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| Journal: | Environmental Science: Processes & Impacts |
|-------------------------------|---|
| Manuscript ID: | EM-ART-08-2014-000455.R1 |
| Article Type: | Paper |
| Date Submitted by the Author: | 02-Oct-2014 |
| Complete List of Authors: | Dartey, Emmanuel; University of Education, Winneba, Faculty of Science & Environment Education Thomassen, Y; Statens Arbeidsmiljo Institutt, Pb 8149 Dep Berlinger, Balazs; Statens Arbeidsmiljo Institutt, Pb 8149 Dep Ellingsen, Dag; National Institute of Occupational Health, Odland, Jon-Øyvind; University of Tromsø, Department of Community Medicine Nartey, Vincent; University of Ghana, Chemistry Yeboah, Francis; Kwame Nkrumah University of Science and Technology, Molecular Medicine, School of Medical Sciences Weinbruch, Stephan; Technical University Darmstadt, Institute of Applied Geosciences |
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Bioaccessibility of lead in airborne particulates from car battery repair work

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Abstract

The bioaccessibility of Pb in air particulate matter from two car battery repair workshops in Kumasi (Ghana) was measured (64 full shift personal aerosol samples). An artificial lung lining fluid simulant (Hatch solution) was applied for leaching the bioaccessible fraction in half of the samples, the other half was leached with synthetic gastric juice. At both locations, the Pb solubility (median) in gastric juice (89 % and 92 %) is substantially higher than in Hatch solution (4.9 % and 5.6 %). The high solubility of Pb in gastric juice may be related to the presence of Pb oxides. The low bioaccessibility of Pb in Hatch solution is in good agreement with previous work on mine tailings, urban aerosol, car exhaust, welding fumes and indoor dust. The high bioaccessibility of Pb in the gastrointestinal tract underpins the importance of improving the personal hygienic behavior at the workplace. It is recommended that air monitoring of Pb should include the extrathoracic aerosol fraction using inhalable aerosol samplers, as particles of this size fraction are most likely transferred to the gastrointestinal tract in addition to the non-lung-soluble particles transported from the lung by muccoiliary and phagocytosis clearance.

1 Introduction

The principal consumption of lead (Pb) is for production of Pb-acid batteries which accounts for approx. 80% of the global Pb production¹. The increasing consumption of Pb driven by industrialization and new technologies with use of batteries in automobiles, solar energy production and telecommunication will consequently also increase the repair and recycling of Pb batteries. Battery repair and recycling are valuable commercial activities for many in the developing world. The unawareness of the toxic effects of Pb combined with lack of other viable economic alternatives has led to serious environmental and occupational exposure to Pb in many

developing countries^{2,3}. Gottesfeld and Pokhrel² have reviewed the Pb exposure studies in battery manufacturing and recycling in 37 developing countries. Both workroom air and whole blood Pb concentrations among workers were considerably higher than those reported from industries in the developed world. Geometric mean air concentrations ranged from 33 to 355 μ g/m³ of Pb while whole blood arithmetic mean concentrations ranged from 22 to 128 μ g/dL of Pb with a median value of 42 μ g/dL of 61 cohort mean values. From the limited data available for battery repair workshops it appears that Pb concentrations in air (A-Pb) are significantly lower compared to battery manufacturing and recycling. For example, Matte et al.⁴ report a range of 0.03 – 5.3 mg/m³ of Pb for battery manufacturing in Jamaica compared to 0.003 – 0.066 for battery repair. Still, concern about Pb exposure in the neighbourhoods of battery repair workshops has been expressed^{4,5,6}.

Environmental and occupational Pb exposure predominantly occurs through inhalation and ingestion⁷. The contribution of ingestion to the total exposure can be significant due to smoking and/or eating habits when personal hygiene is poor^{8,9,10,11,12}. Lead can cause toxic effects in a large number of organs and tissues including the nervous system, blood, kidney, cardiovascular system, endocrine system, and gastrointestinal tract⁷. The bioavailability of Pb in the lung and the gut from airborne particulate matter has been shown to be dependent on the particle size distribution with increasing absorption with decreasing particle sizes^{13,14,15,16}. The assessment of Pb's bioavailability and bioaccessibility is thus important for human health risk characterization. The *bioaccessibility* of a substance is the fraction that can be dissolved by the digestive fluids. This is the theoretical fraction available for adsorption from either the lung and/or the gastrointestinal tract. This fraction can be investigated in vitro by measuring their solubility in

artificial human tissue fluids or in samples of natural tissue fluids. The amount dissolved in these fluids is defined as the *bioaccessible fraction*^{17,18,19,20,21}.

