all of the unsuitable and insufficient risk assessments contained little information on the processes in which MbOCA was handled and on the measures used to control exposure. Five of the assessments were generic and the information provided didn't represent the actual workplace.

5.5 Most of the assessments had never been reviewed even though a plant may have been modified or the volume of work changed significantly over several years.

5.6 The satisfactory risk assessments from manufacturers and suppliers varied in the quantity of detail they contained but they all managed to include relevant data, eg routes of MbOCA/isocyanate exposure, level, type and duration of exposure etc. One of the companies employing 12 workers and handling MbOCA manually (I) uses a rating system to assess the risks to health, ie 1 to 10. The rating values are added and are incorporated into the overall assessment.

5.7 A competent person should produce the company risk assessment. This was generally the case. The competent person(s) producing the risk assessment

may have been the company health and safety professional, an outside consultant, the manager, or owner of the company or a combination of these.

5.8 However, the use of a competent person did not guarantee the production of a suitable and satisfactory risk assessment. The reasons for this are unclear but in most cases they probably relate to the fact that the 'competent' person did not have sufficient knowledge of the industry and/or wasn't familiar with the requirements of COSHH.

Results

Statistical analysis

5.9 The individual results of personal inhalation exposure to MbOCA, background concentrations, urinary MbOCA and urinary isocyanate metabolite concentrations, surface sampling and glove MbOCA concentrations for each polyurethane elastomer manufacturer and MbOCA/resin supplier are not included within this report.

5.10 However, a full statistical analysis of the data has been carried out (see Appendix 2 and HSL Report ESS/2006/07). The specific aims of the statistical analysis were to:

- provide an exploratory analysis of the MbOCA data collected from urine, air, surface and glove samples;
- assess for differences in concentrations between different jobs and different companies;
- investigate the relationship between MbOCA in air and urine samples;
- investigate the relationship between surface and glove concentrations;
- investigate the relationship between MbOCA concentrations on inner and outer gloves;
- calculate the 90th percentile of the MbOCA in urine concentrations and to evaluate the evidence for a revision of the BMGV;
- investigate relationships between MbOCA concentrations in surface and glove samples and MbOCA in air and urine samples;
- assess whether companies using automated processes had different concentrations of MbOCA than the companies using purely manual processes;
- investigate the concentrations of MbOCA on drums held in storage at two MbOCA suppliers and to assess if these differed from concentrations on drums in storage at the manufacturing companies; and
- investigate the isocyanate metabolite concentrations in urine and the relationships between isocyanate concentrations and jobs and isocyanate concentrations and MbOCA concentrations.

Personal inhalation exposure/fixed place background levels

5.11 A total of 210 airborne samples were collected at the MbOCA user companies of which 80 were to measure personal exposure to airborne MbOCA during the handling of the substance. The background static (fixed place monitoring) samples were collected from various locations in and around the MbOCA handling areas where it was expected that MbOCA could become airborne.

5.12 Only 13 (16%) personal exposures were above the level of detection for MbOCA. And only two exposures exceeded the WEL of 0.005 mg/m^3 8-hour TWA. Both high exposures, ie 0.0111 mg/m^3 (company A) and 0.0058 mg/m^3 (company O) were measured during tasks that included the pouring of moulds on an open bench without extraction. Two exposures exceeded half the WEL, ie both were 0.0035 mg/m^3 8-hour TWA (companies O and U). Both workers carried out most MbOCA processing tasks including the pouring of the moulds.

5.13 Fourteen (11%) of the background concentrations measured at the MbOCA user companies were above the level of detection for the chemical with the highest being 0.01 mg/m^3 (company 0). This high concentration was measured inside an extraction booth where MbOCA was weighed, heated and mixed.

Table 3 Summary of statistical analysis of MbOCA airborne samples

MbOCA personal exposures and background concentrations - mg/m^3								
Exposure	n	Max	Min	Median	Arithmetic mean	Arithmetic standard deviation	Geometric mean	Geometric standard deviation
Personal exposure	13	0.011	0.0004	0.001	0.002366	0.00309	0.00246	3.404
Background concentrations	14	0.0111	0.00015	0.00355	0.00366	0.00286	0.00131	2.9082

5.14 The results indicate that at most companies personal airborne exposure to MbOCA can be controlled ie 67 (84%) personal exposures were below the level of detection or had no detectable MbOCA. Exposure to airborne MbOCA was only high where appropriate exposure control was not applied, eg failure to provide LEV to control exposure to MbOCA vapour during the pouring of moulds.

Surface wipe sample analysis

5.15 A total of 334 surface samples were taken from all MbOCA user and MbOCA supplier sites. At the MbOCA user companies, samples were mainly collected from those areas where direct exposure to the chemical was likely for example, around a hopper, inside a partial booth, on the floor near an open drum, inside an oven etc (259 samples). But those areas not likely to be in direct contact with MbOCA were also sampled such as the canteen or office to assess the spread of the substance (75 samples).

5.16 At the two suppliers R and T samples were collected from recently imported kegs and from the surrounding storage area. Prior to the sampling it was expected that there would be no measurable MbOCA on the kegs. At one of the suppliers (R) surface samples were also collected from inside the laboratory where MbOCA was handled inside a fume cupboard, for example from the floor next to the fume cupboard to detect any spillage and lack of containment.

5.17 One hundred and fifty-six (60%) direct samples had concentrations of MbOCA above the limit of detection whereas only eight (11%) of indirect samples had concentrations of the chemical above the LOD. The 156 direct samples were grouped into eight categories, ie fume cupboard, storage, weighing/pouring, mixing, oven, hopper, casting and other (see Table 4 for statistical analysis).

Table 4 Statistical analysis of MbOCA concentrations on various surfaces

Concentration of MbOCA on surfaces mg/cm2								
Exposure	n	Max	Min	Median	Arithmetic mean	Arithmetic standard deviation	Geometric mean	Geometric standard deviation
Fume Cupboard	27	0.0514	0.00001	0.0004	0.00295	0.00985	0.00038	8
Storage	34	0.0665	$9x10^{-6}$	0.0003	0.0042	0.0124	0.00027	12.07
Weighing/ pouring	21	0.1116	$4x10^{-6}$	0.0005	0.0114	0.026	0.000266	18.26
Mixing	9	0.0145	$1.3x10^{-5}$	0.0001	0.0033	0.0061	0.000191	12.88
Oven	21	0.425	$7.4x10^{-6}$	0.0001	0.0207	0.0926	0.000191	11.78
Hopper	4	0.0209	0.0033	0.011	0.0116	0.0072	0.0096	2.163
Casting	6	0.0003	$1.7x10^{-5}$	0.0001	0.00011	0.0001	0.000079	2.8
Other	34	0.0205	$7x10^{-6}$	0.0002	0.0015	0.004	0.000234	7.168

5.18 From the statistical analysis presented in Table 4 it can be seen that the levels of surface MbOCA concentrations from the various locations are very similar, ie medians and geometric means. However, the contamination around the hopper was generally above that of the other sites with a higher median and geometric mean. This is due to excess spillage of MbOCA during hopper filling and a failure to clean it up immediately.

5.19 At one company (J) the surface concentration of MbOCA on an oven was high because mixed liquid polyurethane was being splashed during pouring and left to harden. There were also high surface concentrations of the MbOCA on weighing scales and in the surrounding area, ie where MbOCA pellets were spilled and not cleaned immediately.

5.20 Interestingly, of the 17 surface samples taken at supplier T, only two had small traces of MbOCA, ie 0.0002 and 0.0008 mg/cm^2 on the warehouse floor and on the pallet holding MbOCA drums respectively. There was no evidence of any MbOCA on the kegs or drums sampled. The company indicated that occasionally a keg may be damaged and MbOCA granules would be released. But the spillage would be cleaned up immediately.

5.21 Eleven surface samples were taken from supplier R. Four contained traces of MbOCA, ie 0.0184, 0.0233, 0.0058 and 0.0011 mg/cm^2 from the rim of a keg, the side of a keg, the rim of a pallet and the surrounding floor respectively. These results indicate that imported MbOCA drums from the Far East may still be contaminated with the chemical. This issue needs to be addressed.

Glove sample analysis

5.22 A total of 147 glove samples were taken. Where possible they were classified as inner gloves worn next to the skin and outer gloves worn over the top

of the inner gloves and with the potential for direct exposure to MbOCA. Not all gloves worn, however, could be classified as inner or outer gloves because some companies disputed this definition.

5.23 But as expected the MbOCA concentrations on the outer gloves identified were higher than those of the inner gloves. The respective medians were 0.09 mg/glove for the inner compared with 4.534 mg/glove for the outer gloves. Because the sample numbers were small it was not possible to determine if there was a correlation beween the inner and outer gloves. But, in general, the concentrations on the outer gloves were several orders of magnitude larger than the concentrations on the inner gloves.

Table 5 Statistics of MbOCA concentrations on gloves – mg/glove

MbOCA concentrations on inner and outer gloves mg/glove								
Exposure	n	Max	Min	Median	Arithmetic mean	Arithmetic standard deviation	Geometric mean	Geometric standard deviation
Inner	15	6.3	0.01	0.09	0.5619	1.604	0.107	4.854
Outer	51	74.44	0.016	4.534	9.2766	14.45	2.555	7.885

5.24 A statistical analysis was undertaken to determine if there was a correlation between the concentration of MbOCA on the gloves and urinary MbOCA concentrations. The results appear to show that the concentration of urinary MbOCA is related to the quantity of the chemical present in particular on the outer gloves. Therefore if these gloves are frequently replaced and/or put on and taken off correctly then urinary MbOCA levels should be reduced.

Urine sample analysis

5.25 A total of 78 urine samples were collected from workers at 19 companies, ie 18 MbOCA users (not S or V) and 1 supplier (R) to determine the concentration of urinary MbOCA. Approximately 59 (75%) of the samples were collected from workers directly involved with the manufacture of polyurethane elastomers whilst 19 (25%) were collected from workers not directly exposed to MbOCA but may have been exposed to the substance if best practice was not followed. These workers were used as controls. Of the above samples, 71 (from 17 companies) were tested for isocyanate metabolite concentrations.

5.26 Forty (51%) of the urine samples analysed had MbOCA concentrations above the LOD. But only 3 (4%) of these samples were above the BMGV of 15 µmol/mol creatinine (companies D, P and U). Ten urine samples had urinary MbOCA concentrations around or above half the BMGV (companies G, K, M, N, O and Q). This British Rubber Manufacturers' Association Ltd (BRMA) indicate that any excursion above the BMGV or even readings approaching half the limit should result in a full investigation into control measures and MbOCA handling procedures.

5.27 There were noticeable differences in the urine MbOCA concentrations between the directly and indirectly exposed groups. Surprisingly, 21% of those indirectly exposed to MbOCA (controls) had urinary MbOCA concentrations above the limit of detection whereas 61% of those directly exposed to MbOCA had a detectable concentration. A Fishers exact test was used to determine if directly exposed workers were more likely to have measurable urinary MbOCA concentrations; they were more likely (p=0.003).

Table 6 Statistical analysis of urinary MbOCA concentrations by exposure

Urinary MbOCA concentrations - µmol/mol creatinine								
Exposure	n	Max	Min	Median	Arithmetic mean	Arithmetic standard deviation	Geometric mean	Geometric standard deviation
All exposed	40	24.99	1.33	4.27	6.597	5.73	4.965	2.092
Indirectly exposed	4	7.17	1.33	2.535	3.3925	2.60	2.781	2. 033
Directly	36	24.99	1.35	4.33	6.95	5.896	5.291	2.058

5.28 The range of urinary MbOCA concentrations for the directly exposed group was between 1.35 and 24.99 µmol/mol creatinine (median 4.33) whereas for the indirectly exposed group it was between 1.33 and 7.17 µmol/mol creatinine (median 2.535). For both groups, the distributions of urinary MbOCA concentrations were positively skewed.

5.29 Although the indirectly exposed workers had lower urinary MbOCA concentrations than those workers directly exposed to the substance they were still high, eg max 7.17 µmol/mol creatinine. As controls it was expected that these workers would have had none or little concentrations of urinary MbOCA. In these employees it is highly likely that exposure was through the skin via surface contamination, ie evidence of poor housekeeping.

5.30 Exposed workers were sub-classified into seven groups to reflect the different stages of the manufacturing process and hence potential exposure to MbOCA. The groups were handling/scooping, weighing/mixing/melting, casting, moulding, maintenance, other non-specific and all parts of the process. These categories describe the main type of exposure.

5.31 There is a highly significant association between the job classification and urinary MbOCA concentrations (p=0.002). Potential exposure to MbOCA is more likely to occur during casting (pouring into moulds only) and moulding (includes removal and trimming of moulds). Table 7 gives a statistical analysis of the 36 samples where the urinary MbOCA concentration was above the LOD.

Table 7 Statistical analysis of urinary MbOCA concentrations by job classification

Urinary MbOCA concentrations µmol/mol creatinine and job classifications								
Exposure	n	Max	Min	Median	Arithmetic mean	Arithmetic standard deviation	Geometric mean	Geometric standard deviation
Handling	-	-	-	-	-	-	-	-
Weighing	4	4.92	1.35	3.155	3.145	1.763	2.74	1.872
Casting	3	17.01	3.3	7.35	9.22	7.04	7.44	2.27
Moulding	12	24.99	2.23	5.67	8.34	6.84	6.265	2.19
Maintenance	2	3.92	3.07	3.495	3.495	0.60	3.469	1.18
Other	1	2.37	2.37	2.37	2.37	-	2.37	-
All parts	14	24.2	1.91	4.965	7.185	5.88	5.787	1.896

5.32 The current BMGV for MbOCA is 15 µmol/mol creatinine. It was set at the 90th percentile of available validated data collected from representative workplaces in 1993. Most companies with good occupational hygiene practices should be able to achieve urinary MbOCA levels below the BMGV.

5.33 However, there has been a downward trend in the 90th percentile for many years. Since 1995 it has been below 10 µmol/mol creatinine. The 90th percentile of the current study based on all 78 samples is 8.85 µmol/mol creatinine, suggesting that the present BMGV for urinary MbOCA is set at a high level and could be revised downwards.

5.34 To assess overall exposure to the isocyanate(s) used in the pre-polymer resin (mainly toluene diisocyanate (total TDA)), 71 urines were analysed for the corresponding diamines, ie 2,4 toluenediamine (2,4 TDA), 2,6 toluenediamine (2,6 TDA), 2,4 hexanediamine (HDA), isophoronediamine (IPDA (u)) and 4,4'-diaminodiphenylmethane (MDA).

5.35 Those urinary isocyanate metabolite levels > LOD for 2,4 TDA, 2,6 TDA, total TDA (2,4 and 2,6 combined) and HDA also had levels above the BMGV of 1 µmol isocyanate-derived diamine/mol creatinine. No readings for IPDA (u) and MDA were above the BMGV. Table 8 is a summary of the statistics for the four main isocyanates identified in the urine samples.

Table 8 Statistics of urinary isocyanate levels

Urinary isocyanate levels µmol/mol creatinine								
Exposure	n	Max	Min	Median	Arithmetic mean	Arithmetic standard deviation	Geometric mean	Geometric standard deviation
2,4 TDA	14	5.55	0.32	0.7	1.37	1.40	0.96	2.28
2,6 TDA	22	13.23	0.45	0.77	1.64	2.69	1.037	2.19
Total TDA	23	15.5	0.32	1.26	2.40	3.23	1.54	2.40
HDA	13	10.11	0.22	1.67	3.41	3.38	1.81	3.69

5.36 The quantities of the two TDA isomers had similar magnitudes with median concentrations for 2.4 TDA and 2,6 TDA of 0.7 and 0.77 µmol/mol creatinine respectively. For both TDA and HDA approximately 70% of samples where a measurable concentration of diamine was detected were above the BMGV (at companies B, D, E, F, G, M, N, P, Q and R).

5.37 None of the workers involved in handling and scooping MbOCA only had isocyanate metabolite levels above the LOD. Those workers involved with weighing, mixing and melting MbOCA had measurable quantities of HDA. Those workers handling MbOCA during all stages of the polyurethane elastomer manufacturing process had measurable quantities of TDA. This latter result reflects the handling of pre-polymer resin containing mainly TDA and the failure to use effective controls to reduce exposure for example, during the decanting of heated resin from the drum.

5.38 From the statistical analysis there is evidence of a correlation between urinary MbOCA and urinary isocyanate diamine concentrations in particular between TDA and MbOCA. Furthermore, the observation that many workers were above the BMGV for urinary isocyanate diamines is a new and important finding and indicates the need for improved exposure control.

Exposure control

Substitution

5.39 At present there are no safe and effective elastomers to replace the use of MbOCA in the production of high-grade polyurethane products. Several substitute substances have been evaluated in trials, eg liquid diamines but they do not produce the resilient products that customers require. Until a safe substitute for MbOCA is found and the need for its use is eliminated it will continue to be the elastomer of choice in the UK polyurethane industry.

Segregation

5.40 All work areas where MbOCA is handled should be segregated to minimise the spread of surface contamination and reduce the potential for exposure of those workers not involved with MbOCA handling. The spread of the chemical throughout the plant should be prevented or minimised at all times, eg by good housekeeping, personal hygiene.

5.41 Almost all the companies visited carried out MbOCA work in a dedicated work area. However, at certain times of the day at most sites visited workers from other parts of the factory would walk through the area and thereby increase their risk of exposure.

5.42 Two companies (E and P) indicated that MbOCA was handled at outside locations during contract or repair work. Employers expect that during these tasks the chemical will be handled by experienced workers in segregated areas. No further details were provided because of the varied nature of each job.

Storage of kegs

5.43 Ideally most MbOCA drums should be stored in a dedicated dry storage area. This will reduce the potential for surface contamination of the kegs with MbOCA during polyurethane elastomer production and also contain any spillage from accidental damage to the keg (see Photo 4).

Photograph 4 Storage area for MbOCA kegs

5.44 However, there is still a low risk of a keg becoming contaminated when it is lifted onto a trolley and wheeled into the work area ie hand to keg contact. A keg may be damaged by a fork-lift truck (FLT) and the MbOCA spill onto the surrounding surfaces when it is to be lifted for transfer to the work area. But this is not a common occurrence.

5.45 Most companies do store the kegs in a dry, dedicated storage area. They mainly use a FLT to lift and carry a keg to the work zone. The number of kegs stored at the twenty MbOCA users varied from one only to a full pallet (eight 50 kg kegs); it depended on the quantity of MbOCA being used at the time.

5.46 Three firms employing less than 10 workers (D, F and Q) store one or more kegs under a bench in the work area prior to use. There is therefore, a greater risk of MbOCA contamination of the keg(s) during the polyurethane elastomer production process. At most firms the kegs in use are usually stored in the work area under a bench or in a dedicated storage area.

5.47 The surface sampling results indicate that kegs stored in the work area and in dedicated stores do become contaminated with MbOCA; those in the dedicated store tend to be more lightly contaminated. The kegs in the dedicated store may become contaminated via contact with a MbOCA handler for example, when being taken to the store.

5.48 But it is likely that the kegs are imported and distributed within GB with MbOCA contamination on the outside surface. A recent HSE study in 2004 indicated that kegs imported from the Far East, in particular from China, were contaminated on the outside with MbOCA. An HSE investigation confirmed that this was due to the drum-filling procedure at Chinese manufacturers; MbOCA was added to the containers from a height with little control.

5.49 The present survey has evidence that a very small percentage of supplied kegs may be lightly contaminated with MbOCA on the outside. This could be due to kegs being contaminated prior to import into the UK and/or to damage during transit from the dock to the distributers and/or to damage during storage.

MbOCA transfer from kegs

5.50 Intact MbOCA pellets produce little dust when handled. But when they are removed from a keg, either manually using a scoop or by other manual means, there may be some airborne dust generated albeit in small concentrations. Kegs or drums should only be opened under local exhaust ventilation, eg a partially enclosed extraction booth to control airborne exposure.

5.51 Fifteen companies use manual methods to process MbOCA. At the start of the manufacturing process a scoop is used to transfer MbOCA from an opened keg to a container for weighing. The keg is usually stored near the weighing area. At several companies the lid was not placed onto the keg once the MbOCA had been removed. There was the potential for a major spillage if it was knocked over.

5.52 In most instances this part of the process is not carried out under extraction. There is therefore the potential for inhalation exposure to dust when scooping the MbOCA, dermal exposure via skin contact with the pellets and/or airborne dust and surface contamination from any spillage.

5.53 Spillage of the pellets onto the floor can lead to them being crushed with the foot. There is the potential for airborne dust to be generated that may contaminate clothing and also for parts of the crushed pellets to be transported from the soles of the shoes to other parts of the building. There was extensive evidence of crushed pellets around most opened kegs.

5.54 All workers in the industry wear gloves to prevent skin contamination during the manual scooping of the pellets and their subsequent transfer to a container for weighing and melting. And about half of the operatives also wear suitable respiratory protective equipment (RPE), eg a half-face mask respirator FFP2 during this task.

5.55 Five companies use automated methods to process MbOCA, therefore it is not necessary to use a scoop. If a glove box is used the keg is opened inside the glove box and any spillage is contained. The hands are protected from contamination by putting the hands into the gloves attached to the portals.

5.56 A hopper is filled by manually tipping the contents of a keg into it or by using an FLT to lift the keg and then filling. In both cases there is the potential for the area surrounding the hopper to become heavily contaminated with MbOCA

pellets. Those firms using hoppers provide LEV above the filling point to control inhalation exposure to airborne dust. Most workers also wear appropriate gloves and suitable RPE ie mainly a half-face mask respirator FFP2.

5.57 During the charging of the hopper with MbOCA by whatever method there will be local spillage. Unless it is cleaned up immediately it can quickly accumulate, be crushed and the debris spread throughout the work area and beyond. An industrial vacuum is widely used to remove spillage on a daily basis. However, some companies are not so vigilant. There was visible evidence of heavy contamination on surfaces around the hopper.