The bioaccessibility of Pb in particles emitted during car battery repair work has not been investigated. In addition, data on Pb exposure at workplaces in African countries are very limited. The Suame Magazine and Asafo Fitam industrial slums in the region of Kumasi (Ghana) belong to the largest agglomerations of small scale cluster engineering in sub-Saharan Africa with an estimated income earning population (including women) of about 200,000 (Suame Magazine) and 12,000 (Asafo Fitam), respectively. The main activities at both locations are manufacturing, vehicle repair, metal working, welding of metals, repair of lead-acid batteries, sale of engineering materials, sale of automobile spare-parts, and sale of food (the latter mainly by women). Several thousand inhibitants have their total income earnings from vehicle repair and maintanance (including Pb battery repair) as major activities. As part of a larger exposure assessment study to Pb among car battery repair workers, the present study aims to employ simulated lung fluid (Hatch solution) and gastro-intestinal juice (gastric solution) to investigate the respiratory and gastric bioaccessibility of Pb in airborne particulate matter collected among battery repair workers.

2 Materials and Methods

Process description

Car Pb batteries consist predominately of Pb alloys (with Sb and Ca), Pb dioxide (PbO₂) and diluted sulfuric acid. When the battery is working properly, a thin layer of sulfate forms on the battery plates during discharge, and dissolves back into the battery acid during charging. With

use, sulfation occurs when the sulfate forms a hard crystalline shell that is not dissolved during charging. This process will reduce the capacity of the battery to a non-useful level.

The Pb-acid battery recovery small-scale operation uses simple technology involving pasting of Pb oxide (PbO) to battery plates, gas welding for assembling cells and to attach connectors to rebuilt cells. During these processes it is expected that particles are emitted to the workroom atmosphere containing predominately Pb in the metallic form, as PbO, PbO₂ or as PbSO₄. If the temperature is high as for example during welding operations, Pb may evaporate and form ultrafine particles by condensation.

Sampling

Two small scale workshops at Suame Magazine (Site A) and Asafo Fitam (Site B) were approached and agreed to participate. Personal aerosol samples of sixty four male Pb battery repair workers who voluntarily agreed to participate, were collected using 25 mm "total dust" air sampling cassettes (Millipore, Bedford, MA, USA) equipped with 5 μ m pore size polyvinyl chloride membrane filters. The aerosol cassettes were mounted in the breathing zone of the workers (for details see Ellingsen et al., 2013)²². Air sampling was performed with SKC Sidekick pumps (SKC Ltd. Dorset, UK) operated at a flow rate of 2 ± 0.1 L/min. The sampling time was six hours. The workers neither used gloves nor any personal respiratory protection during the repair work. During the full-shift working period the workers typically did the same repair work for about six hours (depending on the amount of work available), otherwise they stayed outside the workshop area with no source ventilation or general workroom air ventilation system. The job functions of the battery workers investigated included charging of Pb-acid batteries, breaking of batteries to replace damaged Pb plates, repair of Pb plates and replacing the

Pb terminals of the battery by welding. Based on oral interviews and on inspection of the premises it was obvious that much less batteries are handled at site B (Asafo Fitam) than at site A (Suame magazine). However, this difference cannot be quantified.

Blood samples were taken from the same sixty four Pb battery repair workers and from thirty three unexposed male controls (17 from site A and 16 from site B). The controls were selected among workers in the environments of the workshops studied, selling items such as automobile spare parts and engineering materials (excluding Pb-acid batteries). Blood samples were collected by authorized health staff. The procedure was explained to all subjects and the sampling conducted with their informed written consent. The blood samples were frozen and stored at -20 °C at Komfo Anokye Teaching Hospital (KATH), Kumasi, prior to shipment to the National Institute of Occupational Health (NIOH) in Oslo for determination of trace metals.