Melting/mixing of MbOCA and dispensing – reactor vessels

5.58 The risks of exposure to airborne MbOCA/isocyanate vapour will be lowest at those companies using automated methods because the heating and mixing of chemicals will be carried out within a total enclosure (see Photo 5). However, if the outlet safety valve on the reactor is poorly maintained a vapour release may go unnoticed.

Photograph 5 A typical automated system for mixing MbOCA and pre-polymer resin

5.59 The venting area(s) should be extracted or the surrounding atmosphere will become contaminated with vapour. Two companies have installed LEV above the vent with ducting leading to the outside of the building. Any released vapour is passed through a carbon filter before release to the outside.

5.60 MboCA melting machines contain a thermally activated cut-off device so that the temperature can be regulated to not exceed 130ºC. When the molten MbOCA is dispensed into a container usually steel (eg a teapot) there is a high risk of inhalation exposure to vapour and potential skin exposure and burning from any spillage. If dispensing of the hot mixed liquid polyurethane is not controlled then the dispensing valve, the floor (if a drip tray is not provided) and the container can all become contaminated with hot polyurethane.

5.61 An air deflector in front of the valve and careful pouring will protect the worker from splashing and LEV at the dispensing point will remove vapours and thereby mitigate exposure.

5.62 At one company (O) a reactor vessel is used to melt and mix MbOCA and pre-polymer resin to up to 110ºC. The vessel is filled with MbOCA via a hopper. Fixed flexible ducting with an inlet hood is positioned near the dispensing nozzle to remove airborne vapour during pouring. A drip tray is situated underneath the dispensing point. It was heavily contaminated with polyurethane that had hardened. The dispensing valve lever was also heavily contaminated. The risk of skin exposure and subsequent dermal absorption was high.

Weighing and melting of MbOCA – manual methods

5.63 At all companies where MbOCA is handled manually the weighing and melting of the substance and its subsequent mixing with the heated isocyanate based pre-polymer resin is carried out under an LEV system (see Photo 6). Ten companies use partially enclosed booths, six use canopy hoods installed above an open bench and four use fume cupboards for melting and mixing MbOCA. The number and type of LEV systems used at each site will differ.

Photograph 6 Weighing and melting MbOCA inside an extraction booth – notice heavy contamination on booth

5.64 For example, one company employing over 60 workers (B) weighs, heats and then mixes molten MbOCA with pre-polymer resin in up to six open-fronted partially enclosed extraction booths. In contrast a smaller company (H) uses two fume cupboards to complete these tasks. The two suppliers of MbOCA use a fume cupboard when handling the chemical for qualiy control purposes etc.

5.65 It is essential that all types of LEV systems used should provide adequate control during MbOCA processing. This should be achieved if the capture velocity does not fall below a minimum of 0.8 m/s (recommended by BRMA/RAPRA Code of Practice 2001). The average face velocity of a fume cupboard and a partially

enclosed extraction booth should not fall below 0.5 m/s. And adequate make-up air should be provided to replace that lost through extraction.

5.66 The work areas where the polyurethane elastomer is manufactured vary in size. But, in general, the larger companies have the largest surface area for carrying out the manufacturing process tasks. General ventilation is provided in a plant by keeping doors and windows open, by providing roof supply/extraction fans, through gaps in the fabric of the building structure etc or by a combination of these. The general ventilation at almost all factories visited was adequate.

5.67 Most of the LEV systems tested during the survey had poor capture and/or ineffective average face velocities. Some were poorly designed. For example, at one firm (J) a canopy hood was used to capture MbOCA vapour at source during melting. The canopy was not situated low enough to capture airborne contaminants. The average capture velocity was approximantely 0.3 m/s. At another firm (A) the average face velocity of a fume cupboard in use was 0.1 m/s. This was not an adequate velocity to ensure effective containment of airborne contaminants.

5.68 MbOCA vapour will be released during the melting of pellets within an open vessel such as a pan on a hot plate. If the heater is not provided with a thermally activated cut-out device (ideally with an audible alarm) or other temperature control system to prevent overheating, the MbOCA will continue to be heated to a high temperature and high concentrations of vapour will be evolved. If the LEV is not effective some of the vapour will be released into the surrounding environment.

5.69 Recently, there was a release of high concentrations of MbOCA vapour into the workplace at one micro-company (D). Following the incident one of the workers in the vicinity of the melting area had a urinary MbOCA level well above the BMGV. The company had failed to install a suitable temperature control device on the heater and the MbOCA had overheated. A thermostat has now been installed on the heater.

5.70 All heaters used for melting MbOCA have a temperature control device fitted to prevent overheating and the subsequent generation of high levels of MbOCA vapour into the surrounding environment. However, they need to be well maintained to ensure that they continue to work.

Mixing of MbOCA/pre-polymer resin

5.71 The effective mixing of molten MbOCA with pre-polymer resin (heated to 60ºC in an oven) is an important part of the polyurethane production process. It is essential for a good quality product and requires an experienced worker. Mixing is carried out either under extraction or within an enclosure at all the sites visited including the suppliers when required.

5.72 Most of the pouring of MbOCA into the resin is manual. The melted MbOCA is poured carefully into the resin to avoid spillage; the two materials are of a different viscosity so there is a risk of splashing. But at almost all sites there was evidence of spillage some heavy around the mixing vessel.

5.73 Some of the contamination around the mixing vessel was of a fine dusty material ie the deposition of small MbOCA globules that had ‘bounced’ off the resin surface during pouring of the melted MbOCA and had settled on the surrounding area. Adequate worker training and experience of the process can reduce this type of contamination.

5.74 The MbOCA/resin mix is stirred using a stirring rod or similar device for about one to two minutes to produce the correct consistency. When the stirrer is removed from the mixed/resin it is usually heavily contaminated.

5.75 Most operators will let the excess liquid polyurethane drain back into the container but a high number place the stirrer onto the disposable material (eg polypropylene or cardboard) used to line the surface. This causes a build up of contamination and is poor practice.

5.76 Once the MbOCA/resin is thoroughly mixed and cooled most companies remove excess gas bubbles in a Bell jar to improve the final final quality of the product, ie de-gassing. At several companies the mixing vessel was not lidded during transfer to the Bell jar. There was extensive evidence of liquid polyurethane splashing on the Bell jar and in the surrounding area.

Casting, moulding (includes trimming etc) and curing

5.77 Once the MbOCA/resin has been adequately mixed and the liquid polyurethane de-gassed, the container should be lidded before transfer to the casting/moulding area (see Photo 7). This will prevent splashing and the release of vapour. Some companies (eg J) use a teapot to transfer the heated mixed liquid polyurethane to the casting/moulding area. A teapot is used because it contains an attached lid.

Photograph 7 Casting area

5.78 Three of the companies (K, N and O) using reactor vessels to mix the MbOCA and pre-polymer resin use unlidded containers to transport the dispensed liquid polyurethane to the casting/moulding area(s). At one of these firms (O) there was evidence of repeated splashing on the floors leading from the automated dispenser to the casting area.

5.79 At four of the firms, eg A and O, dedicated operatives will carry out the pouring of the liquid polyurethane into the heated moulds; they will do this task

only. At other companies casting and the removal of the cured moulds (and any other process task) will not be carried out by dedicated staff.

5.80 The casting of smaller items is generally undertaken in the MbOCA/resin mixing area under extraction, eg a fume cupboard. However, any large moulds may be cast on extracted benches, on open benches or directly inside the curing ovens (by 15 companies).

5.81 An extracted bench at one of the companies visited (l) had almost no capture because it had been poorly maintained. There was therefore the potential for inhalation exposure to vapour during casting.

5.82 The curing of the moulds is carried out in an oven(s). At most companies the ovens have fitted extraction, ie 65%. The most common type of extraction system is a canopy hood positoned above the oven door. Vapour will be captured if the casting is carried out in the oven or when the oven door is open to check or remove the curing or cured moulds.

5.83 Some of the ovens have internal extraction with venting direct to the atmosphere via ducting. The average capture velocities of the extraction systems above the oven doors were generally poor. There was the potential for MbOCA vapour to escape to the surrounding atmosphere during casting in the ovens or when the doors were open during the curing process.

5.84 Almost all the casting benches and curing ovens were contaminated with hardened polyurethane. There was little evidence that the spillages were being cleaned up promptly using an appropriate method for example, a solution of Decon 90 (2% vol/vol) or sulphamic acid (1% weight/vol). At some companies the pre-polymer resin is stored in a casting oven. At such sites there was hardened resin contamination where it had dripped from the drum nozzle during dispensing and not been removed.

5.85 After a suitable time period usually overnight, the moulds are taken from the curing ovens, carried to a bench and removed. It is expected that at this stage if curing has been satisfactory that there should be no potential for inhalation exposure to MbOCA vapour or for skin absorption of the substance.

Personal protective equipment (PPE)

5.86 All operatives who handle MbOCA wear personal protective equipment (PPE) to prevent skin exposure to the substance and to protect from burning if molten MbOCA or heated liquid polyurethane is spilled. The type of PPE worn does vary from company to company but in general it consists of overalls (re-usable and/or disposable) worn mainly over day-to-day clothing, safety shoes or boots, safety glasses (optional) and gloves.

5.87 Occasionally an apron may be worn over the overalls made from polypropylene or or polyethylene. The re-usable overalls worn are mainly made of polyester/cotton material with elasticated wrists. The disposable overalls or coveralls are mainly made from a spunbonded polypropylene material for greater dust protection. At three firms a laboratory coat (polyester/cotton) is worn as an alternative to overalls.

5.88 If the type of PPE as described above is worn correctly and is well maintained it should protect workers from potential skin exposure to MbOCA and isocyanates during the production of polyurethane elastomer products.

5.89 At three of the companies visited it was evident from the lack of suitable PPE worn that the risks associated with MbOCA skin exposure were not understood. For example, at one of these companies during the scooping, weighing and melting of MbOCA, T-shirts were worn and the arms were therefore

exposed. At another shorts were worn instead of overalls thus exposing the legs to potential MbOCA contamination.

5.90 Most workers change their overalls frequently, eg at least once a week, but some only change them once a fortnight. Disposable overalls or coveralls tend to be used at those companies with a heavy and fluctuating workload and where the risks of exposure may be high. Laundry facilities are available at most sites to wash PPE but some workers are still required to wash their own overalls at home. This is not acceptable.

5.91 During the site visits it was noticed that safety shoes or boots were likely to be heavily contaminated with hardened liquid polyurethane; they were not cleaned often. One worker informed me that he had never cleaned his safety shoes in over two years or more and they were completely coated in hardened polyurethane; a new pair was immediately produced. At another site, several of the operatives removed their overalls before breaks but continued to wear their boots thus potentially contaminating outside areas such as the canteen.

Gloves

5.92 The primary means for preventing skin contamination and the burning of the hands during the handling of MbOCA is by the wearing of suitable gloves or gauntlets. Because the chemically impervious gloves provide such poor thermal insulation it is neccesary to wear inner gloves when handling the hot moulds.

5.93 The type of gloves worn should consider the need for dexterity and the ability to handle the MbOCA satisfactorily during all stages of polyurethane elastomer production. For example, mixing of the molten MbOCA with pre-polymer resin to produce the correct polyurethane mix requires worker dexterity.

Table 9 Types of outer gloves and inner gloves worn during the handling of MbOCA at polyurethane elastomer producers and MbOCA suppliers

COMPANY	OUTER GLOVES	INNER GLOVES
A	Leather	Disposable latex or nitrile
B	Terry towelling	Disposable latex or vinyl
C	Cotton	Disposable nitrile
D	Rubber gauntlets, Terry towelling	Disposable vinyl
E	Terry towelling	Disposable latex (occas.)
F	Rigger	Cotton liners
G	Leather	Disposable latex or cotton liner
H	Cotton	Cotton liners
I	Leather	Cotton liner or disposable PVC
J	Leather	Disposable latex
K	Disposable latex	Cotton liners
L	Leather and disposable nitrile	Cotton liners
M	Terry towelling	Cotton liners
N	Disposable Nitrile	Cotton liner
O	Leather, Rigger or Rubber	Disposable latex or vinyl or cotton liner
P	Terry towelling gauntlets	Disposable latex or cotton liners
Q	Cotton/leather, Polythene	Disposable vinyl
R (Supplier)	Disposable latex or PVC	None
S	Terry towelling	Disposable nitrile
T (Supplier)	PVC gauntlets	None
U	Rigger	Disposable latex
V	Cotton gauntlets/gloves	Disposable latex or nitrile

Table 10 The types of gloves/gauntlets worn and the number of firms using them

TYPES OF GLOVES/ GAUNTLETS	OUTER GLOVES No of firms using them	INNER GLOVES No of firms using them
Leather	7	0
Terry towelling	5	0
Cotton liners	4	10
Rigger	3	0
Disposable nitrile	3	4
Disposable latex	1	9
Disposable PVC	1	1
Polythene	1	0
Rubber	1	0
Cotton gauntlets	1	0
Terry towelling gauntlets	1	0
Rubber gauntlets	1	0
PVC gauntlets	1	0
Disposable vinyl	0	4

5.94 Table 9 shows the range of under and inner gloves worn by the polyurethane elastomer manufacturers and the MbOCA suppliers. Table 10 shows the number of companies using specific types of gloves.

5.93 There is no standardisation to the types of gloves worn in the polyurethane industry; each company uses those that best suit their workers and as selected by trial and error over a number of years. The RAPRA/BRMA Approved Code of Practice indicates that the most suitable glove combination is two pairs of cotton gloves where the top pair can be changed. Only one company (H) uses this glove combination.

5.94 The most common inner gloves worn are cotton liners and disposable latex. The cotton and latex inner gloves are commonly used because they are light and can be easily removed and replaced. The potential for latex to cause skin sensitisation was not known. Companies using such gloves indicated that they would find suitable alternatives, eg disposable nitrile.

5.95 The most common outer gloves are leather and Terry towelling. Companies indicate that the leather and Terry towelling gloves provide the required dexterity during use. They are easy to remove and are of a general thickness to protect the skin from heat. However, the Terry towelling gloves are not recommended for use because they can become heavily contaminated.

5.96 Three MbOCA user companies and one supplier each provide gauntlets for use by their workers. The gauntlets worn at each firm are made of different material. They are worn to protect the hands and forearms from MbOCA contamination. They are used in preference to gloves for most tasks.

5.97 At most firms it was observed that most workers put on and removed their outer gloves at least four times a day. This number increased if there was an additional workload, there were other unrelated tasks to perform or extra breaks were taken. The gloves were mainly placed on a contaminated surface rather than being stored. When put on there was a high risk of skin contamination and contamination of the inner gloves.

5.98 The inner gloves in particular the disposable gloves, eg latex and vinyl, do tend to be changed frequently so the risks of contamination are lower than for the upper gloves. The outer gloves are changed when they are judged by the operative to be heavily contaminated with MbOCA (the glove sample analysis confirms this). It was observed that the procedures for putting on and taking off both the inner and outer gloves were not consistent with good practice (see www.hse.gov.uk/printing for information on the correct removal of gloves etc).

5.99 During the manual handling of MbOCA (eg scooping, weighing, pouring) it is common for the face and hair to be touched with the contaminated outer gloves. The workers need to be informed that such behaviour can cause significant skin exposure. Furthermore, also all workers observed tended to remove their gloves before taking off their overalls and respiratory protective equipment thus contaminating the equipment. On occasions boots and/or safety shoes were removed without gloves thus contaminating the skin.

5.100 After use disposable gloves are thrown into a waste container such as a plastic bag. Empty MbOCA kegs are sometimes used for putting in dirty gloves and other waste materials. Such kegs may contain MbOCA contamination.

5.101 At the end of a shift most workers ensure that the re-usable upper gloves are stored in lockers, drawers or cupboards either in a plastic bag or not. It is company policy at several sites to place the gloves into a plastic bag and leave them on the open bench overnight. It is highly likely that the benches will be contaminated with MbOCA.

5.102 When the pre-polymer resin is decanted from a drum into a container the same inner and outer gloves to be used for handling MbOCA may be worn. However, this is not always the case and it is common to decant the resin without gloves. Gloves will be worn when the MbOCA is then handled.

5.103 Some companies supply barrier creams and/or emollients (moisturisers) for use with the gloves. It is believed that the creams will provide additional skin protection. This is not so. A cream will be removed from skin areas when the gloves are put and during manual tasks. There was no evidence that barrier creams were being used as substitutes for the wearing of gloves.

Respiratory protective equipment (RPE)

5.104 Respiratory protective equipment is rightly provided by 16 of the MbOCA user companies to control inhalation exposure to MbOCA during short-term tasks for example, the filling of hoppers, the scooping of pellets from a keg, the sweeping up of spillage, general maintenance tasks etc.

5.105 The remaining firms (E, F, S and U) have considered the wearing of suitable RPE in particular when scooping the MbOCA from the drum and for basic maintenance tasks. However, they have decided against the use of RPE as they believe that the inhalation exposure risk is minimal during these tasks. But suitable RPE for example, a half-face mask respirator FFP2 should be worn during these tasks as the exposure risks are not minimal.

5.106 The polyurethane elastomer manufacturers and the suppliers of the pre-polymer resin are of the opinion that the risk of inhalation exposure to isocyanate during the decanting of resin (and other tasks where handled) is negligible. The evidence from the urine samples analysed for urinary isocyanate metabolites suggest otherwise. One company, however, does provide a half-face mask respirator with a single A1 filter for wearing during decanting to control vapor exposure only; it is worn infrequently.

5.107 One supplier provides RPE ie a disposable half-mask respirator with FFP3 classification and an assigned protection factor (APF) of 20 to be worn when a drum is damaged and the spilled MbOCA pellets need removed. During cleaning the risk of inhalation exposure to dust is expected to be high.

5.108 Nine companies provide disposable half-mask respirators with classifications ranging from FFP1, FFP2 and FFP3 (mostly FFP1 and FFP2 worn) and APF's of 4, 10 and 20 respectively. They are worn mainly when scooping MbOCA from drums and during maintenance work.

5.109 Six companies provide half-face mask respirators with either single (eg P2) or dual cartridge filters (eg A2P2) for protection against particles and vapour/particles respectively during short-term tasks. At one firm a half-face mask respirator with dual cartridge filters A2P3 is worn when pouring the mixed liquid polyurethane into moulds whereas at another firm a similar respirator but with dual cartridge filters B1P1 is worn during maintenance tasks. One company provides a full-face mask respirator with a single P3 cartridge filter for maintenance work only.

5.110 The operatives at three companies (J, L, O) wear air-fed breathing apparatus with visors during all stages of MbOCA handling to provide additonal protection from airborne MbOCA exposure. Two of these companies and one other also provide powered (fan-assisted) respirators with hoods and single A2P2 cartridge filters to be worn during the full polyurethane manufacturing process.

5.111 Both the air-fed and powered respirators will provide the maximum protection from airborne MbOCA exposure if they are well maintained. But the companies need to ask whether such protection is necessary in particular if the MbOCA is handled under extraction.

5.112 It is essential that when wearing filtering facepieces, half-face and full-face mask respirators that they are tight-fitting to provide a good face seal and of the correct size and shape to fit the wearer's face. The performance of RPE with a loose-fitting facepiece such as visors and hoods is less dependent on a tight seal but still needs to be of the correct size to ensure an adequate fit and protection.

5.113 Fit testing of facepieces will ensure that the selected tight-fitting facepiece (eg disposable half-face mask respirator) is the correct device. For such filtering facepieces a qualitative test will suffice but for full-face masks a quantitative fit test will be required. Only two of the companies that use RPE and require fit testing of the facepieces have actually done so.

5.114 These two companies employ over a hundred workers and have dedicated health and safety personnel. There was a lack of awareness of the need for facepiece fit testing at the other companies including one supplier. This lack of awareness could explain the fact that a number of workers who were not clean-shaven wore RPE in particular the disposable half-face mask respirators. A good face seal can only be obtained if the wearer is clean-shaven in the region of the seal.

Control of MbOCA spread - on surfaces

5.115 During all stages of MbOCA handling there will be the potential for the contamination of surfaces, for example from dust and pellets during scooping into a container/pouring into a hopper, from the liquid during the melting and mixing with pre-polymer resin and from the liquid polyurethane during casting (see Photo 8). The use of disposable materials such as card can contain the contamination in particular in those areas more likley to have a build up of contamination, eg the inside of a fume cupboard.

Photograph 8 MbOCA pellets around hopper

5.116 Furthermore, the installation of stainless steel surfaces and/or polypropylene plastic can ensure that the cleaning and decontamination of surfaces is made easy and can be carried out before visible accumulation occurs.

5.117 The work areas of all user companies have visible evidence of contamination, especially in those areas where build-up is expected, ie around a hopper and keg, in the melting, mixing and casting areas and in the curing ovens. But it is around the hoppers, the weighing areas and the ovens in particular where concentrations of contamination are the highest.

5.118 One large company uses sheets of card placed on the floors around a partially enclosed extraction booth and in the casting area to contain the levels of contamination (see Photo 9). It was expected that the card would be changed daily but this was not the case and there was a build up of hard material on the card. Another company handles the MbOCA on stainless steel surfaces but the contamination is not frequently cleaned from the surfaces.

Photograph 9 Sheets of card on and around a booth to contain spillage

5.119 The standard of housekeeping at most companies is not adequate. At almost 80% of companies (n=16) it is poor. For example, surface contamination is not immediately cleaned up. It is allowed to accumulate with the potential for skin exposure and transfer to other parts of the plant. At many sites pellets are allowed to accumulate on the floor, with the potential to be stood on and crushed.

5.120 Ovens used for curing the moulds tend to be coated with dried liquid polyurethane that has hardened on oven doors and handles. The fitting of plastic polypropylene in such accessibly contaminated areas would allow easy wipe down. But even in those factories where it is installed, the contamination is not regularly removed or spillages immediately cleaned up.

5.121 At those few companies with reasonable housekeeping there is still evidence of significant contamination. Care is taken, however, when decanting pre-polymer resin and when pouring molten MbOCA to ensure minimal or no spillage.

5.122 Some polyurethane producers successfully use a commercially available wipe sampling technique to detect MbOCA surface contamination. It is a colourimetric technique and it is simple to use. It is mainly used for detecting if any MbOCA is still on a surface after cleaning and to check for spread in areas where MbOCA should not be present.

5.123 However, the test will not only detect MbOCA but other amines. One large company was not aware of this limitation and was reporting positive results in areas where MbOCA was not being used. The amine causing the positive reaction was identified as 4,4'-methylenedianiline.

5.124 Another company (N) uses UV light to detect MbOCA contamination on surfaces and on workers' skin and clothing. Contaminated surfaces fluoresce so they are easy to detect and clean. Workers' hands are scanned before washing so that the level and location of MbOCA contamination can be detected and after the hands have been thoroughly washed to check that the hands are clean.

5.125 The use of such methods in particular wipe sampling to detect MbOCA surface contamination are very useful. All companies should consider their use as part of their overall risk assessment.

5.126 All contaminated waste including card, rags, gloves and overalls are placed in empty MbOCA kegs and/or similar receptacles. When full they are regularly removed by specialised contractors. At a couple of the smaller user companies, the waste material is not regularly collected. There was widespread evidence of containers being overfilled. A specialised contractor is not usually employed to remove the waste and it may be collected and disposed of as normal waste

5.127 It is common for 'empty' MbOCA kegs to be used as waste receptacles. At one company the keg still contained MbOCA pellets. In other parts of the plant 'empty' MbOCA kegs were being used as tables for the placing of tools, drinks etc. This was an irresponsible practice that was stopped immediately.

Control of MbOCA spread – other means

5.128 There are other means to reduce the spread of MbOCA in the workplace, these include:

- removing PPE/RPE before leaving the MbOCA work area for whatever reason (eg breaks and lunch time);

- preventing other workers not involved with polyurethane manufacture from entering the workplace;
- limiting the PPE/RPE worn during MbOCA processing to those tasks only;
- providing each worker with their own PPE/RPE that should not be shared;
- providing changing facilities and lockers for PPE/RPE storage;
- preventing eating, drinking and smoking in the work area;
- providing adequate washing facilities that are in the workroom; and
- ensuring good personal hygiene.

5.129 Approximately 12 (60%) of companies try to utilise all the above means to reduce the spread of MbOCA outside the workplace whereas the remainder have problems trying to ensure the use of three or more. The use of good personal hygiene is the most difficult for companies to enforce because it requires self-discipline and good staff supervision.

5.130 For example, at one factory a member of the MbOCA processing staff was allowed to wear a heavily contaminated piece of clothing for several months before internal disciplinary action was required to make him remove it. During this time there was significant skin absorption resulting in a high urinary MbOCA level.

5.131 Washing facilities are provided in the MbOCA work areas of most companies. But during the survey many workers were observed to leave the work area without washing their hands or removing their PPE after having handled MbOCA and/or resin.

5.132 One company does not have local washing facilities. MbOCA handlers have to open two doors and walk through another part of the plant to reach the nearest washing facilities. There is therefore the potential for MbOCA to spread to other parts of the factory and contaminate surfaces.

5.133 At many MbOCA users there was widespread evidence of drinking and eating in the MbOCA handling areas although company policies forbid it. Supervision at such sites is not satifactory and needs to be improved.

6 Use of controls

6.1 It is necessary that all employees handling MbOCA wear the PPE provided by the employer, in particular the gloves and overalls, to prevent skin absorption. And all workers should handle the chemical using the control procedures as outlined by the company, eg weighing and melting MbOCA within the extraction system provided. This was the case at most sites visited but there were occasional lapses by the workforce due to poor supervision or poor hygiene.

6.2 Because of the nature of MbOCA and the potential for skin absorption each worker should practice a high standard of personal hygiene. For example, this may include changing gloves when heavily contaminated or damaged, cleaning surface contamination when it arises and washing the hands before eating and drinking.

6.3 The standards of personal hygiene vary between companies and individuals. Some workers handling MbOCA wash their hands frequently and do not eat or drink

in the workplace, ie they observe good hygiene practices. Other workers are lax in their hygiene standards. Such lax behaviour does put other workers at risk of exposure. Many companies turn a 'blind eye' to such behaviour rather than try to enforce any discipline.

6.4 The employer should ensure that the employees use the control measures provided to mitigate MbOCA exposure. They should also provide adequate supervision to ensure that the defined methods of work are being followed and that the control measures used, such as the LEV systems, are effective when in use (in the majority of companies this was not always the case).

6.5 There was evidence of poor supervision at many sites visited. There were several reasons given for this. For example, the workers were experienced and knew the job so did not need to be closely supervised, they would not do the tasks correctly even if told how to etc. Improvements need to be made in employer/employee relationships to ensure better and more robust supervision.

7 Maintenance of control measures

Local exhast ventilation systems

7.1 Regular maintenance of a LEV system is essential to ensure that it contains and extracts the airborne contamination effectively. This can be achieved by:

- checking the airflow speed into the LEV system using, for example, a hand-held anenometer;
- observing the capture efficiency where the airborne contamination is generated using a smoke tube;
- checking the filters for blockage; and
- the integrity of the ducting if capture is reduced etc.

7.2 Any reductions in the effectiveness and/or efficiency of a LEV system should be reported to an appropriate person and immediately rectified, eg by replacing a filter if blocked, by cleaning the fan etc. All damages detected in a LEV system, such as holes in the ducting, should be repaired immediately. Records should be kept of any tests and remedial/maintenance work carried out.

7.3 Most of the companies carry out regular internal maintenance of their LEV systems, eg changing of filters where appropriate. Ten companies use an anenometer or smoke tube to check the air velocities or capture efficiencies respectively of their LEV systems. This is mainly on a weekly or monthly basis. However, only two of these companies keep regular records of the results.

7.4 During the survey, HSE measured the average airflow velocities on appropriate LEV systems using a hand-held anenometer. Interestingly, the average face velocities of most partially enclosed extracted booths and fume cupboards were less than 0.5 m/s. The capture velocities of the extraction systems tested were mainly below 0.8 m/s (BRMA/RAPRA recommend a minimum of 0.8 m/s).

7.5 For example, two companies (E and J) using canopy hoods to provide extraction during weighing, heating and mixing of MbOCA had measured capture velocities of less than 0.5 m/s. Another company (I) using a fume cupboard for

weighing, heating and mixing the chemical had an average face velocity of 0.3 m/s; it was therefore not likely to be effective at containing any vapours or dust released during handling.

7.6 All LEV systems used for controlling exposure to MbOCA should be thoroughly examined and tested at least once every 14 months by a competent person to ensure that the system is performing effectively and efficiently. Any faults detected during the examination and testing should be promptly rectified. The employer should keep a record of the examination and testing for at least five years.

7.7 The survey revealed that 14 (70%) of the MbOCA users had not carried out a thorough examination and testing of their LEV systems as required by COSHH regulation 9. The operatives handling the MbOCA during weighing, heating and mixing procedures were therefore at an increased risk of exposure to MbOCA dust and/or vapour. There was also likely to be an increased risk of exposure to isocyanates during the mixing process. However, the two distributers who use fume cupboards for handling MbOCA both complied with COSHH regulation 9.

7.8 One large polyurethane elastomer producer (B) carried out in-house examination and testing of all of their LEV systems in the factory. It was believed that this was sufficient to comply with the legislation. On further investigation it was discovered a thorough examination and testing was not being carried out on the LEV systems but just basic maintenance checks.

7.9 Six (30%) of the MbOCA users had had thorough examination and testing of their LEV systems but 4 (67%) of these companies had failed to improve/repair any faults reported by the examiner for example, cleaning the fan, replacing filters. In the industry there appears to be a lack of awareness of the need for thorough examination and testing of LEV systems as required by COSHH regulation 9. The reasons for this are not clear.

7.10 Companies that were not complying with the legislation were asked to have their LEV systems thoroughly examined and tested by a competent person within four to six weeks. As part of this 'live intervention' any faults identified were to be promptly repaired to ensure that the LEV systems were effective and efficient and would control exposure to MbOCA.

7.11 The appropriate documentation was sent to HSE within the set time period to indicate that the appropriate LEV examinations and tests had been carried out. There is evidence mainly from the industry trade association that all companies are now complying with the legislation to ensure that all their LEV systems are thoroughly examined and tested at least once every 14 months.

PPE including RPE etc

7.12 Employers should ensure that accomodation is provided for the PPE so that it can be safely stored or kept when not in use. Fourteen (70%) of the manufacturers provide lockers for storing PPE including overalls, safety shoes/boots etc. The lockers of three (15%) of these companies are situated outside the work area; surfaces may therefore become contaminated when the PPE is removed.

7.13 The six (30%) MbOCA users not providing lockers do provide pegs or shelves for hanging worker's overalls. They are located in the work areas so that any potential contamination is contained and does not spread.

7.14 The two MbOCA suppliers provide lockers. They are located outside the laboratories where MbOCA is handled. There is therefore the small risk for contaminating the surrounding surfaces when the laboratory coats are removed.

7.15 In general, both re-usable and disposable overalls tend to be replaced frequently or immediately if they become heavily contaminated with MbOCA (see Photo 10). However, not all companies have adequate laundering facilities. Some workers therefore need to take contaminated overalls home to wash. There is the potential for their homes to become contaminated.

Photograph 10 A heavily contaminated overall

7.16 Most workers handling MbOCA change their disposable gloves frequently. The reusable gloves are checked for contamination regularly during routine work. They tend to be replaced if the contamination is visible or they are damaged in any way.

7.17 At fourteen (70%) of the companies visited there was evidence of the reusable gloves being left on a bench, with the potential for contamination whilst workers had a break or went for lunch. When not in use all gloves should be adequately stored so that they do not contaminate surfaces themselves or become contaminated with MbOCA.

7.18 The RPE should be effectively maintained to ensure that the equipment continues to provide the protection for which it was designed. This will include cleaning, disinfection, examination, repair, testing, safe storage and record keeping.

7.19 Most companies provide disposable half-face dust mask respirators. This type of RPE requires little maintenance but they should be stored safely. Furthermore, they should only be worn for short-term tasks (ie up to a hour), such as pouring MbOCA into a hopper, changing filters etc and then replaced. However, there was extensive evidence that this type of respirator was being worn for several tasks over a full shift.

7.20 Re-usable RPE, eg powered (fan-assisted) respirators, require cleaning and disinfection after each use and then should be stored in a suitable storage area rather than left on a bench in the open. And where appropriate, the replaceable filters should also be changed on a regular basis to ensure their effectiveness.

7.21 However, at all those companies using re-usable RPE with a replaceable single or dual filter cartridge system there was confusion as to the time required before filters needed to be replaced. The manufacturers instructions were not always clear. It is common for replaceable filters to be changed when the odour of the workplace can be detected through the filter. At one company the replaceable filters are replaced when breathing becomes laboured indicating a heavily contaminated filter.

7.22 For general use the filters should last for a week or more before replacing. But it depends on the frequency and quantity of MbOCA handled. For half-mask and full-face mask respirators the filters may need changing daily. Advice on how often replaceable filters should be changed is given in HSE's guidance HSG53 *Respiratory protective equipment at work: A practical guide*.

7.23 At three sites air-fed breathing apparatus is worn by workers to provide additional exposure protection during the handling of MbOCA. At two of the firms the quality of the air delivered is tested every three months. But at the other firm the air supply quality is carried out only every six months. The quality of the air supplied to the breathing apparatus should be tested at least once every three months and more frequently when the quality of the air supplied cannot be assured.

7.24 Defined working procedures are needed to ensure that MbOCA is not spread throughout the workplace. Such procedures include cleaning of contamination on surfaces, maintaining personal hygiene, not eating and smoking in the work area etc. The procedures in place should be checked regularly to ensure that they are still being followed, are still workable or can be improved.

7.25 For example, at company N swipe tests are carried out regularly to detect surface contamination. The surfaces are cleaned thoroughly by the workers if MbOCA contamination is found. Any break down in this procedure could result in a build up of MbOCA surface contamination, with the potential for skin absorption.

8 Monitoring of exposure

Personal inhalation exposure/fixed place monitoring

8.1 Monitoring of personal inhalation exposure to MbOCA is required to ensure that the WEL of 0.005 mg/m^3 8-hour TWA is not exceeded, to check that the control measures in use are effective and/or to determine if changes in handling conditions such as an increase in use and quantity may effect worker exposure.

8.2 But the main route of exposure to MbOCA is skin absorption; significant inhalation exposure may only occur if the non-volatile MbOCA is agitated or heated. COSHH ACOP para 203 (d) indicates, therefore, that if biological monitoring confirms that the total absorption by all routes, skin, inhalation and ingestion is below the BMGV then air monitoring is unnecessary.

8.3 In this survey personal inhalation exposure to MbOCA only exceeded the WEL in two situations (when the heated mixture was poured into mouldings without the use of exposure controls, eg appropriate LEV). So if MbOCA is effectively controlled during all stages of handling then there should be little airborne exposure and no need to monitor personal exposure.

8.4 However, if during urine testing the BMGV is exceeded (or is at half the BMGV or above) then the use of airborne monitoring may be part of the investigation of the cause(s).

8.5 Only seven (35%) of the MbOCA user companies have carried out personal inhalation exposure monitoring mainly to check compliance with the WEL. The monitoring is carried out about once a year by an outside occupational hygiene consultant. Those few exposures exceeding the WEL have been due to ineffective control measures or to a breakdown in procedures for handling MbOCA.

8.6 The use of fixed place monitoring can be mainly used to check on the effectiveness of the measures to control exposure to MbOCA in particular the LEV systems. If the LEV is ineffective then airborne MbOCA vapour may not be contained and contaminate the surrounding air.

Biological monitoring

8.7 Biological monitoring for MbOCA is useful because it will measure absorption of the chemical by all routes in particular through the skin. It is recommended that the concentration of urinary MbOCA should be monitored every six months for those workers directly handling MbOCA. This will determine if the measures to control exposure are effective.

8.8 Urine samples should be taken in appropriate containers at the end of the shift. The detection of MbOCA indicates that there has been exposure to the chemical by one or more exposure routes. The MbOCA should be measured in relation to the creatinine level in urine. If controls are effective there should be little or no urinary MbOCA detected.

8.9 The BMGV for MbOCA is 15 µmol/mol creatinine (set at 90th percentile). The BRMA/RAPRA Code of Practice indicates that ‘any excursion above this level or even readings approaching half the limit should result in a full investigation into control measures and MbOCA handling procedures’. Once the full investigation of exposure has occurred then repeat urine samples should be taken to show that the controls in force are now effective.

Surface wipe sampling

8.10 The cleanliness of workplace surfaces should be monitored on a daily, weekly or other time period using surface wipe sampling. Such sampling should be used to determine if MbOCA contamination is present on a surface(s) and/or to determine the spread of contamination.

8.11 Three companies regularly use a commercial system for surface contamination monitoring. Where contamination is detected the surface(s) is cleaned. And one company uses UV light to successfully monitor for contamination on surfaces and on worker’s skin. No companies use a quantitative test for monitoring the concentration of MbOCA on surfaces and for assessing the spread of contamination.

9 Health surveillance

9.1 The BRMA recommend bi-annual urine cytology screening for bladder tumours for those workers potentially exposed to MbOCA. However, only one large polyurethane elastomer manufacturer carries out exfoliative urine cytology screening (every six months). No positive results have so far been discovered.

9.4 Most manufacturers including suppliers where appropriate use health care professionals either an occupational health nurse, a registered medical practitioner

(eg occupational health physician) or both, to provide health surveillance. Several of the larger companies provide in-house health surveillance, mainly by an appointed occupational health nurse.

9.5 The appointed health care providers are mainly employed to carry out lung function tests (LFTs) on those workers handling isocyanates. This includes MbOCA workers. A reduction in the functioning of the lungs may indicate repiratory disease and should be further investigated by a medical practitioner.

9.6 In general, urine samples are collected for monitoring urinary MbOCA on the day the workers have their LFTs. Urine monitoring is therefore integrated into the health surveillance. The results of the urine monitoring for MbOCA are returned either to the health care provider or more commonly the employer.

9.7 It is recommended by HSE that workers handling isocyanates should be routinely tested annually while exposure continues. But of the 20 polyurethane elastomer producers 12 carry out routine LFTs etc on workers once every six months, two carry out the tests once a year as recommended and six only when appropriate or not at all. Some of the latter six companies are therefore putting the health of their workers at risk of developing respiratory disease.

9.8 Furthermore, the frequency of biological monitoring for urinary MbOCA as carried out by many companies is not once every six months as recommended by HSE (see Table 11).

Table 11 Frequency of biological monitoring for urinary MbOCA in polyurethane elastomer manufacturers

Frequency of monitoring for urinary MbOCA				
Monthly	6 Monthly	Yearly	Other	Never
2 (10%)	12 (60%)	2 (10%)	2 (10%)	2 (10%)

[X] One company had LFTs and sampled for urinary MbOCA every three months
One company had LFTs and sampled for urinary MbOCA when high workload

9.9 One of the companies (B) who do not carry out LFTs or monitor workers for urinary MbOCA levels employs over 50 workers and handles over 30 kg of MbOCA per day; the other company (G) employs four workers and handles about 20 kg of MbOCA per week. The larger company provides the services of an occupational health nurse every three months for advice. Both companies could provide no valid reason for not monitoring urinary MbOCA.

9.10 Those companies carrying out biological monitoring monthly for urinary MbOCA do so because of the high volume of the substance handled and to regularly check the control measures for effectiveness. One of these companies issues a pre-employment heath surveillance questionnaire to new staff and carries out regular LFTs.

9.11 The two companies who monitor workers for urinary MbOCA on a yearly basis do so because the risk of exposure to MbOCA is perceived to be low. Both companies indicate that the BMGV has never been exceeded.

9.12 Four of the smaller companies, ie employing less than 15 workers, are failing to take the urine samples for monitoring urinary MbOCA at the end of the working day shift. The results therefore may not reflect the true MbOCA exposure.

9.13 At some companies there has been confusion about the interpretation of the urinary monitoring results. This is because results have been returned from the

analyst without calculating the concentration of MbOCA in relation to the creatinine levels. This has led to urinary MbOCA levels being reported as high. Furthermore, one analyst calculated the urinary MbOCA based on hydration rather than creatinine. The returned results could not be compared with the BMGV.

9.14 Concerns have been voiced in the industry that maintenance personnel (some who are sub-contracted) are never monitored for urinary MbOCA or included in health surveillance programmes. If there is the potential for exposure to MbOCA, for example during LEV maintenance, then they should be monitored for urinary MbOCA at the end of the shift. If there is likely to be exposure to isocyanates then it will need to be assessed if they should be included in health surveillance.

9.15 Records of health surveillance including the results of biological monitoring should be kept for a minimum of 40 years. Each worker's individual record will be important to relate the effects of potential exposure to MbOCA and isocyanates with possible future health effects. The results will also be important for future epidemiological studies on the relationship of bladder cancer and MbOCA exposure.

9.16 Those companies that employ in-house occupational health providers have better systems of record retrieval than those companies that use outside providers. Some of the smaller companies in particular had difficulties in retrieving information on individual worker's health surveillance.

9.17 Over half of the polyurethane elastomer producers have been established for over 10 years or more. If these or any of the newer firms decide to cease trading then health surveillance records may be lost unless they are given to HSE for safe keeping.

10 Information, instruction and training

10.1 It is essential that all operators handling MbOCA and isocyanate-based pre-polymer resins are aware of the possible health effects from workplace exposure to these chemicals. They should also know about and how to use the measures to control exposure and thereby reduce the risks to health

10.2 This requires a programme to provide effective information, instruction and training. Unless such a programme is implemented and updated as new information is available, then the workers may increase their exposure risk to MbOCA/isocyanates during handling. Records should be kept of training etc given to workers.

10.3 The survey has revealed that 8 (40%) companies do not provide any formal information, instruction and training on MbOCA and isocyanate handling. One of these is a large company (C) and employs over 120 workers with several directly involved with polyurethane elastomer manufacture.

10.4 Nine (45%) companies provide induction courses only on the hazards associated with production and on the measures used to control exposure to the hazards. There is no additional updating of information etc.

10.5 Three (15%) companies provide induction courses and also regular update training. The MbOCA handlers (over 21 workers) at one of these companies are provided with an initial induction programme. It includes a discussion of the health hazards and on the means to reduce exposure. The workers also attend an external course on COSHH. They are also provided with regular information updates. Each worker retains as a signed record of the training etc given.

10.6 In general, companies that have provided induction courses and regular updates of information have less MbOCA surface contamination and more effective exposure control. Those companies providing no training etc tend to have the poorest record of controlling exposure to MbOCA.

10.7 The two suppliers of MbOCA and isocyanate pre-polymer resin both provide general information, instruction and training to operatives who handle kegs. The information etc includes details on the chemical nature of the kegs contents and the potential health effects of exposure. Only one of the suppliers (R) provides formal refresher courses.

11 Conclusions

General

11.1 The use, exposure and management of the risks from handling MbOCA in the polyurethane elastomer industry was studied as part of HSE's Disease Reduction Programme (Carcinogens Project). The results of the study can be used to revise HSE's guidance on the control of MbOCA, eg *COSHH essentials*, to provide recommendations on MbOCA exposure control for use by the polyurethane elastomer industry and to provide evidence from which HSE and stakeholders can develop a model for intervention activity and thereby reduce occupational exposure to carcinogens.

11.2 MbOCA is used in the production of high-quality, abrasion-resistant polyurethane products, for example gaskets, shock absorbers and gearwheels. At present there are no safe and effective elastomers to replace the use of MbOCA. It is unlikely that satisfactory substitutes for the chemical will be found in the near future though they are being sought.

11.3 The three potential routes of exposure to MbOCA during handling are inhalation, skin absorption, and ingestion. Skin absorption is the major route of entry into the body.

11.4 Most company COSHH risk assessments are unsuitable and insufficient; they could be improved. Most companies provide inadequate information, instruction and training on the risks associated with handling MbOCA (and isocyanates) and on the measures to control exposure etc. During handling many workers are therefore at a high risk of exposure to MbOCA and isocyanates.