Leaching procedures

An artificial lung lining fluid simulant (Hatch's solution)²³ was applied for leaching of the bioaccessible fraction in thirty two (out of the sixty four) filter samples randomly selected among the samples collected at Site A and Site B. The composition of the Hatch leaching solution is presented in Table 1. In short, the leaching of the air particulates on each filter was done in a 50 mL VectaSpin 20TM PP centrifuge tube equipped with a 25 mL volume cup insert with 0.45 mm pore size Nylon membrane (Whatman International Ltd., Maidstone, England, UK) with 10 mL of Hatch solution. The tube was heated in a laboratory oven at 37 °C for 24 hours. The leaching solution was then filtered by centrifugation at 2075 G with a 12 tube capacity centrifuge (Model 4K15, Sigma, Osterode/Harz, Germany). The large amount of organic materials in the Hatch leachate required a following simple acid digestion procedure; 1 mL of the leachate was

transferred to a 14 mL polypropylene (PP) tube (Sarstedt AG, Nümbrecht, Germany) and 2 mL of 65 % ultrapure HNO₃ and 100 μ L of internal standard solution containing 1.0 mg/L thallium (Tl) were added before heating in a laboratory oven at 90 °C for 90 minutes. After cooling, the solutions were diluted to 14 mL with de-ionized (DI) water. A two-step acid digestion procedure was required to dissolve the non-Hatch soluble particles. Two mL of 65 % HNO₃ (p.a. quality) and 100 mL of an internal standard solution containing beryllium (Be) were added to the cup insert which were put into SV-140 Teflon autoclaves (Milestone, Sorisole, Italy). The open autoclaves were placed into a laboratory oven at 120 °C for 120 minutes. After this step, a mixture of 2.0 mL aqua regia and 0.2 mL 40 % HF was added to each autoclave, which after closing, were kept at 120 °C for 150 minutes in a laboratory oven. The digested samples were finally diluted with DI water to 14 mL. Further details of the leaching procedures can be found elsewhere²².

The other thirty two aerosol samples were subjected to leaching with synthetic gastric juice with some modifications following the United States Pharmacopeia (UPS) methodology described by Hamel et al.²⁴. The leachate was prepared by dissolving 2.0 g of NaCl in a solution of 7 mL of ultrapure hydrochloric acid and 250 mL of deionised water in a 1 L volumetric flask, 3.2 g of pepsin from porcine gastric mucosa was added, and the solution was brought to 1000 mL for immediate use. The leaching was done in the VectaSpin 20TM PP centrifuge tubes by adding 10 mL of gastric juice to the PVC filter samples. Each tube containing the filter and the leaching solution was placed in a laboratory oven set to a temperature of 37 ± 1 °C for 2 hours. The obtained solutions were then filtered by centrifugation at 2075 G. After centrifugation, 100 µL internal standard solution containing 140 µg/L of Be and a mixture of 2.0 mL aqua regia and 0.2

mL 40 % HF were added to the filter cup inserts which were put into the SV-140 Teflon autoclaves. After the digestion procedure, the sample solutions were transferred to 14 mL PP tubes and filled up to 14 mL with DI water.

Analytical procedures

Lead and Sb in the Hatch and gastric solutions as well as in the "gastric non-soluble" fraction after 10 times dilution were determined using high-resolution inductively coupled plasma mass spectrometry (ICP-SF-MS) (ThermoFinnigan Element 2, Bremen, Germany), meanwhile inductively coupled plasma optical emission spectrometry (ICP-OES) (Perkin Elmer Optima 7300, Waltham, USA) was used to determine the same elements in the "Hatch non-soluble" fraction. Both instruments were calibrated with matrix matched (Hatch solution / gastric solution / acids) solutions. The accuracy was assessed by comparing the analytical data obtained by analyzing realistically exposed welding aerosol filters by a previously validated method to the total amounts of metals (Hatch soluble + Hatch non-soluble and gastric soluble + gastric nonsoluble) obtained using ICP-SF-MS and ICP-OES procedures²⁵. All measurements were carried out at the National Institute of Occupational Health in Oslo, Norway. The obtained detection limits (DL) of Pb and Sb in $\mu g/m^3$ were as follows: gastric non-soluble fraction: Pb: 0.012 and Sb: 0.003; gastric soluble fraction: Pb: 0.003 and Sb: 0.002; Hatch non-soluble fraction: Pb: 0.22 and Sb: 0.26; Hatch soluble fraction: Pb: 0.009 and Sb: 0.013.