11.5 There is widespread evidence of the use of ineffective, inefficient and poorly maintained LEV systems during polyurethane elastomer production, eg the weighing, melting and mixing of MbOCA. **This is a major issue.**

11.6 Much of the hand scooping of MbOCA from a keg is carried out in the open workroom. The pouring of MbOCA pellets into a hopper is carried out under extraction. The handling of a keg within a glove box is within an enclosed system and therefore there is negligible MbOCA exposure.

11.7 The standards of housekeeping between the manufacturing companies vary but generally they are poor for example, spillage is not being immediately cleaned and is allowed to accumulate. In all instances there is major room for improvement.

11.8 Many companies fail to ensure that their employees practise good personal hygiene. They do not provide suitable supervision. There is widespread evidence of workers eating and drinking in the MbOCA handling areas and leaving the work area without washing their hands. Most of the firms provide adequate washing facilites.

11.9 Most producers provide health surveillance because their employees handle isocyanates. Biological monitoring for urinary MbOCA is incorporated into the health surveillance.

11.10 At many companies there is a general misunderstanding as to the frequency of urinary MbOCA monitoring with only 60% carrying out sampling on a recommended six monthly basis. There is a concern that maintenance personnel are not being included in the urinary MbOCA monitoring programme.

PPE/RPE

11.11 Operatives who handle MbOCA and isocyanate pre-polymer resins wear PPE for example, overalls, gloves, safety shoes, safety glasses to prevent skin exposure (and burning from molten MbOCA). The types of PPE worn differ between companies and therefore there is no overall standardisation. For example, five types of inner gloves (mainly cotton liners) and 12 types of over gloves (mainly leather) are worn. But they do provide adequate exposure control if correctly worn.

11.12 There is a need for better training and supervision to ensure that the PPE provided is worn when required, changed at frequent intervals and stored and maintained adequately. This is not always the case.

11.13 Respiratory protective equipment for example, a half-face mask respirator FFP2 is worn by employees at most polyurethane manufacturers especially for short-term tasks such as the filling of hoppers.

11.14 The types of RPE worn and the degree of protection differ betweeen the various companies. Few companies wear RPE for handling pre-polymer resins for example when decanting from a drum. It is believed that the exposure risks are negligible; **they are not.**

11.15 Only two companies have carried out fit-testing of the facepieces worn. Most companies are not aware of the need for fit-testing.

Personal inhalation exposures

11.16 Due to a combination of the use of pellets/granules, the low volatility of the chemical **and the use of LEV**, exposure to airborne MbOCA (dust and vapour) should be controllable.

11.17 A total of 80 personal inhalation exposures to MbOCA were measured. Only 13 (16%) personal exposures were above the level of detection and two of these exceeded the WEL. The high personal exposures were from workers who poured mixed liquid polyurethane into moulds on an open bench without extraction.

Surface sampling results

11.18 One hundred and fifty-six (60%) surface wipe samples had evidence of MbOCA contamination; it was heaviest around the hoppers where MbOCA pellets/granules were poured and on surfaces around the weighing and pouring areas.

11.19 One of the suppliers provided evidence of MbOCA contamination on imported kegs. The contamination was high in relation to that recorded from kegs sampled at most producers. It is highly likely that imported kegs will continue to be contaminated.

11.20 The concentrations of MbOCA on the outer gloves were in general much larger than those on the inner gloves. It was not possible to statistically assess for correlation between inner and outer gloves. However, it was possible to show that the concentration of urinary MbOCA was related to the quantity present on the outer gloves only. This would indicate a lack of good hygiene practice eg in removal of gloves.

Urinary MbOCA results

11.21 A total of 78 urine samples were collected to determine the concentration of urinary MbOCA in those directly and indirectly exposed to the chemical. Over half of these urine samples had measurable MbOCA concentrations.

11.22 There were noticeable differences between the directly and indirectly exposed groups. Surprisingly, urinary MbOCA concentrations in the indirectly exposed group were higher than expected (median 2.53 µmol/mol creatinine). This may reflect skin exposure via surface contamination.

11.23 Three of the urine samples in the directly exposed group were above the BMGV of 15 µmol/mol creatinine (set at 90th percentile). The 90th percentile of the present study is 8.85 µmol/mol creatinine, suggesting that there have been improvements in occupational hygiene practice within the industry since 1995. A BMGV revised to 10 µmol/mol creatinine would reflect today's good practice in the polyurethane industry.

11.24 The urine samples were also analysed for isocyanate diamines eg 2,4 toluenediamine. Many results were above the BGMV of 1 µmol/mol creatinine for isocyanate metabolites thus indicating poor exposure control to the substance.

11.25 There was a strong statistical association between urinary MbOCA and urinary isocyanate diamines.

11.26 It can be finally concluded that if the principles of good practice as outlined in COSHH regulation 7(7) Schedule 2A are **applied at all times** then exposure to MbOCA (and isocyanates) should be well controlled during polyurethane elastomer manufacture.

12 Recommendations

Risk assessment

12.1 Each company needs to ensure that they have a suitable and sufficient assessment of the risks to health whilst handling MbOCA and isocyanates and on the measures to prevent or control exposure. It is important that the COSHH risk assessment applies specifically to the work carried out, ie it should not be a generic risk assessment.

12.2 Relevant information to include in the risk assessment can be found in the Safety Data Sheets supplied by the suppliers of MbOCA and isocyanate-based pre-polymer resins. A competent person should carry out the risk assessment. An experienced MbOCA handler may be the most relevant person to undertake the assessment in some cases.

12.3 The risk assessment should be reviewed regularly. This is critical especially if the results of monitoring frequently indicate 'high' urinary MbOCA levels (> 8 µmol/mol creatinine). It should also be reviewed if there are regular changes in the volume or rate of elastomer production etc.

12.4 Further information to help with producing the COSHH risk assessment can be found in HSE's COSHH essentials available on www.coshh-essentials.org.uk and in HSE's publication *A step by step guide to COSHH assessment* HSG97 (Second edition) HSE Books 2004. The trade association, ie Polyurethane Elastomers Group, also provides relevant information.

Exposure control – general

12.5 Because MbOCA has been assigned the risk phrase R45 'May cause cancer' all the principles of good practice for the control of exposure to substances hazardous to health, ie COSSH Schedule 2A should be applied **at all times**. If applied conscientiously the principles of good practice will prevent or adequately control exposure to MbOCA and isocyanates.

12.6 Although all companies use some of the principles of good practice to mitigate exposure to MbOCA, for example the use of LEV, wearing gloves to prevent skin exposure etc there are still some specific areas that need addressing (see below).

12.7 No unspecified person(s), for example office workers and visitors, should be in the segregated area(s) when MbOCA is being handled unless supervised. There is a risk of exposure to MbOCA via inhalation, skin or by ingestion. It is unlikely they will be wearing PPE.

12.8 Where appropriate, in-use MbOCA kegs should be lidded when not required and stored in a dedicated dry area ideally away from the main MbOCA work area. This will prevent or reduce the risk of contamination to the outside of the keg(s) during handling.

12.9 Manual scooping of MbOCA from kegs should be carried out under extraction to reduce the risks of airborne dust exposure. Any spillage of MbOCA pellets or granules in particular in the area surrounding hoppers should be immediately cleaned up using an industrial vacuum.

12.10 Companies with automatic dispensers should pour the liquid carefully to prevent splashing, provide LEV at or around the dispenser to remove airborne contaminants and have an appropriately positioned drip tray to capture any drips. Molten liquid polyurethane should be covered with a lid if it is to be tansported to another part of the work room.

12.11 The weighing, melting, mixing and casting of MbOCA should be carried out under LEV, for example a partially enclosed extraction booth, fume cupboard, canopy or downdraft table that is effficient and effective. For a fume cupboard or booth the average face velocity should be not less than 0.5 m/s. The average capture velocity for appropriate LEV systems should not fall below 0.8 m/s.

12.12 The molten MbOCA should be poured carefully into the pre-polymer resin to prevent surface contamination. The stirrer should not be placed onto the surface liner, eg polypropylene, as it will contain excess mixture; it should be allowed to rain back into the mixture. Any splashing should be cleaned immediately with a rag otherwise a build-up of material may develop.

12.13 The heated mixture should only be transferred from one part of the work area to another in a lidded container to prevent spillage onto the skin and onto surrounding surfaces and to prevent airborne exposure to vapour.

12.14 During casting, any local spillage should be immediately cleaned. This includes the cleaning of any spillage on and/or inside the curing ovens. There should be extraction on the inside or outside of the curing ovens to remove evolved vapours during curing. The removal of moulds following curing does not need to be under extraction. It is highly unlikely that there will be any MbOCA vapour release from the moulds or any free surface MbOCA that may be absorbed.

Exposure control - PPE/RPE

12.15 It is essential that during the handling of MbOCA the skin is protected from contamination and subsequent dermal absorption. All operatives handling MbOCA should wear appropriate PPE at all times, eg overalls, safety shoes, safety glasses and gloves.

12.16 There is no standardisation of the types of gloves to be worn but cotton lined inner gloves and leather outer gloves would provide suitable protection during the handling of MbOCA. Terry towelling outer gloves are not recommended for wearing as they are easily contaminated and retain the contaminants.

12.17 All gloves should be put on and removed correctly to reduce the potential for skin contamination. Under no circumstances should gloves be left on a bench or other contaminated surface when not in use.

12.18 The outer gloves should be changed frequently, ie when heavily contaminated or damaged to prevent a build-up of contaminants on the surface that may be permeate through the glove. It is expected that disposable gloves will be changed at least four times daily.

12.19 Barrier creams may be worn to provide additional skin protection. There use should not replace the wearing of gloves.

12.20 It is essential that the wearers of tight-fitting facepieces, eg disposable dust mask respirators, half and full-face mask respirators, are facepiece fit tested.

12.21 For disposable dust mask and half-face mask respirators a qualitative fit test should suffice but for full-face masks a quantitative test should be used. Users of powered (fan-assisted) respirators with hoods and those using airfed breathing apparatus with hoods or visors will not requre fit-testing. Further information can be found in *Fit testing of respiratory protective equipment facepieces* OC 282/28 HSE 2003 available on www.hse.gov.uk.

Exposure control - housekeeping and welfare

12.22 Standards of housekeeping tended to be poor and therefore in need of improving. This can be achieved by one or a combination of the following:

- installing stainless steel surfaces and/or polypropylene plastic where appropriate to make the cleaning of surfaces easier;
- cleaning liquid spillages immediately with rags;
- using an industrial vacuum to remove dust regularly; and
- placing all contaminated material in a dedicated waste bin.

12.23 Companies need to ensure that their employees have high standards of personal hygiene. This can be achieved by preventing eating, drinking and smoking in work areas, removing all PPE when leaving the work area, washing the hands etc. All companies should ensure that adaquate washing faclities are provided at all times.

Use of controls

12.24 Employees should ensure that the measures provided to control exposure to MbOCA (and isocyanates) by all routes are used for example, wearing gloves when handling MbOCA and follow the defined methods of work.

12.25 Employees should practice a high standard of personal hygiene.

12.26 Employers should provide adequate supervision during all stages of MbOCA handling to ensure that the defined methods of work are carried out. They also need to ensure that any controls provided to reduce the risks of exposure to MbOCA (and isocyanates) are properly used.

12.27 Any reported faults or defects in the control measures used should be promptly dealt with, for example providing sufficient pairs of gloves to replace those that are damaged or heavily contaminated.

Maintenance

12.28 All polyurethane elastomer producers should ensure that their LEV systems are thoroughly examined and tested at least once every 14 months. Any defects found in the systems and reported by the examiner should be promptly repaired.

12.29 LEV systems should be checked on a regular basis, eg about once a week, using an anenometer and/or smoke tube to ensure that the air velocity required to contain or capture the airborne contaminants is adequate and to monitor airflow patterns respectively.

12.30 The average face velocity of partially enclosed booths and fume cupboards should not drop below 0.5 m/s to ensure effective containment within the system. The capture velocity of a LEV system should not fall below 0.8 m/s otherwise the airborne contaminants will not be effectively extracted and could escape into the local environment.

12.31 Those companies that use pegs to hang PPE should consider the use of lockers. The lockers should be in the workshop so that contamination on clothing is not spread when the clothing is removed.

12.32 Laundry facilities should be provided to wash contaminated clothing where appropriate. No worker should take contaminated clothing such as overalls home to wash.

12.33 All PPE should be checked during use to ensure that it is not damaged or heavily contaminated, particularly gloves.

12.34 RPE should be well maintained to include cleaning, disinfection, examination, repair, testing, safe storage and record keeping. This is especially important for reusable RPE, eg powered (fan-assisted) respirators that require the use of replaceable filters or cartridges.

Biological monitoring

12.35 Biological monitoring for urinary MbOCA should be carried out on relevant employees **once every six months**. The urine samples should be collected towards the end of the shift from all personnel handling the MbOCA.

12.36 **Suppliers of MbOCA** should carry out biological monitoring of personnel who handle MbOCA for quality control purposes, on those who need to split kegs and transfer MbOCA to smaller containers and on those involved in cleaning MbOCA from surfaces following an accidental release.

12.37 If there are any excursions above 15 µmol/mol creatinine or even readings approaching half the limit then a full investigation into the effectiveness of the control measures used should be carried out. Once the investigation is complete then repeat urine sampling should be undertaken.

12.38 There is the risk of high exposure to MbOCA during maintenance duties such as cleaning the LEV systems and reactor vessels. Maintenance personnel carrying out such work should have their urines collected at the end of the shift for measurement of urinary MbOCA

12.39 Biological monitoring should be considered for isocyanate urinary metabolites when samples are collected for urinary MbOCA monitoring. A urinary concentration of urinary diamine above the BMGV of 1 µmol/mol creatinine would indicate poor control practice and warrant an investigation of the handling of the isocyanate based pre-polymer resin.

Personal inhalation exposure monitoring etc

12.40 Regular airborne monitoring for MbOCA is not required. However, if following biological monitoring the BMGV for urinary MbOCA is exceeded or regarded as high (based on a companies previous results), then monitoring personal inhalation exposure to MbOCA may be useful as part of an overall investigation of the effectiveness of the control measures.

12.41 Those companies that carry out regular monitoring of airborne exposure to MbOCA as part of their annual risk assessment review should continue to do so.

12.42 Regular monitoring of surfaces using a wipe sampling technique to detect and assess MbOCA surface contamination and to assess the spread of contamination should be undertaken and the results incorporated into company workplace risk assessments.

Health surveillance

12.43 All workers handling isocyanates should have appropriate health surveillance. Health surveillance will include lung function testing, completion of a suitable questionnaire etc.

12.44 It is recommended that health surveillance for isocyanate handlers should include a pre-exposure examination, examination at about six weeks and 12 weeks after work has started and then at annual intervals while exposure continues.

12.45 A number of companies provide health surveillance for their isocyanate workers on a more regular basis (eg every six months); this is fine. It fits in with the recommended time for urine sampling for the monitoring of urinary MbOCA.

12.46 Furthermore, workers should be informed that if they develop symptoms such as wheezing, coughing, breathlessness etc whilst working with isocyanates it should be reported. Further exposure should be avoided and medical advice obtained.

12.47 A health record should be kept for each worker having health surveillance. It must be kept for at least 40 years.

Information, instruction and training

12.48 The provision of information, instruction and training in the polyurethane elastomer industry is poor and in need of improvement.

12.49 It is important that all future employees who may handle MbOCA and pre-polymer resin are provided with information on the nature of the hazards, the routes of exposure and the measures to control exposure as part of induction training. Where necessary, present employees handling MbOCA/resin should also be provided with the same information.

12.50 Instruction and training should be provided to all MbOCA/resin handlers on how to use the control measures provided for example, the correct method for removing gloves, how to maintain RPE etc. Refresher courses should be provided as and when required. This may be when a new control method is introduced or there is a change in the defined method of work.

12.51 It may be useful to keep records of each workers training and add to it as circumstances arise, eg attending a course, obtaining a professional qualification etc. All records (employers and employees) should be kept for an indefinite time period.

12.52 Relevant information on the handling of MbOCA, the exposure control measures used etc must be made available to safety representatives at an appropriate time. This may be at a regular health and safety meeting or through a Trades Union representative. In those smaller companies such information may be transferred personally on a one-to-one basis.

Appendix 1: Brief descriptions of workplaces and exposure control

Company A – The firm employs about 30 people; four work with MbOCA directly, ie about 1.25 kg/day. The MbOCA is handled inside a fume cupboard that extracts to atmosphere and is used for work with other chemicals. The oven used for curing the castings is situated inside a fume cupboard. Both fume cupboards are thoroughly examined and tested yearly. There is a reduced airflow into the cupboards.

MbOCA handlers wear overalls, lab coats, safety glasses, disposable latex or nitrile inner gloves and leather heat-resistant outer gloves. A disposable half-mask respirator FFP1 is provided but not worn. There is little surface contamination. It is mainly inside the fume cupboard. Urinary MbOCA concentrations are generally low.

Company B – This company employs over 60 workers and even though there are five dedicated MbOCA handlers, other staff may be involved with handling the substance directly. Approximately 30 kg is used on a daily basis. It is weighed,

melted and mixed in five extraction open-fronted booths and poured in an area on heated benches with overhead canopy extraction. The moulds are placed in ovens to cure. The five ovens are inside the booths because they contain no extraction. The LEV systems are in need of maintenance.

Workers wear disposable overalls with hoods, safety shoes, safety glasses, disposable latex or vinyl inner gloves and heat-resistant Terry towelling outer gloves. A disposable half-mask respirator FFP2/3 is worn during cleaning of surfaces whereas a half-mask respirator with a changeable A1 filter is worn for handling resin. There was surface contamination on the floor and on the sides of the booths. No urine samples have been collected from workers for many years to measure urinary MbOCA levels.

Company C – This company employs 120 workers but only three to five of these handle the MbOCA manually in a dedicated room and within a large partially enclosed extracted booth situated on a bench. About 5 kg of MbOCA is used daily. The poured moulds are placed in one or more ovens to cure. There is a canopy hood above the ovens to extract any vapour generated from the moulds.

The LEV is not effective and in need of improvement. MbOCA handlers wear day-to-day clothing, a plastic apron and safety shoes. Disposable nitrile gloves are worn. Some workers also wear cotton gloves to protect the skin from the heat. Disposable half-mask respirators FFP2 are provided but not worn. Urine MbOCA concentrations are mainly below 8 µmol/mol creatinine.

Company D – This long established company employs four workers and they all handle MbOCA directly, ie 12 kg daily within an extracted partial booth. The average face velocity of the booth was <0.5 m/s and therefore did not provide adequate containment (it was thoroughly examined and tested in 1998). The MbOCA/resin mixture is poured into the moulds in five ovens with canopy extraction above their doors.

During MbOCA handling the workers wear an apron over their day-to-day clothing and safety shoes. Safety goggles and a disposable overall may occasionally be worn. Rubber gauntlets are worn when filling the hopper. Disposable vinyl inner gloves and Terry towelling outer gloves are worn for other operations. A half-mask respirator with twin A2P3 cartridges is worn when pouring the molten MbOCA into the resin. Workers have not been fit-tested. There is some surface contamination in particular around the hopper into which MbOCA pellets are poured. There have been no urine samples collected to measure urinary MbOCA for over 6 years even though some could have been high.

Company E – This company employs over 60 workers with four handling the MbOCA. There is some handling of MbOCA outside the plant. Between 1.25 kg and 2.0 kg MbOCA are used daily. The chemical is handled on a partially enclosed bench with a large canopy hood that extracts via a fan direct to atmosphere. Casting is carried out on an open bench with overhead canopy extraction. Both LEV systems are ineffective due to poor maintenance and design. The moulds are cured in vented ovens.

The male workers wear lab coats over their day-to-day clothing, safety shoes and disposable latex gloves. The female workers wear their day-to-day clothing, aprons, ordinary shoes and disposable latex gloves. Terry towelling gloves are provided but not worn. No RPE is worn. There is extensive evidence of surface contamination. Urinary MbOCA concentrations have been high, eg 30 µmol/mol creatinine, due to poor hygiene and housekeeping.

Company F – This company employs four workers and they all handle MbOCA directly, ie 200 gm/day. A partial booth with extraction is used when weighing, melting

and then mixing MbOCA and for subsequent degassing of the mixture. A dedicated bench with an overhead canopy is used for casting. The LEV systems have not been thoroughly examined and tested for several years. The moulds are cured in ovens.

Operatives wear disposable ovalls, safety shoes, cotton liners and Rigger-type outer gloves when handling MbOCA. No RPE is worn. Surface containation is particularly noticeable near the casting bench. Urine samples are tested for urinary MbOCA every six months. Previous urinary MbOCA concentrations have been above half the BMGV ie >7.5 µmol/mol creatinine.

Company G – This small company employs four workers; all handle the MbOCA. Approximately 4 kg of the chemical are used per day. MbOCA is fed from a hopper and is handled in three extracted partial booths linked to one set of ducting. The castings are poured and cured in one of seven ovens with no extraction. The LEV has never been thoroughly examined and tested. The average face velocities at two of the booths were below 0.5 m/s.

Workers wear overalls, safety shoes, safety glasses, disposable latex or cotton inner gloves and leather outer gloves. A disposable half-mask repirator FFP2 is worn (not fit tested) during MbOCA handling. There is surface contamination, it is heavy near the hopper. There is no regular urine testing for MbOCA exposure but previous results were above half the BMGV.

Company H – This is a small company employing six workers, four of which handle 0.5 kg/day MbOCA manually within two fume cupboards. Though not checked for over five years, the average face velocities were about 0.65 m/s. There is no extraction in or on the outside of the curing ovens.

The employees wear cotton coats over their day-to-day clothing, safety shoes, and a pair of cotton gloves (cotton liners provided but not worn). Overalls are provided and may be worn. Disposable half-mask respirators FFP2 are worn when scooping the MbOCA from a drum. Urine samples are only taken when the employer wishes to check on control effectiveness during MbOCA handling.

Company I – This company employs 12 workers and they handle up to 30 kg of MbOCA and 200 kg pre-polymer resin weekly. The MbOCA is weighed in one of two fume cupboards (never been thoroughly examined and tested) and heated in an automatic heater. A bench with downward extraction is used for pouring the moulds but some moulds are also poured on an open bench. The moulds are cured in one of four ovens with no extraction.

The workers wear lab coats or short-sleeved overalls, safety shoes, cotton liners or disposable PVC inner gloves with leather outer gloves. A half-mask respirator with replaceable B1P1 cartridge filters is worn when filling the hopper (no worker has been fit-tested). Urine samples are not tested every six months for urinary MbOCA. But there have been high levels because of poor housekeeping.

Company J – This company employs 15 workers and handles up to 10 kg MbOCA per day but can be as high as 70 kg in particular if specific circular products are produced. MbOCA is manually handled in a partially enclosed booth with a canopy hood; it is not effective as it is poorly maintained.

The curing ovens have no extraction. Workers handling MbOCA wear cotton overalls, Tyvek disposable overalls, safety shoes, safety glasses, disposable latex inner gloves and leather outer gloves. An airline breathing apparatus with a helmet is worn during MbOCA handling. Some urinalysis results for MbOCA have been high.

Company K – This company employs about 10 employees and uses between 100 and 150 kg MbOCA a week. The substance is weighed and mixed with resin under extraction in one part of the plant and casting and curing is carried out in ventilated ovens on the opposite side.

During the handling of MbOCA the workers wear nylon overalls, safety shoes, safety glasses, cotton liners and disposable latex overgloves. Sometimes leather-palmed gloves may be worn. Powered respirators with helmets and A2P3 cartridges are worn when mixing, weighing and casting. There is little surface contamination and urine MbOCA concentrations are generally very low.

Company L – This company employs over 112 workers and up to six may be involved with handling MbOCA directly. This number would increase if the workload was high. Approximately 3 kg are used daily. The MbOCA is handled in four partially enclosed extraction booths. They are checked yearly. However, any faults detected are not immediately dealt with. Casting and subsequent curing is undertaken in ovens with no ventilation.

During MbOCA handling including removing moulds from ovens workers wear reusable or disposable overalls, safety shoes, safety glasses, cotton inner gloves and disposable vinyl or nitrile or leather outer gloves. When handling MbOCA an airline breathing apparatus with a full–mask is worn. A full or half-mask with replaceable twin A2P3 cartridges is also used. There is little surface contamination. Urines samples are tested monthly. Most are negative for urinary MbOCA but have had very high concentrations in recent years.

Company M – This company employs 20 workers of which five handle MbOCA directly in manual processes. Approximately 50 kg/MbOCA and 500 kg pre-polymer resin are used daily. The MbOCA is weighed, melted and mixed in three small booths. The mixture is poured on a heated bench under extraction and the moulds are cured in ovens with extraction.

The LEV is ineffective (no recent thorough examination and testing) and needs the design improved eg better enclosure. There was evidence of extensive surface contamination, ie poor housekeeping. Workers wear overalls, safety shoes and cotton inner gloves and Terry towelling outer gloves during MbOCA handling. A disposable half-mask respirator FFP2 is worn when scooping MbOCA from the keg. Urine samples are collected every six months but not at the end of the shift as recommended.

Company N – This company employs over 60 workers and a third of these may be involved with the production of polyurethane products. Over 150 kg MbOCA are used per week. MbOCA is handled in a glove box under negative pressure and fed to a reactor vessel where it is heated and mixed with resin prior to dispensing. The worker wears a disposable half-mask respirator FFP3.

A hose is used to pump directly into the moulds in a partial booth. There is extraction above the doors of the curing ovens that operate when the doors are open. The workers are provided with disposable overalls. On the day of the visit they wore jeans, T-shirts, safety shoes, safety glasses, cotton undergloves and nitrile outer gloves. There is surface contamination around and on the reactor vessel due to spillage. Recently, there were urinary MbOCA levels above the BMGV.

Company O – There are 280 employees at this company and 10 or more are directly involved with polyurethane production. About 40 kg of MbOCA is handled daily. MbOCA is fed via a glove box into a reactor vessel where it is heated and mixed with resin, colourants etc. The mixture is dispensed into moulds that are positioned on an extracted conveyor system. They are cured in a vented oven or

on a bench (not extracted). Some MbOCA may be manually weighed, melted, mixed and poured on a bench with extraction.

During MbOCA handling workers wear overalls, disposable overalls, safety shoes or boots, safety glasses, safety goggles or a full face visor, and various combinations of gloves for example, cotton or disposable latex inner gloves and leather or rubber outer gloves. There is evidence of heavy surface contamination from spillage during casting. Urinary MbOCA concentrations have been well above the BMGV due to poor personal hygiene and poor housekeeping.

Company P – Over 70 employees work for this company with up to five handling MbOCA directly. Some MbOCA is handled offsite by several workers. Up to 12 kg of MbOCA can be handled on a busy day. The MbOCA is manually handled, eg weighing, melting etc in three small booths, all under extraction and cured in ovens with extraction above the doors. This extraction is poorly designed.

There is evidence of high surface contamination in the booths and on surrounding surfaces. Workers wear separate trousers and matching tops, an apron if workload is high, safety shoes, disposable latex inner gloves and Terry towelling outer gloves (gauntlets may also be worn). No RPE is worn even though provided. Recently, urinary MbOCA levels have been above the BMGV.

Company Q – This firm employs seven employees. About 8 kg MbOCA are used daily and approximately 80 kg isocyanate pre-polymer resin. Most of these workers handle the MbOCA manually during scooping, weighing etc in a partially enclosed extracted booth. The average face velocity of the booth is very low. The pouring of the mixture is carried out on two benches. Each bench has access to a flexible hose with an attached hood to remove any airborne contaminants. The capture velocity of the flexible LEV system is poor.

The workers wear disposable or re-usable overalls, a rubber or disposable vinyl apron, safety shoes, safety glasses, disposable vinyl inner gloves and fibrous cotton/leather palmed outer gloves. A re-usable half-mask respirator with twin P3 filters is worn when scooping the MbOCA pellets. There is heavy contamination on the floor. Urinary MbOCA concentrations have been high but latest company results have been well below the BMGV.

Company R (Supplier) – This company is a MbOCA and resin supplier. It employs over 100 workers. Three workers will handle up to 200 gms/MbOCA/day for quality control purposes within a fume cupboard. The moulds are cured in a small oven with extraction above the door. Both LEVsystems are effective. Workers handling MbOCA wear overalls, safety shoes, safety glasses, and disposable PVC or latex gloves. No RPE is worn. There is little surface contamination. There is no testing of urine for evidence of MbOCA exposure.

Company S – This company employs approximately 90 workers. Between four to seven people directly handle up to 10 kg of MbOCA daily. The MbOCA is added (via a glove box), melted in a reactor vessel and mixed with resin, colourants etc. The mixture is dispensed into a container. Flexible ducting with an extraction hood is used to remove airborne contaminants during dispensing. The mixture is poured into the moulds on two heated tables with downward extraction and cured in ventilated ovens. All the LEV systems are tested/examined in-house.

Workers wear overalls, safety shoes, safety glasses, disposable nitrile inner gloves and Terry towelling outer gloves. No RPE is worn. There is surface contamination on and around the hot tables and on the floor at the dispensing point. Urinary MbOCA concentrations are monitored every six months and tend to be below the BMGV.

Company T (Supplier) – This company is a major supplier of MbOCA and imports the chemical mainly from Japan. Small quantities of MbOCA may be handled for quality control purposes but this is infrequent. When MbOCA testing is required one person will handle it within a fume cupboard. The person will wear a lab coat and either disposable latex or nitrile gloves.

About two to three workers will handle the pallets containing MbOCA kegs. If a keg is damaged (the last major spillage was four years ago) the MbOCA spillage will be cleaned up by workers wearing Tyvec disposable overalls, safety shoes, safety glasses and disposable gloves. A disposable half-mask respirator FFP3 will also be worn. Urine samples will be collected from those workers dealing with spillage.

Company U – This company employs 12 workers and up to half may handle MbOCA directly (7.5 kg daily). The MbOCA is handled in a 'walk-in' extraction booth. The MbOCA/resin mixture is poured into moulds inside an oven that is situated in the booth. Some may be poured into moulds outside the booth. A second extraction booth is used when weighing MbOCA and when crushing the empty drums. Both booths had not been thoroughly eamined and tested as required under COSHH regulation 9. There was evidence of extensive contamination in both booths.

Operators wear disposable overalls, safety shoes, Rigger and/or disposable latex gloves. No safety glasses or RPE are worn. Urine samples are tested for MbOCA every three to six months. Urinary MbOCA concentrations above 20 µmol/mol creatine were recorded recently; MbOCA had been overheated.

Company V – This company employs 13 workers. It uses over 50 kg of MbOCA and 500 kg resin daily. An automatic reactor vessel is used to melt MbOCA and then mix with the pre-polymer resin prior to dispensing into moulds or a container. There is a flexible hose with an extractor hood located above the funnel hopper that is used to feed MbOCA and resin into the reactor vessel.

There is extraction above the oven doors where the moulds are cured. The workers wear lab coats, aprons, safety shoes, safety glasses, cotton outer gloves and disposable latex or nitrile inner gloves during MbOCA handling. Gauntlets may occasionally be worn over the gloves. Re-usable half-face mask respirators are worn with dual A2P3 filters. The employees have not been fit tested. There is evidence of poor housekeeping eg heavy surface contamination. Previous urinary MbOCA concentrations have exceeded the BMGV.

Appendix 2: Statistical analysis of survey results

1 Methodology

1.1 Analysis of MbOCA and isocyanates

Urine samples were analysed for MbOCA (and its labile conjugates) and isocyanate metabolites using methodology described in detail in Cocker et al. (1996) and Williams et al. (1999). Air, surface and glove samples were analysed for MbOCA; the filters from the air samples, the surface wipes and the glove samples were dissolved in a solvent (acetonitrile) and then analysed using either liquid or gas chromatography.

1.1.1 Limits of detection

The limits of detection (LOD) for urine analysis were 0.5 µmol/mol creatinine and 0.1 µmol/mol creatinine (assuming a typical creatinine level of 9 µmol/l) for MbOCA and isocyanate metabolites respectively. The LOD for MbOCA using liquid chromatography was:

Air - 1 µg m^{-3} for a 200 litre sample
Surfaces - 5 µg/sample for 22 ml desorption volume
Gloves - 80 µg/sample for a 400 ml desorption volume

The LOD for some of the samples, analysed using the more sensitive gas chromatography method was approximately ten fold lower than those quoted above. The LOD on surface and glove concentrations was influenced by the desorption volume so the differing quantities of solvent used to dissolve the sample resulted in differing limits of detection.

1.2 Data cleaning

Prior to statistical analysis some amendments were to be made to the data by analysts at HSL. All readings denoted as ND (Non Detected) or less than LOD in the urine, air, surfaces and gloves data were re-coded as Non Detected. Some of the air, surface and glove concentrations were corrected since the units of measurement were erroneous, after consultation with relevant experts from HSL. The measurements from air, surfaces and glove samples were all converted to milligrams prior to analysis.

1.3 Derivation of variables

In order to thoroughly analyse the data from urine, air, surface and glove samples and to achieve the aims of the study, the descriptions about the samples, recorded by the on site occupational hygienists, were used to derive variables.

1.3.1 Urine

All workers were categorised as directly exposed or controls. Directly exposed workers were working in the manufacturing environment whereas controls were working within the same building but in jobs (such as office based work) where they should not be exposed to MbOCA. Those workers thought to be directly exposed were further sub-classified into seven groups based upon different types of possible exposure; handling/scooping, weighing/melting/mixing, casting, moulding, maintenance, other (non-specific) exposure and all parts of the process. These categories denote the main type of work undertaken by workers as recorded by the HSE inspectors on site although it is likely that many workers were involved in all parts of the process.

1.3.2 Air

The air samples were categorised into personal and static samples. The static samples were classified into those taken from directly exposed and control areas of the workplace. The controls samples were taken from areas such as offices and canteens. The exploratory analysis of the data showed that MbOCA was detected in air in few samples and a further sub-classification into workplace areas was not necessary.

1.3.3 Surfaces

Surface samples were classified into those taken from directly exposed and control surfaces. The control samples were taken from surfaces in areas such as canteens, offices and toilets. The directly exposed areas were sub-classified, based on the description of the sample, into fume cupboard/degassing, storage, weighing/pouring, mixing, ovens, hopper, casting and other (non-specific).

1.3.4 Gloves

Glove samples were classified, where possible, as inner or outer glove samples. When the description of the sample did not specify inner/outer explicitly, the sample was taken to be an outer glove when the concentration of MbOCA on the sample was in excess of 1 mg. When the sample concentration was less than 1 mg no classification was made.

1.4 Statistical methodology

The data on each of the measurements had a mixed categorical/continuous form. Resultantly, a two-phased statistical approach was used to analyse the data. The first of these involved recoding all continuous data to the categorical value of greater than LOD and analysing the data using statistical methods for ordered categorical data. The second method concentrated on the continuous data only, those samples where a concentration was recorded and more sophisticated numerical analyses were used on this subset.

Fishers exact test was used in order to test for association between categorical variables; the test is the exact test for associations in contingency tables and is often approximated by the chi-squared test. For the continuous data correlations were calculated using Kendall's tau, a non-parametric test of correlation based on data that is ranked in order of magnitude. The Mann-Whitney U test, the non-parametric equivalent of a two-sample t-test, was used in order to test for a difference in median between two subsets. The Kruskall-Wallis test, the non-parametric equivalent of a one way Analysis of Variance (ANOVA), was used to test for a difference in medians when more than two subsets were being compared.

1.4.1 Data Sensitivity

Prior to statistical analysis, the 20 companies where data was available, were each allocated a letter A – U. Due to commercial sensitivity, when the results from different companies have been compared, the companies have been referred to by letter rather than by name. A list mapping letters to companies is provided in a separate document for the use of the HSE authorising officer.

2 Survey results

The statistical analysis is presented in four sections each focusing on the locations where samples were made.

2.1 Urine samples

A total of 78 urine samples were taken from workers at 19 companies although no urine samples were taken from one of the companies using MbOCA (company S). All the samples were tested to determine the concentration of MbOCA in the urine and 71 samples (from 17 of the companies) were also tested to determine isocyanates concentrations. Approximately 75% (n=59) of the samples were taken from workers who could be classified as directly exposed (ie involved in at least one aspect of the manufacturing process) and the remainder (n=19) were controls who were not involved in any part of the manufacturing process, but who may have been exposed to MbOCA if best practice was not followed.

2.1.1 MbOCA in Urine

Table 1 reports the frequency of urine samples where the sample was recorded as ND or greater than LOD (in excess of 0.5 µmol/mol creatinine). In addition, the frequency of samples that were in excess of the present BMGV of 15 µmol/mol creatinine is reported. Note the percentages in the first two columns equal 100, the cases where the readings were in excess of 15 µmol/mol creatinine are a subset of those greater than LOD.

Table 1 Frequencies for MbOCA concentration in urine

MbOCA concentrations in urine		
ND	> LOD	> BMGV
38 (49%)	40 (51%)	3 (4%)

Table 1 shows a little over half (51%) of the samples analysed had a level of MbOCA that was above the limit of detection. The rest of the samples had levels within the range of 0 – 0.5 µmol/mol (49%). Of all the samples only 4% (n = 3) were above the BMGV whereas by the definition of the BMGV, 10% of samples might be expected to be above this value if controls had not improved since the BMGV was set in 1996.

A numerical analysis of the 40 samples where the MbOCA concentrations were above the limit of detection was conducted with some summary statistics presented in Table 2. The analysis showed a large range of concentrations (1.33 to 24.99 µmol/mol creatinine) with a respective arithmetic mean and median of 6.597 and 4.27 µmol/mol creatinine. The readings were positively skewed with statistical tests indicating that the data could be approximated by a log normal distribution. The majority of readings were concentrated around the lower end of the range; the large differences between the arithmetic and geometric means and arithmetic and geometric standard deviations reflect this feature of the data. Two readings were well in excess of the current BMGV (24.4 and 24.99 µmol/mol creatinine respectively).

Table 2 Summary statistics of MbOCA concentration in urine

MbOCA concentrations in urine							
n	Max	Min	Median	Arithmetic mean	Arithmetic standard deviation	Geometric mean	Geometric standard deviation
40	24.99	1.33	4.27	6.597	5.73	4.965	2.092

2.1.1.1 Analysis by Exposure

Table 3 reports the frequency of urine samples where the sample was recorded as ND or greater than LOD and the frequency of samples that were in excess of the BMGV for the groups of workers classified as directly exposed to MbOCA and controls. For each of the two groups the percentages in the first two columns reported in Table 3 equal 100, the cases where the MbOCA concentration was in excess of the BMGV are a subset of those greater than LOD.

Table 3 Frequencies for MbOCA concentration in urine by exposure

MbOCA concentrations in urine			
Exposure Control	ND	> LOD	> BMGV
	15 (79%)	4 (21%)	- -
Directly exposed	23 (39%)	36 (61%)	3 (5%)

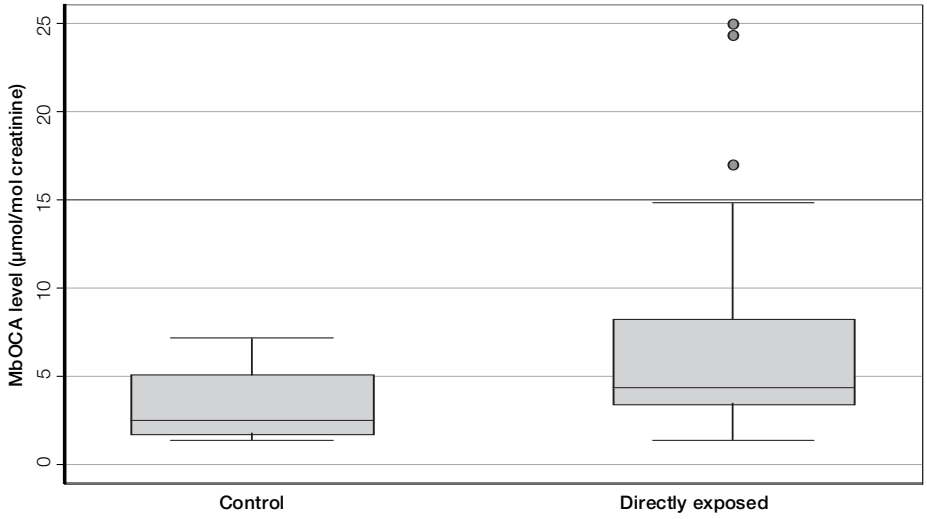
It can be seen from Table 3 that there were noticeable differences between the directly exposed workers and the controls with the former more likely to have a urine reading above the limit of detection. Only 21% of the controls had levels in their urine greater than the limit of detection, whereas 61% of those directly exposed to MbOCA had a detectable concentration. Workers directly exposed were statistically more likely to have a measurable concentration of MbOCA in urine (p=0.003). In addition, as can be seen from Table 3, all of the urine samples exceeding the BMGV could be identified as originating from those working in directly exposed jobs. However, despite the obvious differences between the two groups it is surprising that 21% of the controls had a detectable concentration of MbOCA in their urine and may be an indication that best practice was not followed. A numerical analysis of the subset of 40 samples where the MbOCA concentration was above the limit of detection was also performed, with some summary statistics presented in Table 4.

Table 4 Summary statistics of MbOCA concentration in Urine by exposure

MbOCA concentrations in urine								
Exposure	n	Max	Min	Median	Arithmetic mean	Arithmetic standard deviation	Geometric mean	Geometric standard deviation
Control	4	7.17	1.33	2.535	3.3925	2.60	2.781	2.033
Directly exposed	36	24.99	1.35	4.33	6.95	5.896	5.291	2.058

Figure 1 shows boxplots of MbOCA levels in urine for the controls and directly exposed workers. Also shown in Figure 1 is the BMGV for MbOCA. A detailed note on how to interpret a boxplot is included in appendices.

Figure 1 MbOCA concentrations in urine by exposure



Both the summary statistics presented in Table 4 and Figure 1 clearly show concentrations of MbOCA were higher in the directly exposed group. The median concentrations were 4.33 and 2.35 µmol/mol creatinine for the directly exposed and control groups respectively and the arithmetic mean concentrations were 3.39 and 6.95 µmol/mol creatinine respectively. The range of MbOCA concentrations was much larger for the directly exposed workers than the controls, (1.35, 24.99) compared with (1.33, 7.17) µmol/mol creatinine. For both groups the distributions of MbOCA concentrations were positively skewed. The urine samples exceeding the BMGV are shown as the dots above the red line, which the statistical analysis indicated as outlying (unusually large) observations.

Workers directly exposed had significantly higher levels of MbOCA in their urine than controls (p=0.039). Although the controls had lower concentrations of MbOCA in urine, the magnitude of the concentrations was surprisingly large with a largest recorded concentration for a control of 7.17 µmol/mol creatinine, which was just below a half of the current BMGV.

2.1.1.2 Analysis by job

As previously described in section 2.3.1, the exposed workers were sub-classified, using information about the worker, into seven groups which were chosen to reflect the different stages of the manufacturing process and hence potential differences in exposure to MbOCA. These were: handling; weighing/melting/mixing; casting; moulding; maintenance, other non-specific exposure and all parts of the process. As discussed in 2.3.1 most workers would be involved in more than one stage of the process so these categories describe the main type of exposure at the time of the inspection.

Table 5 below reports the frequency of urine samples in which the sample was classified as ND or greater than LOD and the frequency in which the BMGV of 15 µmol/mol creatinine was exceeded for the seven classes of exposed workers. For each row in Table 5 the percentages in the first two columns equal 100.