Lead was determined in the whole blood samples at the National Institute of Occupational Health in Oslo, Norway. The samples were prepared by adding 2 mL of 65 % ultrapure nitric acid and 100 μ L of an internal standard solution containing 1 mg/mL of europium (Eu) to 1 mL of whole

blood in a polypropylene tube. After heating to 90 °C for 90 minutes and cooling to room temperature, the samples were diluted to 14 mL with deionized water. The analysis was performed by inductively coupled plasma high-resolution mass spectrometry (ICP-SF-MS) calibrated with whole blood matrix matched standard solutions. The method detection limit for Pb in whole blood was 0.2 μ g/L. For the quality control of the Pb determinations Seronorm Trace Elements Whole Blood L-2 (LOT: MR9067x) reference material (Sero AS, Billingstad, Norway) was used. The measured Pb concentrations (N = 24) had an average of 421 μ g/L with a standard deviation of 15 μ g/L while the reference value given by the producer was 395 ± 22 μ g/L.

Data analysis

As a significant fraction of the air samples investigated contained Pb at concentrations below the detection limit, our statistical analysis generally followed the recommendations given by Helsel for censored data²⁶.

Total air concentrations (TC) were calculated as the sum of the concentrations of the soluble (C_{sol}) and insoluble fraction (C_{insol}) , for both gastric juice and Hatch solution. If both fractions are below DL, TC can vary between zero and the sum of the two detection limits ($0 \le TC < (DL_{sol} + DL_{insol})$). If only one fraction is below DL, TC can vary between the measured concentration (C) of the fraction with a concentration above DL and the measured concentration plus the detection limit of the other fraction: $C_{sol} \le TC < (C_{sol} + DL_{insol})$ or $C_{insol} \le TC < (C_{insol} + DL_{sol})$. With this information, an unequivocal rank could be assigned to each measurement (including those with values below DL) for TC of Pb in both, gastric juice as well as Hatch solution samples.

Nonparametric methods were used to calculate the summary statistics as recommended by Helsel for small samples of censored data.

Correlation between the B-Pb and A-Pb concentrations was estimated with Spearman's rank correlation coefficient after censoring at the highest reporting limit as recommended by Helsel for censored data.

The solubility (S) is defined as the soluble fraction (C_{sol}) devided by the sum of the soluble and insoluble fractions ($C_{sol} + C_{insol}$). If both fractions are below DL, nothing can be said about the solubility ($0 \le S \le 1$). Thus, measurements with both fractions below DL had to be excluded. If the soluble fraction is above DL and the insoluble fraction below DL, S may vary between ($C_{sol}/(C_{sol} + DL_{insol})$) and 1. If the soluble fraction is below dl and the insoluble fraction above DL, S may vary between 0 and ($DL_{sol}/(DL_{sol} + C_{insol})$). However, the range of possible solubilities obtained for samples with one fraction below DL is in most cases very large (in contrast to TC). Thus, these measurements also had to be excluded in the calculation of summary statistics. Still, to keep the analysis consistent, nonparametric methods were used for calculation of summary statistics of the solubility data.

All statistical calculations were performed with R (version 3.0.3), and using the package NADA for R for the analysis of censored data²⁷.

3 Results

Boxplots of B-Pb are shown in Figure 1, separately for the two locations investigated as well as for exposed and controls. Information on the workers investigated is summarized in Table 2. At site A, the B-Pb concentrations are significantly higher (U-test, two-sided, p = 1.41 E-4) in the exposed workers (BAT) than in the controls (CBAT). At site B, the difference between exposed (BBAT) and controls (CBBAT) was not significant (U-test, two-sided, p = 0.673). Similarly, the difference between the two unexposed groups (CBAT, CBBAT) was not statistically significant (U-test, two-sided, p = 0.51).

A censored boxplot of the total A-Pb at the two locations investigated is shown in Figure 2. The horizontal line in the censored boxplot denotes the highest DL at which the data are censored. Summary statistics of A-Pb are given in Table 3. The parameters listed in Table 3 are also estimated with censoring at the highest DL. A-Pb is somewhat higher at site A compared to site B. However, the difference does not reach statistical significance (U-test, two-sided, p = 0.052).

A scatterplot of B-Pb versus A-Pb for the exposed workers is shown in Figure 3. Most high B-Pb concentrations ($\geq 200 \ \mu g/L$) are observed for low A-Pb concentrations ($< 10 \ \mu g/m^3$). Nevertheless, B-Pb in the exposed workers is positively correlated with A-Pb (Spearman's rho = 0.42, p = 4.7 E-4).

The solubility of Pb in gastric juice as well as in Hatch solution is summarized in Table 4. The solubility in Hatch solution is much lower ($\approx 5 - 6$ %) than in gastric juice (about 90 %) and is not depending on the sampling location (gastric juice: two-sided U-test, p = 0.44; Hatch solution:

two-sided U-test, p = 0.52). The solubility of Pb in gastric juice is independent on the Sb content (data not shown). With the exception of one data point, the Sb content (relative to the sum of Pb and Sb) varies between approximately 1 and 10 %. For the Hatch solution, the data base is rather limited, as the insoluble fraction of Sb was mostly below the DL.