Table 5 Frequencies for MbOCA concentrations in urine by job type

MbOCA concentrations in urine			
Job Classification	ND	> LOD	> BMGV
Handling and scooping	5 (100%)	- -	- -
Weighing, mixing and melting	4 (50%)	4 (50%)	- -
Casting	- -	3 (100%)	1 (33%)
Moulding	1 (8%)	12 (92%)	1 (8%)
Maintenance	1 (33%)	2 (67%)	- -
Other exposure	6 (86%)	1 (14%)	- -
All parts of the process	6 (30%)	14 (70%)	1 -

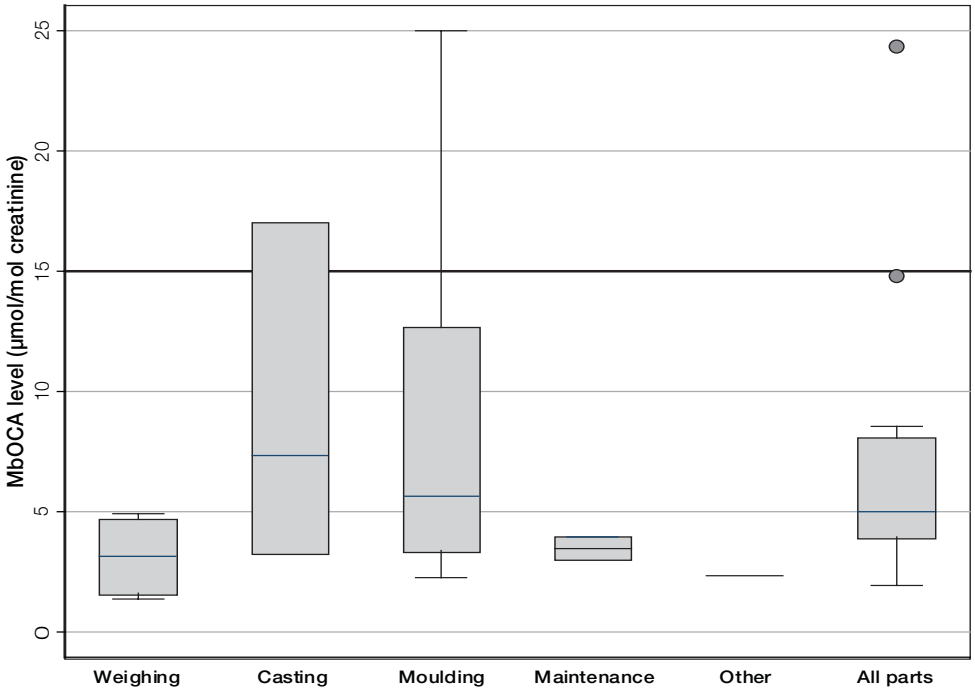
Table 5 shows there were differences between the job classifications in the proportions of workers where MbOCA was above the LOD, with it detectable in the samples from almost all those involved in casting and moulding, whereas those involved in handling or other non-specific exposure often had a concentration below the LOD. A significant association between job classification and MbOCA levels in urine was found (p= 0.002).

A numerical analysis of the 36 samples where the MbOCA concentration was above the limit of detection was also performed. Table 6 shows some summary statistics for the different job categories and Figure 2 shows boxplots of MbOCA levels in urine for each of the job classifications and an indication of the BMGV for MbOCA in urine. Whilst summary statistics are given for all job categories for completeness, the arithmetic and geometric standard deviations should be viewed with caution given the small samples in some of the categories (n <5)

Table 6 Summary statistics of MbOCA concentrations in urine by job

MbOCA concentrations in urine								
Job	n	Max	Min	Median	Arithmetic mean	Arithmetic standard deviation	Geometric mean	Geometric standard deviation
Handling	-	-	-	-	-	-	-	-
Weighing	4	4.92	1.35	3.155	3.145	1.763	2.74	1.872
Casting	*3*	*17.01*	*3.3*	*7.35*	*9.22*	*7.04*	*7.44*	*2.27*
Moulding	*12*	*24.99*	*2.23*	*5.67*	*8.34*	*6.84*	*6.265*	*2.19*
Maintenance	2	3.92	3.07	3.495	3.495	0.60	3.469	1.18
Other	1	2.37	2.37	2.37	2.37	-	2.37	-
All parts	*14*	*24.2*	*1.91*	*4.965*	*7.185*	*5.88*	*5.787*	*1.896*

Figure 2 MbOCA concentrations in urine by job classification



As can be seen from Figure 2, the results showed a contrast between the groups, 'all parts of the process', 'casting' and 'moulding' (highlighted in Table 6 as the categories in italics) and a second group 'maintenance', 'weighing/melting & mixing' and 'Other exposed'. The former of these groups had higher median and more variable concentrations. The second group showed low variability (although the sample sizes were small in all three groups and the measures of variability were sensitive) with all concentrations well the BMGV for MbOCA. 'all parts of the process', 'casting' and 'moulding' all had one sample which was above the current BMGV. A formal statistical test of equality in the medians was performed but did

not show significant differences between concentrations in the different jobs. The samples were very small however and resultantly the power of the test was low.

2.1.1.3 Analysis by company

As previously described, the urine samples in this survey came from 17 companies who used MbOCA directly within their premises and two companies who distributed it. From the information regarding job classification (previously described in section 3.1.1.2) it was possible to group five companies together, where the directly exposed workers that were sampled carried out 'all parts of the process'. In addition, it was possible to group another four companies where the directly exposed workers that were sampled were mainly carrying out the 'moulding' part of the process. Summary statistics of the readings greater than the LOD are given in Table 7 and the data is displayed in Figures 3 'all parts of the process' and 4 'moulding'. Also shown in Figures 3 and 4 is the BMGV for MbOCA.

Table 7 Summary statistics of MbOCA concentrations in urine by company

MbOCA concentrations in urine								
Company	n	Max	Min	Median	Arithmetic mean	Arithmetic standard deviation	Geometric mean	Geometric standard deviation
All Parts								
G	4	14.86	2.14	7.685	8.0925	5.223	6.58	2.25
H	2	5.64	1.91	3.775	3.775	2.638	3.281	2.15
I	3	5.7	4.25	4.29	4.75	0.826	4.70	1.18
J	-	-	-	-	-	-	-	-
U	2	24.4	3.65	14.025	14.025	14.67	9.44	3.832
Moulding								
M	4	11.59	2.23	2.995	4.95	4.44	3.90	2.09
N	6	14.8	2.33	4.44	6.03	4.51	5.027	1.87
P	1	24.99	24.99	24.99	24.99	-	24.99	-
Q	3	13.66	7.17	8.4	9.74	3.45	9.36	1.40

Figure 3 MbOCA concentrations in urine by selected companies

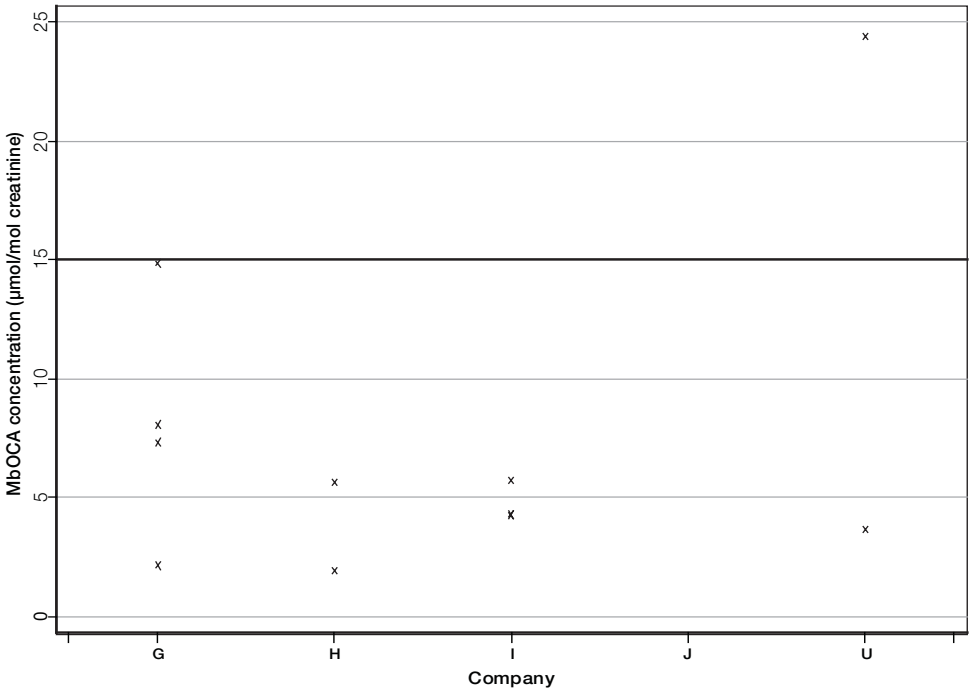


Figure 4 MbOCA concentrations in urine by selected companies

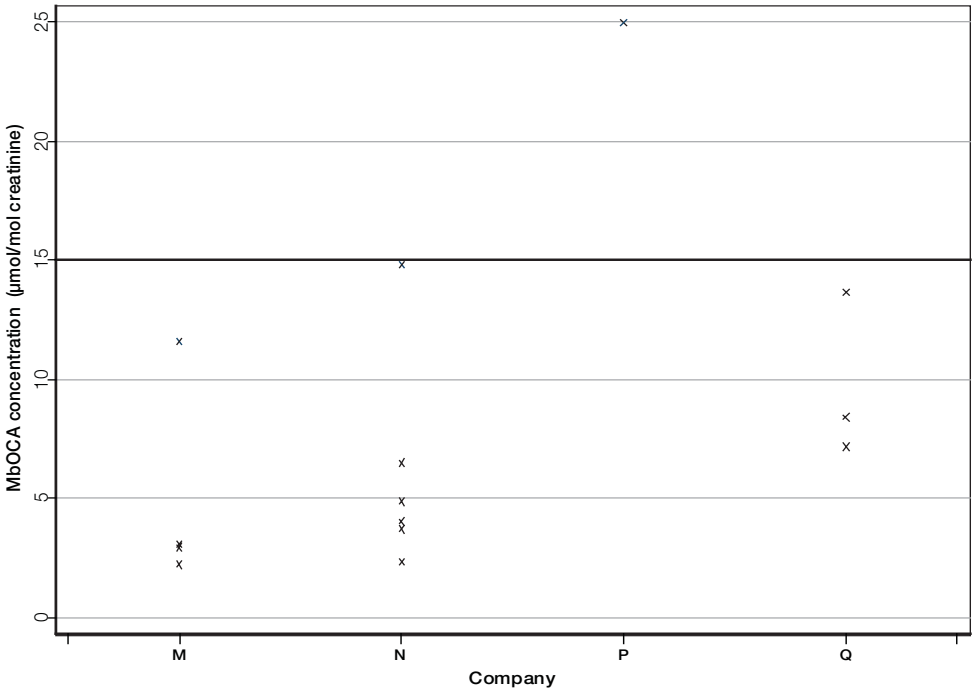


Figure 3 and the summary statistics in Table 7 show there were differences in the variability of concentrations between companies, with G and U having very large ranges. There was no evidence to suggest any of the companies had significantly larger concentrations of MbOCA in urine, which was confirmed by formal statistical tests. Figure 4 suggested that there might be differences between the different companies for the samples taken from Moulders, in particular the samples from company Q were all above the global median, however this was not confirmed by statistical tests. The power of the statistical tests was low due to the small sample sizes.

Company N was the only one of the five companies using automated processes where enough samples were taken to allow for a meaningful analysis. The comparison with other similar companies (similar in terms of the job tasks the workers were carrying out) showed there were no significant differences between the companies using automated and manual processes, however sample sizes were small in all companies and the power of the statistical test was low.

2.1.1.4 Biological Monitoring Guidance Values for MbOCA

The current BMGV for MbOCA is 15 µmol/mol creatinine. This is the good practice guideline that employers should aim for and is set around the 90th percentile of available validated data collected from representative workplaces with good occupational health practices. The BMGV was agreed by The Working Group on Action to Control Chemicals (WATCH) in 1996 based on data from 1993.

Of the 78 urine samples analysed for MbOCA concentrations, three were over the BMGV. By the very definition of the BMGV, 10% of the samples (or eight in this dataset) might exceed the BMGV even in workplaces with good controls so values above 15 µmol/mol creatinine do not necessarily imply that good practice is not followed. However, while only three concentrations were above the BMGV, two of these were far in excess of 15 µmol/mol creatinine.

One of the specific aims of the statistical analysis was to assess how the BMGV agreed by WATCH in 1996 compared to the 90th percentile of data from workplaces with good practice. The 90th percentile of the current study, based on all 78 samples, was 8.85 µmol/mol creatinine, which was far below the current BMGV. Moreover, the 90th percentile from this study was consistent with previous data collected by HSL over the last 10 years. Figure 5 shows the 90th percentile for MbOCA concentrations in urine from samples taken from 1975 up to and including the data in this survey.

Figure 5 90th percentile for MbOCA in urine from 1975 to 2006

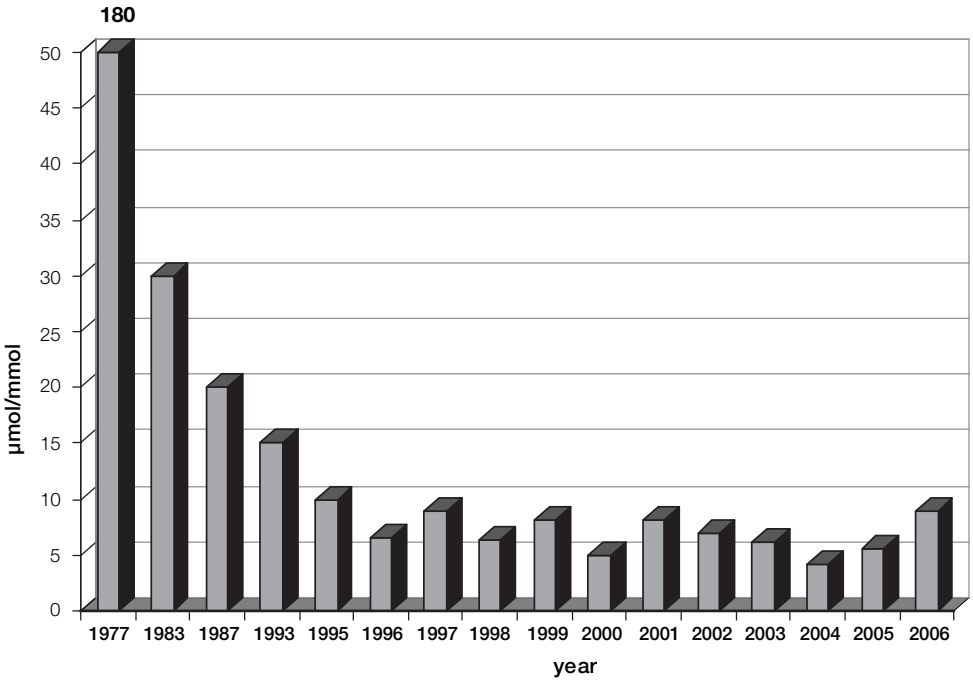


Figure 5 shows there has been a downward trend in the 90th percentile for some years and since 1995 the 90th percentile has been below 10 µmol/mol creatinine. The 90th percentile reported in this survey, which was the largest since 2001, is likely to be an overestimate of the 90th percentile since the data from all companies has been used rather than just those with good occupational health practices (an occupational hygienist would have to make judgements on which data to discard). Although, if data was discarded due to being inconsistent with the other data (the 24.4 and 24.99 µmol/mol creatinine concentrations in particular were identified as 'outliers'), the 90th percentiles of the current and previous data suggest the BMGV may be as low as 7.3 µmol/mol creatinine. The data from this and previous studies suggest that a reduction of the BMGV to10 µmol/mol creatinine would be conservative.

2.1.2 Isocyanate metabolites in urine

The urine samples were analysed for 2,4 Toluenediamine (2,4 TDA), 2,6 Toluenediamine (2,6 TDA), 2,4 Hexanediamine (HDA), Isopherone diamine (IPDAu) and Methylendianinine (MDA). The first two of these, 2,4 TDA and 2,6 TDA, are derived from 2,4 and 2,6 Toluene diisocyanate the individual isomers used in varying proportions in industry, however since these reflect exposure to the same isocyanate the sum of the metabolites is used as a measure of total exposure. The BMGV for isocyanates is 1.0 µmol/mol creatinine.

Samples from 17 companies were tested (none of the samples from companies J and O were assessed for any of the isocyanates), yielding a maximum of 71 samples for testing. A further two samples were not analysed for HDA and IPDA.

As with the statistical analysis of MbOCA in urine, a two-phased analysis was performed. Initially, all samples were coded as ND or greater than LOD before a separate analysis of the numeric samples was performed. Table 8 reports the frequency of urine samples where the sample was coded as ND or greater than LOD and the frequency of samples which were greater than the BMGV. Results are given for HDA, IPDA and MDA, whilst concentrations of 2,4 TDA and 2,6 TDA are reported in addition to their sum, 'total TDA'. In each case the sum of the percentages in the first two columns equal 100 since those greater than BMGV are a subset of greater than LOD.

Table 8 Frequencies for Isocyanates concentrations in urine

Diamine concentrations in urine			
Diamine	ND	> LOD	> BMGV
2,4 TDA	57 (80%)	14 (20%)	6 (8%)
2,6 TDA	49 (69%)	22 (31%)	7 (10%)
Total TDA	48 (68%)	23 (32%)	16 (23%)
HDA	56 (79%)	13 (21%)	9 (13%)
IPDA	66 (96%)	3 (4%)	- -
MDA	65 (92%)	6 (8%)	- -

Table 8 shows a measurable concentration was recorded in a total of 58 samples although in many cases the two TDA isomers were detected in the same sample and after adjusting for this a total of 45 samples were above the LOD for the four distinct isocyanates. In the cases where TDA was detected, 2,6 TDA was measurable in all but one of the samples. A total of 25 samples were above isocyanate BMGV of 1.0 µmol/mol for TDA (16 samples) or HDA (9 samples). Of the samples in which the total TDA was above the BMGV, four samples were above the BMGV for just 2,4 TDA, five above the BMGV for just 2,6 TDA and two samples were above the BMGV for both of the isomers. A further five samples were below the BMGV for both the 2,6 TDA and 2,4 TDA isomers but above the BMGV for total TDA.

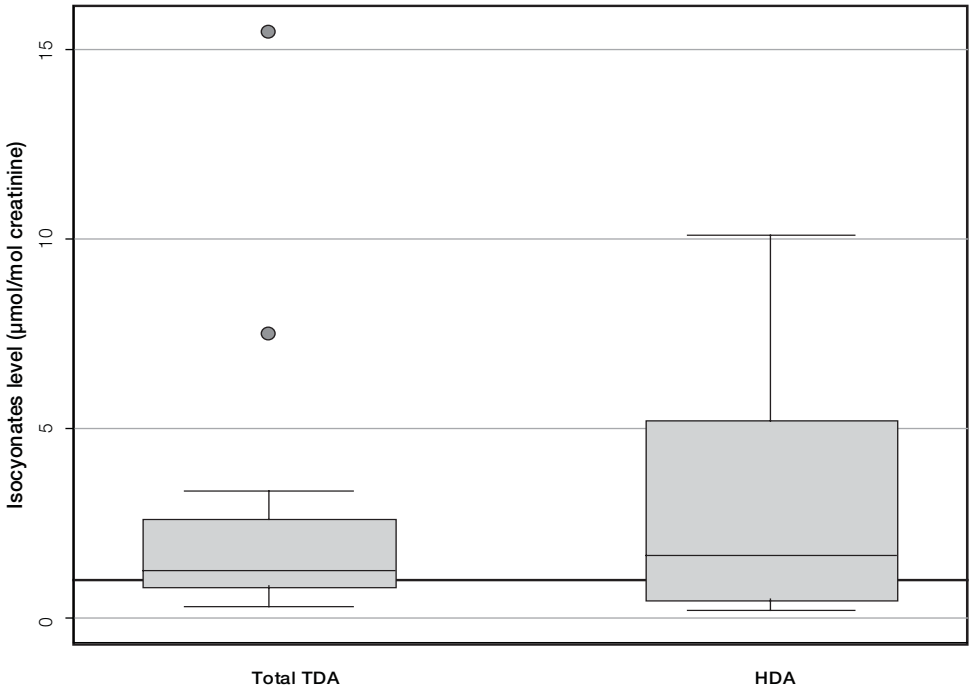
Summary statistics from the second phase analysis, looking at the numerical readings, are given in Table 9. Results are given for HDA, 2,4 TDA, 2,6 TDA and total TDA.

Table 9 Summary statistics of diamine concentrations in urine

Diamine concentrations in urine								
Diamine	n	Max	Min	Median	Arithmetic mean	Arithmetic standard deviation	Geometric mean	Geometric standard deviation
2,4 TDA	14	5.55	0.32	0.7	1.37	1.40	0.96	2.28
2,6 TDA	22	13.23	0.45	0.77	1.64	2.69	1.037	2.19
Total TDA	23	15.5	0.32	1.26	2.40	3.23	1.54	2.40
HDA	13	10.11	0.22	1.67	3.41	3.38	1.81	3.69

Figure 6 shows boxplots of total TDA and HDA readings. The BMGV is included as the red line.

Figure 6 Diamine concentrations in urine



The summary statistics in Table 9 reflect that the quantities of the two TDA isomers, when at a measurable concentration, had similar magnitudes with median concentrations for 2,4 TDA and 2,6 TDA of 0.7 and 0.77 µmol/mol creatinine respectively. The variability was also similar as seen by comparing the geometric standard deviations of 2.28 and 2.19 respectively, which are unaffected by the one very large concentration (13.23 µmol/mol creatinine) of 2,6 TDA. When comparing HDA and total TDA the results were noticeably different with TDA exhibiting low variability (outliers excepted) whilst the HDA concentrations exhibited greater variability. For both of the isocyanates approximately 70% of samples where a measurable concentration was detected were above the BMGV.

2.1.2.1 Analysis by exposure

Table 10 below reports the frequency of urine samples where the sample was coded as ND or greater than LOD and the frequency of concentrations in excess of the BMGV for both controls and workers who were directly exposed to MbOCA. For both controls and directly exposed workers the percentages classified as ND or greater than LOD sum to 100.

Table 10 Frequencies for isocyanates concentrations in urine by exposure

Diamine concentrations in urine						
	Control			Directly exposed		
Diamine	ND	> LOD	> BMGV	ND	> LOD	> BMGV
2,4 TDA	16 (94%)	1 (6%)	- -	41 (76%)	13 (24%)	6 (11%)
2,6 TDA	17 (100%)	- -	-	32 (59%)	22 (41%)	7 (13%)
Total TDA	16 (94%)	1 (6%)	- -	32 (59%)	22 (41%)	16 (30%)
HDA	15 (94%)	1 (6%)	(6%)1	41 (77%)	12 (23%)	8 (15%)
IPDA	16 (100%)	- -	- -	50 (94%)	3 (6%)	- -
MDA	14 (82%)	3 (18%)	- -	51 (94%)	3 (6%)	- -

Table 10 shows that samples where a measurement was obtained, were almost exclusively from the workers who were directly exposed to MbOCA, and 24 of the 25 concentrations that were above the BMGV were in the directly exposed group. MDA was noticeably different from the general pattern with both workers who were directly exposed to MbOCA and controls showing similar results.

2.1.2.2 Correlations between diamine concentrations

The urine samples where both 2,4 TDA and 2,6 TDA were above the LOD and samples where total TDA (meaning that one or both of the isomers were above the LOD) and HDA were above the LOD were examined further to assess for correlations. Figure 7 shows plots of the TDA isomers and total TDA against HDA. Also shown in Figure 7 is the BMGV for isocyanates.

Figure 7 Correlations between 2,4 TDA, 2,6 TDA and HDA concentrations in urine

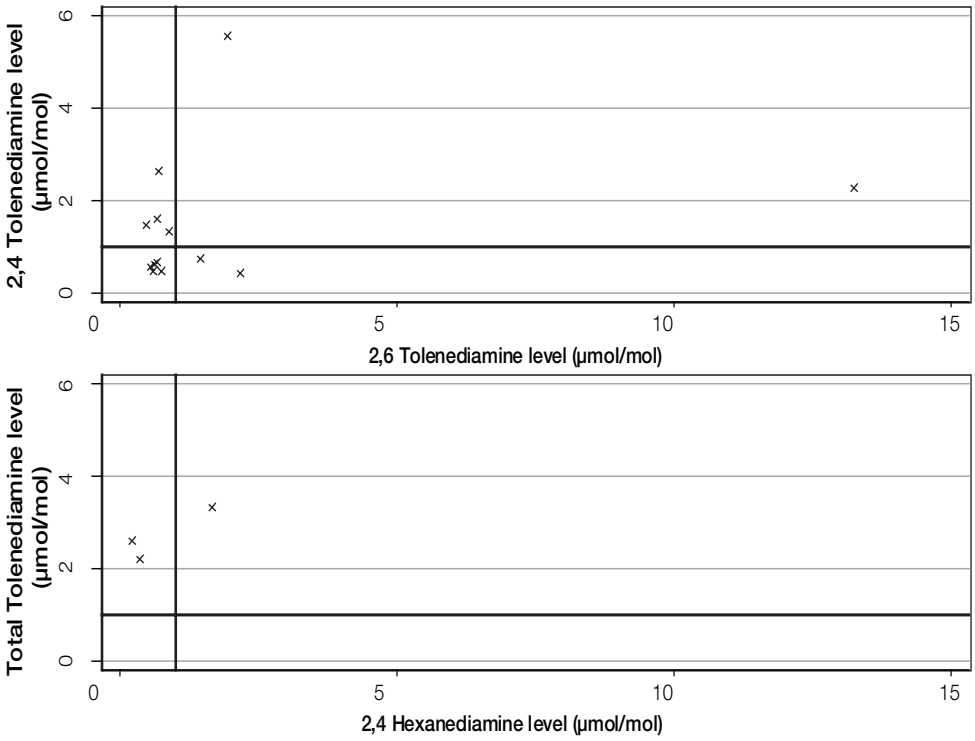


Figure 7 and the earlier discussion show a measurable concentration, of both TDA isomers was often found in the same sample with a measurable concentration of 2,4 TDA present in only one sample when 2,6 TDA was not at a measurable concentration. However, the magnitudes of the two isomers appeared to be independent, as verified by statistical tests (p=0.392). Measurable concentrations of total TDA were rarely found in combination with HDA (only three cases) and statistical tests showed there was no evidence (p = 1.00) to support a correlation between the magnitudes of total TDA and HDA.

2.1.2.3 Analysis by job

Further analysis was performed on the directly exposed workers, sub-classified into the 7 different job categories defined in section 2.3.1.

The following tables report the frequency of urine samples in which the sample was NA or greater than LOD and the frequency of samples which were in excess of the BMGV for total TDA (Table 11), and HDA (Table 12) by job classification. In each table the percentages in the first two columns sum to 100.

Table 11 Frequencies for total TDA concentrations in urine by job type

	Total TDA concentrations in urine		
Job Classification	ND	> LOD	> BMGV
Handling & scooping	5 (100%)	- -	- -
Weighing, mixing & melting	8 (100%)	- -	- -
Casting	1 (50%)	1 (50%)	1 (50%)
Moulding	6 (50%)	6 (50%)	6 (50%)
Maintenance	1 (100%)	- -	- -
Other exposure	3 (43%)	4 (57%)	4 (57%)
All parts of the process	7 (39%)	11 (61%)	5 (28%)

Table 12 Frequencies for HDA concentrations in urine by job type

	Total TDA concentrations in urine		
Job Classification	ND	> LOD	> BMGV
Handling & scooping	5 (100%)	- -	- -
Weighing, mixing & melting	2 (25%)	6 (75%)	4 (50%)
Casting	2 (100%)	- -	- -
Moulding	9 (75%)	3 (25%)	2 (17%)
Maintenance	1 (100%)	- -	- -
Other exposure	4 (57%)	3 (43%)	2 (29%)
All parts of the process	18 (100%)	- -	- -

Tables 11 and 12 show some common features, in particular that moulders were exposed to both isocyanates, whilst those involved in handling/scooping MbOCA had no isocyanate concentrations above the LOD. Those working mainly in weighing, mixing & melting only had measurable quantities of HDA in urine whilst those working in all parts of the process only had measurable quantities of TDA.

2.1.2.4 Analysis by company

An analysis of the results by company helped to explain the differences found in the different diamine concentrations by job type since the isocyanate concentrations in urine were strongly associated with the companies.

The important findings are summarised below.

- Large readings for TDA, with the 2,4 TDA isomer above BMGV, were found for all three samples taken from company R, from workers involved in work classified as ‘other exposed’.

- Two readings taken from moulders working at company Q and the single directly exposed sample taken from company P were above the guidance value for TDA, this time the 2,6 TDA isomer. The latter sample also had a high MbOCA concentration of 24.99.

- Two of the three moulders working at company M had readings above guidance values for HDA whilst all four samples from the workers involved mainly in weighing/mixing and melting at company F had urine concentrations above the BMGV.

- The single worker in the control group with a urine isocyanate concentration above the BMGV worked at company E. All four of the workers who were directly exposed to MbOCA had concentrations below the BMGV for all of the isocyanates.

2.1.3 Correlations between MbOCA and diamines

The results from the urine analysis were subjected to a two-phased analysis to assess for correlations between MbOCA and the presence of isocyanates. The first phase involved coding MbOCA as ND or greater than LOD and a second variable, presence of Isocyanates, was derived as NA if neither TDA nor HDA were detected and greater than LOD if at least one of these was detected. Results from this simple analysis are shown in Table 13.

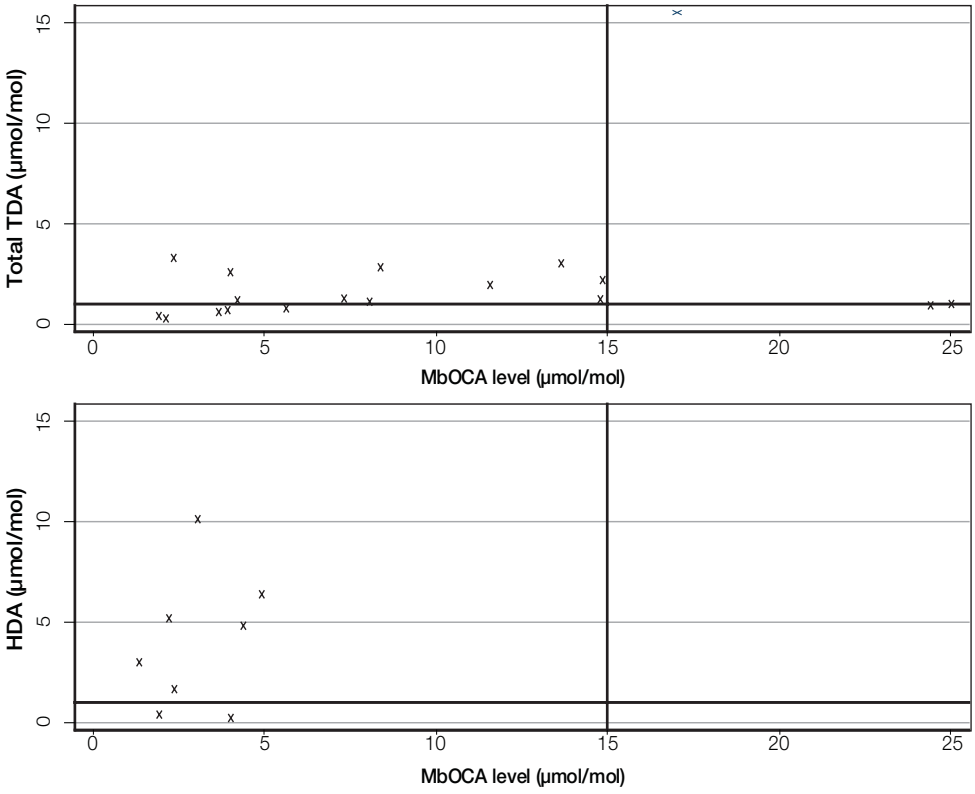
Table 13 Frequencies for measurable quantities of MbOCA and diamines

		Measurable quantity of MbOCA		Total
		No	Yes	
Measurable quantity of diamine	No	24	13	37
	Yes	10	24	34
	Total	34	37	71

Table 13 shows there was a strong association between a measurable quantity of MbOCA and at least one of the diamines (p = 0.004).

The second phase of analysis involved a more detailed examination of the cases where measurable concentrations of MbOCA and TDA or HDA were detected. Figure 8 shows scatter plots of total TDA and HDA against MbOCA. The BMGV limits for both MbOCA and the isocyanates are shown as the red vertical (MbOCA) and horizontal (isocyanates) lines.

Figure 8 Correlations between MbOCA and diamine concentrations in urine



From Figure 8 there appeared to be evidence of positive correlations between the MbOCA concentration and diamine concentrations in urine, particularly between MbOCA and total TDA (p = 0.069). Statistical tests (p=0.53) showed the relationship between MbOCA and HDA concentrations was weak however the number of matched pairs was small.

The 71 samples that were tested for both diamines and MbOCA were used to derive two further variables. Each sample was coded as either less than BMGV or greater than BGMV for MbOCA and the second variable, diamine above BMGV, was derived by categorising each of the samples as having at least one diamine concentration above the BMGV or all diamine concentrations below the BMGV. Table 14 below shows a cross tabulation of the two variables. In workplaces with good occupational health practices the two variables would not be expected to be related, and conversely, a relationship between the two variables could be an indicator of poor occupational health practices in some of the workplaces.

Table 14 BMGV values of diamine and MbOCA

		MbOCA level above BMGV		Total
		No	Yes	
Diamine level above BMGV	No	46	1	47
	Yes	22	2	24
	Total	68	3	71

Table 14 shows there did not appear to be a link between whether diamine concentrations were above the BMGV and MbOCA concentrations above the BMGV, however this clearly depended on the magnitude of the BMGV. In section 3.1.1.4 the analysis showed the BMGV could be reduced and when it was lowered to 10 µmol/mol creatinine and the above analysis repeated, the results showed that those workers above the revised BMGV for MbOCA would be more likely to be above the BMGV for at least one of the diamines.

2.1.4 Summary

- Evidence suggests that the current BMGV for MbOCA could be reduced since the 90th percentile for all companies (including some that may not have good occupational hygiene practices) has been consistently below 10 µmol/mol creatinine for the last ten years.

- Directly exposed workers had higher MbOCA concentrations in urine, particularly those working in casting, moulding and all parts of the process. The observation that many workers were above the BMGV for isocyanates is a new and important finding.

- Correlations between the different isocyanates diamine concentrations were weak.

- Correlations between MbOCA and diamine concentrations were positive and provided some evidence of a relationship, particularly between TDA and MbOCA.

2.2 Air samples

A total of 210 air samples from 20 companies were collected, with samples taken at both static and person level. Person level samples were taken from the working area of one of the employees. Both the static and person level air samples were

then analysed for MbOCA. The WEL for MbOCA in a person level air sample, calculated as an eight-hour average exposure, is currently set at 0.005 mg m^{-3}.

A total of 80 personal air samples were collected. In some cases multiple samples were taken (at different times of the day) from the same working area. A total of 130 static samples were taken from the companies at a variety of locations. The static samples were almost exclusively taken at locations that could be classified as directly exposed whereas all personal samples were taken from directly exposed workers. In general, the samples were taken over a period of approximately 100 minutes although some samples were taken over a much shorter period.

Table 15 below reports the frequency of person level and static level air samples in which the sample was recorded as ND or > LOD

Table 15 Frequencies for MbOCA concentration in air by sample type

		MbOCA concentration in air sample	
		ND	> LOD
Exposure	Personal Samples	67 (84%)	13 (16%)
	Static Samples	116 (89%)	14 (11%)

For both personal and static samples the concentrations of MbOCA were very low and found in only 10% of cases. Neither the Figures in Table 15 nor statistical tests suggested any differences between the static and personal samples.

Some summary statistics of the numeric readings are given in Table 16 and boxplots of the readings are shown in Figure 9. The WEL of 0.005 mg m^{-3} is also shown.

Table 16 Summary statistics of MbOCA concentration in air by sample type

MbOCA concentration in air sample								
Exposure	n	Max	Min	Median	Arithmetic mean	Arithmetic standard deviation	Geometric mean	Geometric standard deviation
Personal Level	13	0.011	0.0004	0.001	0.002366	0.00309	0.00246	3.404
Static	14	0.0111	0.00015	0.00355	0.00366	0.00286	0.00131	2.9082

Figure 9 MbOCA concentration in air by sample type

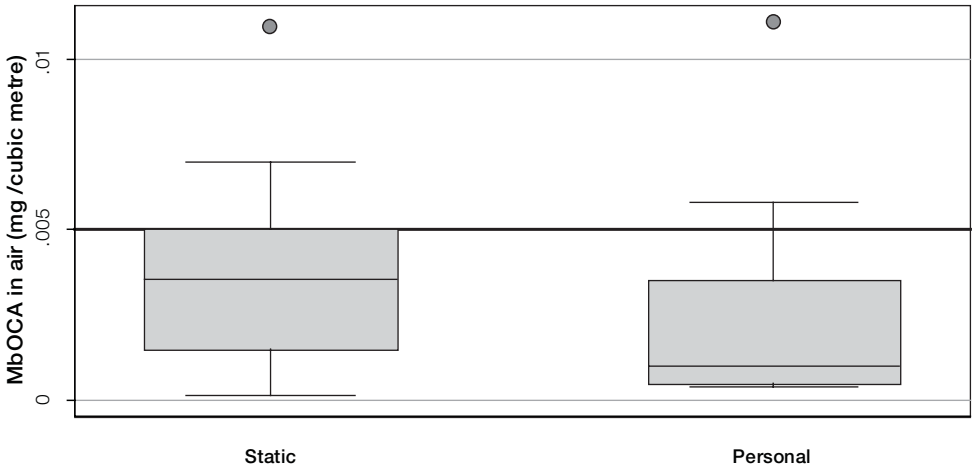


Figure 9 shows the concentrations (where the test was able to determine the quantity of MbOCA in the air sample) were small, with respective medians of 0.0036 and 0.001 for static and personal samples respectively. There was some evidence to suggest that the static samples had higher concentrations than the person level samples (p = 0.0848) however the power of the test was low due to the small number of numeric readings in both groups. Two of the concentrations from personal samples were above 0.005 mg m^{-3}, which, given that 75 samples were collected, would be consistent with good practice. However, the largest concentration observed of 0.011mg m^{-3} was taken over a 20-minute period and may not be representative of a working shift although it is representative of short-term exposure.

2.2.1 Correlation between air and urine samples

Where possible the air and urine samples were matched (n=75) in order to test for correlations between the samples. Air and urine samples could not be matched in all cases.

The results from the first phase analysis are shown in Table 17. Each of the urine and air samples was classified as ND or greater than LOD. The row percentages in Table 17 equal 100.

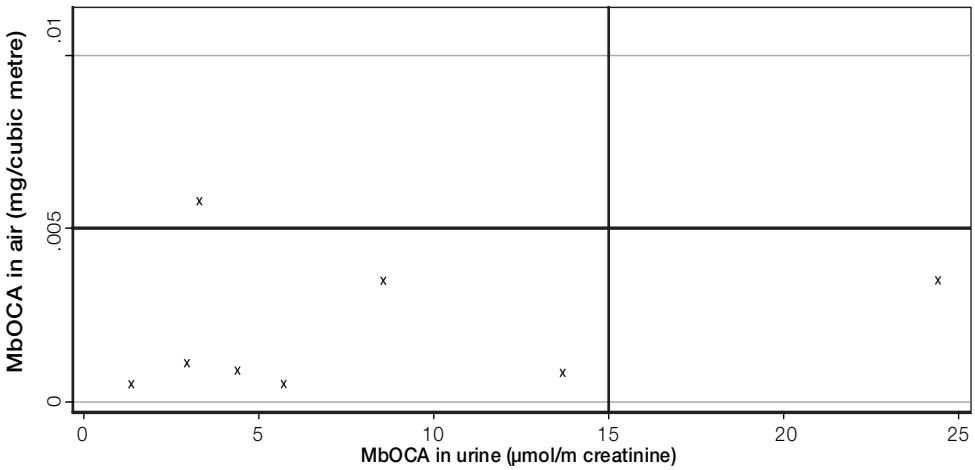
Table 17 Comparison of air and urine results

		MbOCA concentration in air	
		ND	> LOD
MbOCA concentration in urine	ND	28 (87%)	4 (13%)
	>LOD	35 (82%)	8 (18%)

Table 17 shows that there did not appear to be an association between the MbOCA concentrations in urine and personal air samples using this simple analysis. Formal statistical analyses were also performed and showed there was no evidence to suggest an association between MbOCA concentrations in urine and personal air samples (p= 0.54).

A graphical representation of the eight cases where numerical readings were obtained for both air and urine samples is shown in Figure 10.

Figure 10 Correlations between MbOCA and Isocyanate levels in urine



From the small amount of data where numeric readings were obtained for both samples there was no evidence of a relationship. Moreover, there were no cases where an individual was above the BMGV for urine and the WEL for air.

2.3 Surface wipe samples

A total of 334 surface wipe samples were taken from the 20 companies. Samples were mainly concentrated on surface areas that might be classified as directly exposed to MbOCA, with 259 taken from directly exposed areas and 75 taken from control surfaces (surfaces which should not contain traces of MbOCA if good practice was followed) such as canteen or office surfaces. In general the surface wipe was taken from an area of 100 square cm.

Table 18 reports the frequencies that the control and directly exposed surface samples were classified as ND and > LOD.

Table 18 Frequencies for MbOCA level on surface wipes by exposure

		MbOCA concentration on surface wipe	
		ND	> LOD
Exposure	Control	67 (89%)	8 (11%)
	Directly Exposed	103 (40%)	156 (60%)

The differences between the directly exposed and control areas of the workplace were large with the majority of control areas having no MbOCA present on the surface wipe whilst the majority of samples taken from exposed areas had a measurable concentration. However, the eight control samples (which came from a variety of control locations) had measurable concentrations of MbOCA and could be viewed as indication that best practice was not followed at all premises.

Summary statistics of the numeric readings are given in Table 19 by exposure.

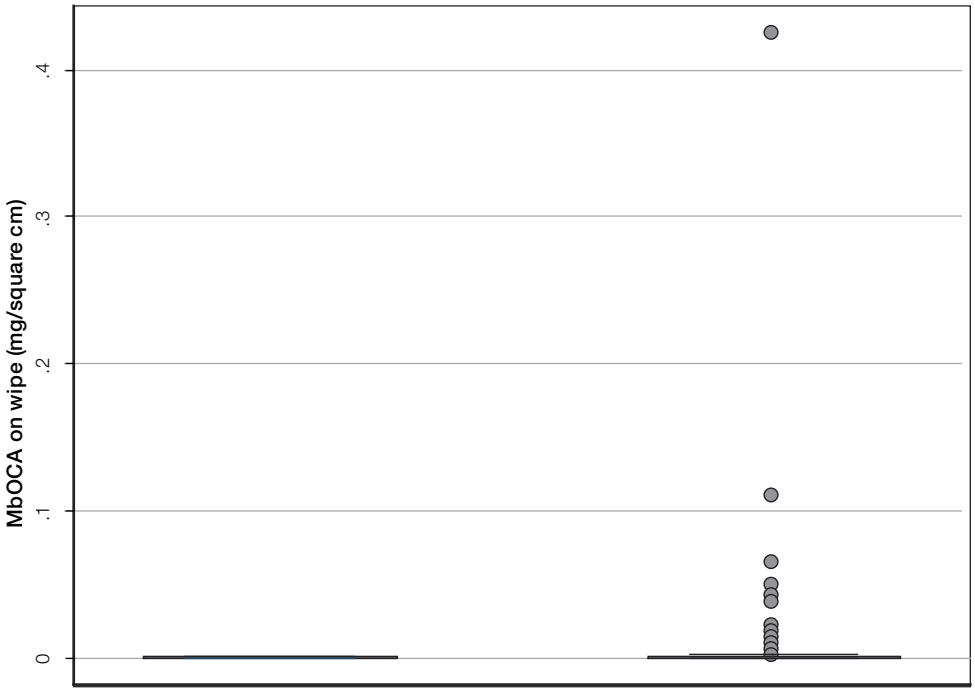
Table 19 Summary statistics of MbOCA concentration on surface by exposure

MbOCA concentrations on surface								
Exposure	n	Max	Min	Median	Arithmetic mean	Arithmetic standard deviation	Geometric mean	Geometric standard deviation
Control	8	0.0074	0.00002	0.0001	0.00026	0.000298	0.00012	4.1494
Directly exposed	156	0.425	0.00001	0.0002	0.00658	0.03597	0.000307	10.7757

Due to the small number of control samples (n=8) a corresponding test was not performed for this group.