4 Discussion

The gastric bioaccessibility of Pb measured in our study is remarkably high (medians of the two locations: 89 % and 92 %). Much lower values between 10 - 16 % for total particulate matter (PM) and 15 - 23 % for PM_{2.5-1} were reported by Uzu et al. for particles from a Pb recycling plant²¹. Since Uzu et al. used an aqueous calcium chloride (CaCl₂) solution in their study, a much lower bioaccessibility of Pb is to be expected. Even a lower bioaccessibility of Pb of 0.5 - 6 % was measured for mine wastes¹⁷. However, the bioaccessible fraction of Pb from mine tailing may be also higher: a range of 17 - 47 % (depending on pH) was reported by Bruce et al.²⁸ and a range of 23 - 69 % by Jaggard²⁹. In soils, the bioaccessibility of Pb in gastric juice is generally higher with values between 62 and 76 %^{18,19,30,31}. The gastric phase bioaccessibility of Pb in the particle size fraction < 50µm in soils has been reported to be from 37.7 to 98.8 % of total Pb³².In house dust, the gastric bioaccessibility of Pb was found to vary between 52 and 77 %³³.

The high bioaccessibility of Pb observed for particulate matter from battery repair workshops most likely results from the Pb phases present. According to Ruby et al.³⁴, high gastric bioaccessibility is observed for Pb halogenides, Pb carbonates and Pb oxides. The latter can be expected to be a major component of the air particulate matter in battery repair work due to the

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use of PbO_2 as positive plate. The bioavailability of Pb from Pb-Sb alloys is not known. Pure metallic Pb is reported to have a low gastric bioaccessibility³⁴.

The low bioaccessibility of Pb in Hatch solution found in the present study (medians of the two locations: 4.9 % and 5.6 %) is in accordance with Jaggard who observed values between 0 and 0.05 % in lung fluid for Pb from mine tailings²⁹, although this comparison may not be relevant since mine tailings usually contain other chemical forms of Pb, e.g. sulfidic Pb. However, the bioaccessibility of Pb in Gamble solution (which mimics the interstitial fluid within the deep lung) of various standard materials of atmospheric particles varied considerably: 14.5 ± 0.9 % (mean value \pm relative standard deviation) for urban atmospheric PM, 45.2 ± 3.5 % for vehicle exhaust, 24.6 ± 3.0 % for indoor dust, and 3.3 ± 0.2 % for coal combustion fly ashes³⁵. Berlinger et al.²⁰ found 1.0 - 2.6 % and 0.1 - 3.2 % bioaccessible Pb in MIG welding fumes applying Hatch and Gamble solution as leaching solutions, respectively. The solubility of Pb was approximately 10 times higher in water than in biological fluid simulants. A moderate bioaccessibility of Pb (16 - 29 %) in urban particulate matter (using a water soluble extraction buffered at pH 7 to simulate the neutral lung environment) was reported by Niu et al.³⁶. Again, these differences most likely reflect the complex phase composition of the different Pb containing particles present in the media investigated.

Our results strongly indicate that in battery repair work gastrointestinal uptake of Pb may be of higher importance than respiratory uptake. This is in contradiction to Uzu et al. who, based on their less relevant CaCl₂ leaching procedure, concluded that the gastric bioaccessibility of Pb is relatively low in aerosols from battery recycling plants²¹. The bioavailability of Pb from the

gastrointestinal tract is, however, rather limited⁷. Thus, it appears that battery repair work represents a unique workplace environment with Pb species of high gastric bioaccessibility. This observation has two important consequences. First, improvement of the personal hygienic behavior (including reduction of eating and smoking at work sites) is of importance as already mentioned earlier^{8,9,37}. Second, air monitoring of Pb should also include the coarser particles $(>10 \ \mu m \text{ aerodynamic diameter } (d_{ae}))$ present in the extrathoracic aerosol fraction, as particles of this size fraction are likely to be transferred to the gastrointestinal tract. The non-lung-soluble particles present in the thoracic sub-fraction will also to a large extent be part of a gastrointestinal exposure due to mucociliary and phagocytosis clearance. Even though B-Pb concentration is generally used as the primary indicator of Pb exposure, air measurement of Pb is recommended, complementary, to evaluate the effectiveness of controls for airborne Pb. Air concentrations have predominantly been assessed using "total" aerosol cassettes shown to undersample the inhalable Pb air concentrations in primary Pb smelters by a factor between 1.39 to 2.14^{38} . Since the mass median d_{ae} of Pb containing particles is considerably higher in Pb battery production compared with Pb smelting, 14.1 and 4.9 µm, respectively, a more serious undersampling of the inhalable fraction is to be expected in the production and repair work of Pb batteries³⁹. Thus, the air concentrations in our study, where a "total" aerosol cassette was used for air sampling, may have been underestimated.