Figure 11 shows boxplots of the data where a numeric reading was obtained by exposure.

Figure 11 MbOCA on surface wipe by exposure



The quantity of MbOCA on surface wipes was broadly similar in the directly exposed and control areas with respective medians of 0.0002 and 0.0001 mg/cm^2 and respective interquartile ranges of 0.001086 mg/cm^2 and 0.000463. The directly exposed group had a median and interquartile range approximately twice as large as the control group, although in both cases these summaries of the data were of the same order of magnitude. However, Figure 11 highlights the differences in the large concentrations with a relatively small number of very high surface wipe concentrations solely in the directly exposed areas; the affect of these can be seen by comparing the arithmetic and geometric means for directly exposed areas which differ by an order of magnitude. Despite the obvious skew, the data from directly exposed areas^2 were not log-normally distributed (both the skewness and kurtosis of the data were too pronounced).

2.3.1 MbOCA concentration on surface wipes by location

As described in section 2.3.3, the areas which surface wipes were taken from were classified into eight areas, with the areas chosen to reflect the stages of the manufacturing process. Results from the first stage analysis are presented in Table 20. All row percentages in Table 20 sum to 100.

Table 20 Frequencies for MbOCA level on surface wipes by location

	MbOCA levels in on surface wipe	
Location	ND	> LOD
Fume cupboard/degassing	10 (27%)	27 (73%)
Storage	34 (50%)	34 (50%)
Weighing/pouring	4 (16%)	21 (84%)
Mixing	6 (40%)	9 (60%)
Oven	14 (40%)	21 (60%)
Hopper	4 (50%)	4 (50%)
Casting	4 (40%)	6 (40%)
Other non-specific	27 (44%)	34 (56%)

Table 20 shows that MbOCA was found in the majority of samples for almost all locations. The weighing/pouring locations had a particularly high proportion of samples where a measurable quantity of MbOCA was present on surfaces.

Further analysis of the numeric readings is given below with summary statistics presented in Table 21 and boxplots shown in Figure 12.

Table 21 Summary statistics of MbOCA concentration on surface by location

MbOCA concentrations on surface								
Exposure	n	Max	Min	Median	Arithmetic mean	Arithmetic standard deviation	Geometric mean	Geometric standard deviation
Fume cupboard	27	0.0514	0.00001	0.0004	0.00295	0.00985	0.00038	8
Storage	34	0.0665	9*10-6	0.0003	0.0042	0.0124	0.00027	12.07
Weighing/ pouring	21	0.1116	4*10-6	0.0005	0.0114	0.026	0.000266	18.26
Mixing	9	0.0145	1.3*10-5	0.0001	0.0033	0.0061	0.000191	12.88
Oven	21	0.425	7.4*10-6	0.0001	0.0207	0.0926	0.000191	11.78
Hopper	4	0.0209	0.0033	0.011	0.0116	0.0072	0.0096	2.1631
Casting	6	0.0003	1.7*10-5	0.0001	0.00011	0.0001	0.000079	2.8
Other	34	0.0205	7*10-6	0.0002	0.0015	0.004	0.000234	7.168

Figure 12 MbOCA on surface wipe by location

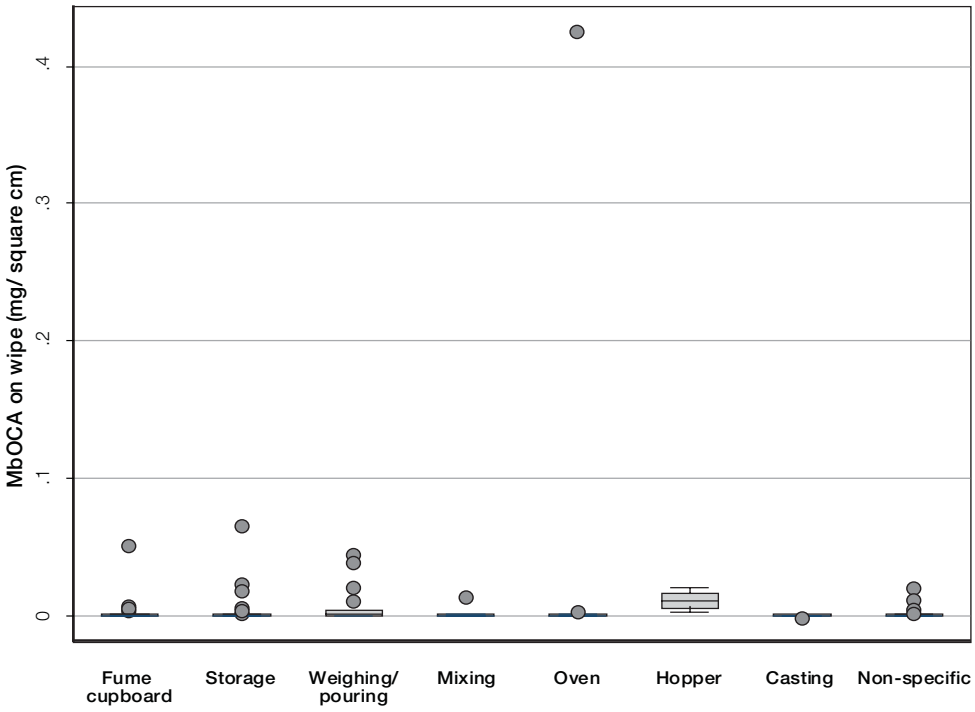


Figure 12 and the summary statistics presented in Table 21 show that the general level of surface concentrations was at a similar level for the different sample locations, with medians and geometric means very similar for different locations; Hopper was the one exception with a much larger median (an order of magnitude larger than at the other locations) and geometric mean. Many of the sample locations had concentrations that could be considered to be 'outlying' or unusual however the descriptions accompanying the samples showed that the very large concentrations usually came from areas where MbOCA contamination would be expected such as weighing scales.

2.3.2 Storage drums

One of the specific aims of the statistical analysis was to investigate the quantities of MbOCA found on wrapped drums in storage at the two distributors, companies R and T. The numbers of samples taken from the companies were not sufficient to allow for a thorough statistical analysis however the results from a simple exploration of the data are presented here. Of the 17 surface samples taken from the storage area at company T, two had small traces of MbOCA, 0.0002 and 0.0008 mg/cm^2 respectively. Of the 11 samples taken from the storage area at company R, four contained traces of MbOCA with respective concentrations of 0.0184, 0.0233, 0.0058 and 0.0011 mg/cm^2 from samples on wrapped pallets and wrapped storage drums. Collectively these samples from company R accounted for all but one of the large observations (see Figure 12) taken in storage facilities in all companies, the largest of all being a sample taken from the side of a drum at company C.

2.3.3 Correlations

It was not possible to correlate surface concentrations with air or urine results due to the way the samples were taken. Surface concentrations were taken from specific work areas and these could not be related to specific workers using the data collected.

2.4 Glove samples

There were a total of 147 glove samples, all of which could be classified as being potentially contaminated by MbOCA. More glove samples were taken from the companies however, due to unspecified reasons a small number of samples were not tested.

2.4.1 Analysis by glove type

Gloves could be classified as an inner glove worn next to the skin and an outer glove, worn over the top of the inner glove and with a potential direct exposure to MbOCA. A two-phase analysis of all the glove data was not possible since not all gloves were explicitly classified as inner or outer by the on-site inspectors and the description accompanying the sample was insufficient for this judgement to be retrospectively made. Only 88 of the 147 glove samples could be classified as inner or outer.

Table 22 below shows the frequencies of glove samples where the measurements were either ND or greater than the level of detection by the glove type.

Table 22 Frequencies for MbOCA concentration on gloves

		MbOCA concentration on gloves	
		ND	> LOD
Glove Type	Inner	16 (52%)	15 (48%)
	Outer	6 (11%)	51 (89%)

Approximately 90% of the outer gloves contained a measurable concentration of MbOCA whereas approximately 50%of the inner glove samples contained a measurable concentration. The difference between glove types was highly significant ($p < 0.001$) .

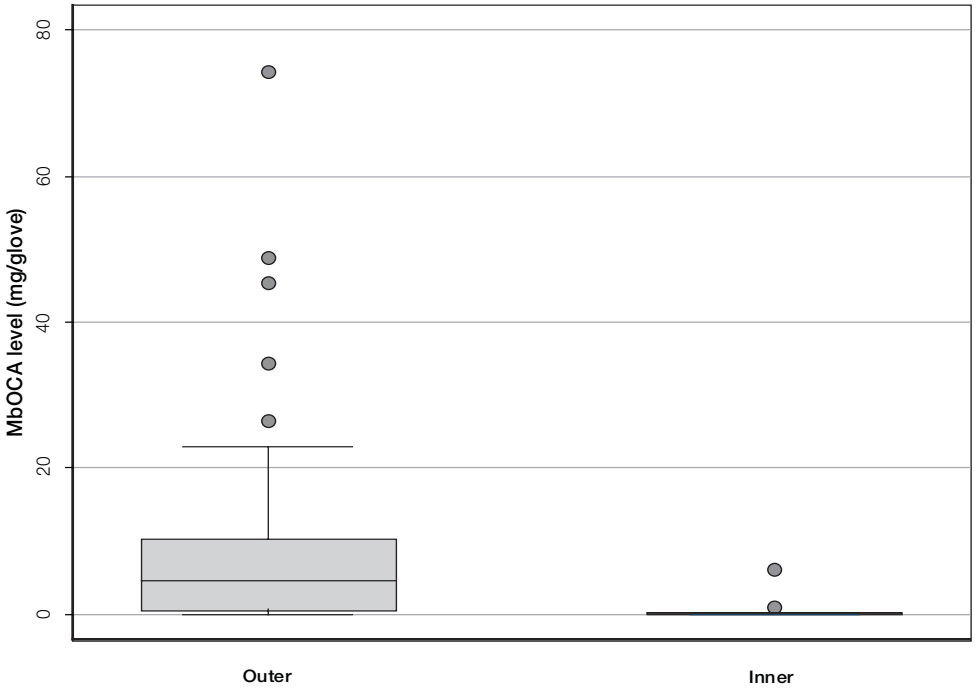
Table 23 shows summary statistics for the measurements from the two glove types.

Table 23 Summary statistics of MbOCA concentration on gloves

MbOCA concentrations on gloves								
Exposure	n	Max	Min	Median	Arithmetic mean	Arithmetic standard deviation	Geometric mean	Geometric standard deviation
Inner	15	6.3	0.01	0.09	0.5619	1.604	0.107	4.854
Outer	51	74.44	0.016	4.534	9.2766	14.45	2.555	7.885

Figure 13 shows boxplots of the concentrations measured in mg/glove found on the inner and outer gloves.

Figure 13 MbOCA concentration by glove type



The differences between the inner and outer glove concentrations are clearly visible from both the summary statistics in Table 23 and the plot in Figure 13 and statistically significant ($p < 0.001$). The respective medians were 0.09 mg/glove for inner compared with 4.534 mg/glove for outer, with respective ranges of (0.01, 6.3) and (0.016 to 78), which reflect that the concentrations on outer gloves were in general much larger than inner gloves; in general the concentrations on outer gloves were several orders of magnitude larger than the concentrations on inner gloves.

2.4.2 Correlation between inner and outer glove samples

One of the specific aims of the statistical analysis was to investigate the correlation between inner and outer glove concentrations. At three of the site inspections, inner and outer (and in one instance middle) glove samples were taken from the same individual whereas the data collected from other premises were not detailed enough to allow samples to be matched. It was only possible to match inner and outer

glove samples for nine individuals and even in these cases the hand the gloves were worn on could not be matched for the inner and outer glove samples, hence a meaningful comparison between inner and outer glove concentrations was not possible. However, in one case where it was possible to match inner and outer gloves, the very large inner glove concentration of 6.3 mg correlated with large outer glove concentrations of 12.8 and 22.9 mg.

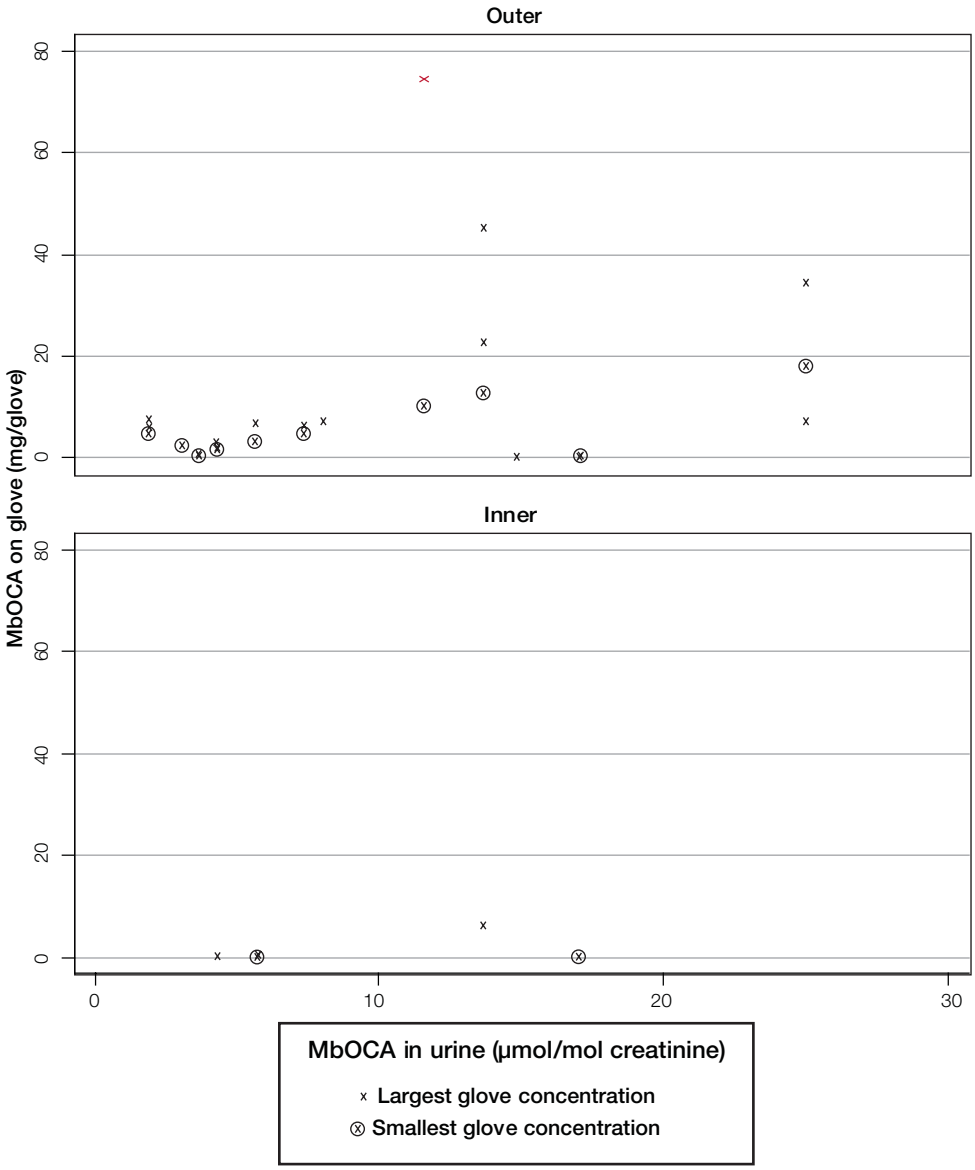
2.4.3 Correlation between glove samples and urine samples

The descriptions that accompanied glove samples did make it possible to match glove samples to urine samples. Figure 13 shows the cases where numeric values were obtained in both glove and urine tests for both outer and inner glove samples. It was possible to match more than one glove sample to a urine reading (left, right hands) for some cases; when this was possible the largest of the readings is identified by the red cross and the smallest glove concentration is identified by the green cross.

Figure 14 shows that it was possible to match urine and outer gloves concentrations much more frequently than for inner gloves. The data on inner gloves was too sparse to establish a relationship however the data indicated that there may be a relationship between the level of contamination of MbOCA on gloves and the concentration of MbOCA in urine, with urine concentrations increasing with increases in the level of contamination of the gloves. In particular the two samples with very high concentrations of MbOCA in urine both had a large contamination on glove samples. A correlation coefficient is not provided since there was not a one-to-one mapping of urine readings to give concentrations. A correlation could be calculated by using a summary of the two glove concentrations (ie maximum or mean) and relating this to the urine, however the correlation would depend on the summary used.

A relationship between the level of contamination on outer gloves and MbOCA in urine would be more complex than Figure 14 suggests. Each point in Figure 14 corresponds to a case where both the level of contaminant on a glove and the concentration of MbOCA in urine were above limits of detection, the cases where one or both of these measurements were below the LOD are not seen. The variability in the data would suggest that factors such as the length of time the gloves were worn (single use gloves for quickly performed tasks versus continuous use), the material of the glove, the job being performed and whether the gloves were reused may be important. The data from the present study did not contain sufficient detail to investigate the relationship further. In order to establish for what combination of factors the relationship between glove contamination and urine concentrations was at its strongest additional research would be required.

Figure 14 MbOCA concentration by glove type and MbOCA in urine



2.5 Interpretation of a boxplot

A boxplot is an effective visual display of key summaries of a continuous variable and is particularly useful for displaying skewed data containing outlying (or unusual) observations, and for comparing two or more variables. The boxplots in this report are comprised of four elements:

- median;
- quartiles – the 25th and 75th percentiles of the data;
- bounds of variability; and
- outliers.

The figure below using the MbOCA in urine readings is used to highlight these elements.

The 25th and 75th percentiles mark the bounds of the shaded area or 'box', the difference between these values being the interquartile range, which is a more reliable summary of dispersion than standard deviation for skewed data. The central line within the box is the median, an estimate of location that is more reliable than the mean for skewed data. The vertical lines or 'whiskers' that emerge from the box (above and below) indicate the maximum and minimum values unless outliers are present, in which case they extend to 1.5 times the interquartile range. The points that are beyond the 'whiskers' are outliers or unusual observations, seen in the above plot as the blue dots.

Further reading

Method validation for MbOCA analysis on nitrile and leather gloves HSL OMS/2006/03

Biological monitoring in the workplace: A guide to its practical application to chemical exposure HSG167 HSE Books 1997 ISBN 0 7176 1279 1

Health surveillance at work HSG61 HSE Books 1999 ISBN 0 7176 1705 X

Control of substances hazardous to health (Fifth edition). The Control of Substances Hazardous to Health Regulations 2002 (as amended). Approved Code of Practice and guidance L5 HSE Books 2005 ISBN 0 7176 2981 3

Monitoring strategies for toxic substances HSG173 HSE Books 1997 ISBN 0 7176 1411 5

Respiratory protective equipment at work: A practical guide HSG53 (Third edition) HSE Books 2005 ISBN 0 7176 2904 X

Maintenance, examination and testing of local exhaust ventilation HSG54 (Second edition) HSE Books 1998 ISBN 0 7176 1485 9

A step by step guide to COSHH assessment HSG97 (Second edition) HSE Books 2004 ISBN 0 7176 2785 3

Aromatic amines in air and on surfaces MDHS75 HSE Books 1993 ISBN 0 11 886370 3

Guidance on Laboratory Techniques in Occupational Medicine (Tenth edition) 2005 HSL

Cocker J, Nutley B P, Wilson H K 'Methylene bis (2-chloroaniline) (MbOCA): Towards a biological monitoring guidance value' Biomarkers 1996, 1, 185-189

Cowie H A, Hughson G W et al 'An occupational hygiene assessment of the use and control of isocyanates in the UK' 2004 HSE Contract Research Report RSU Reference 4305/R51.229

Assessing and managing risks at work from skin exposure to chemical agents: Guidance for employers and health and safety specialists HSG205 HSE Books 2001 ISBN 0 7176 1826 9

Cost and effectiveness of chemical protective gloves for the workplace: Guidance for employers and health and safety specialists HSG206 HSE Books 2001 ISBN 0 7176 1828 5

Health and Safety Commission. Health and safety statistics 2005/06 HSE Books (free publication)

EH40/2005 Workplace exposure limits: Containing the list of workplace exposure limits for use with the Control of Substances Hazardous to Health Regulations 2002 EH40 HSE Books 2005 ISBN 0 7176 2977 5

Fit testing of respiratory protective equipment facepieces OC 282/28 (rev) HSE 2003. Web-only version at www.hse.gov.uk/pubns/fittesting.pdf

Survey findings from a national survey of MbOCA exposure HSL ESS/2006/07

Clapp D E, Piacitelli G M, Zaebst D D and Ward E 'Assessing exposure to 4,4'-Methylene bis (2-chloroaniline) (MbOCA) in the Workplace' Appl. Occup. Environ. Hyg. 1991, 6,2, 125-130

Report on a survey at four users and four suppliers of MbOCA 2004 HSL JS500 9600

Method for 2,2'-Dichloro-4,4'methylene dianiline (MbOCA) in urine HSL January 2005 available at www.hsl.gov.uk

Method for isocyanate metabolites in urine HSL October 2005 available at above website

HSE, (2005b) http://www.hse.gov.uk/aboutus/hsc/iacs/acts/watch/agendas.htm WATCH meeting October 2005

Williams N R, Jones K and Cocker J. 'Biological monitoring to assess exposure from isocyanates use in motor vehicle repair' *Occupational & Environmental Medicine*. 1999, 56, 598-601

Toxicity and Safe Handling of Di-isocyanates and Ancillary Chemicals (Second Edition) – A Code of Practice for Polyurethane Flexible Foam Manufacture and Elastomer Manufacture – BRMA and RAPRA Technology 2001

'MbOCA and You' 1999 HSE Free Leaflet

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