The bioaccessibility behavior of the particulate matter collected in this study may only be valid for contaminants present in workroom atmospheres during Pb car battery repair work and primary production due to specific particle mass size distribution and individual particle composition. The B-Pb concentrations were, particularly in BAT, high when compared with the A-Pb concentrations. The unexpected high B-Pb concentrations is most likely due to contaminated personal and workroom surfaces causing gastrointestinal exposure to Pb^{40} . Lead exposure is associated with a variety of neurotoxic effects, ranging from neuromotor or cognitive impairment to violent behavior and violence⁴¹. The critical exposure level for the induction of neurotoxic effects in adults has been estimated to be around 20 µg/dL of Pb in whole blood⁴². This B-Pb concentration was exceeded by a substantial number of the participants in this study.

Recommendations for future bioaccessibility studies

Since detailed analytical quality control procedures are probably not possible with the leaching procedures applied in this study due to the lack of suitable characterised reference materials (particulate matter), we suggest repeatability studies using split (halved) filters or replicate parallel stationary filter sampling to test the precision of the leaching process which can be influenced by a range of parameters such as leaching time, temperature, solvent/sample mass ratios as well as the physio-chemical properties of the collected particles themselves. If possible, non destructive characterization of bulk filters containing different particle-size fractions by X-ray fluorescence and X-ray-diffraction, in addition to individual particle characterisation using scanning and transmission microscopy, may also be useful in such studies to provide a total element loading and species identification benchmark prior to performing leaching experiments.

Acknowledgements

This research project was financially supported by the Norwegian Ministry of Foreign Affairs through The Climate and Human, Environment and Health Research Strategy Centre, University of Tromsø (Norway) and the Arctic Monitoring and Assessment Programme (AMAP) secretariat in Oslo (Norway).

Ethical approval

The study was approved by both, the School of Medical Sciences, Kwame Nkrumah University of Science and Technology/Komfo Anokye Teaching Hospital Committee on Human Research Publication and Ethics, and the Regional Committee for Medical Research Ethics of Northern Norway (code 2011/729).

References

- 1 International Lead and Zinc Study Group 2014, <u>http://www.ilzsg.org</u>
- 2 P. Gottesfeld and A.K. Pokhrel, J. Occ. Environ. Hyg., 2011, 8, 520.

3 R. Fuller, *Environ. Health Perspect.*, 2009, **117**(12), A535.

4 T.D Matte, J.P. Figueroa, S. Ostrowski, G. Burr, L. Jackson-Hunt, R.A. Keenlyside and E.L. Baker, *Int. J. Epidem.*, 1989, **18**, 874-881.

5 M.L Suplido and C.N. Ong, *Environ. Res.*, 2000, 82, 231-238.

6 P. Haefliger, M. Mathieu-Nolf, S. Lociciro, C. Ndiaye, M. Coly, A. Diouf, A.L. Faye, A. Sow, J.Tempowski, J. Pronczuk, A.P.F. Junior, R. Bertollini and M. Neira, *Environ. Health Perspect.*, 2009, **117**, 1535-1540.

7 S. Skerfving S and I.A. Bergdahl, *Lead*, In: G.F. Nordberg, B.A. Fowler, M. Nordberg and L.T. Friberg, editors. *Handbook on the toxicology of metals*, Amsterdam, Elsevier, 3rd ed.,2007, 599-643, ISBN 978-0-12-369413-3.

8 H.S. Far, N.T. Pin, C.Y. Kong, K.S. Fong, C.W. Kian and C.K. Yan, *Int. Arch. Occup Environ. Health*, 1993, 64, 439-443.

9 M. Kentner and T. Fischer, Int. Arch. Occup. Environ. Health, 1994, 66, 223-228.

10 M. Kentner, T. Fischer and G. Richter, Int. Arch. Occup. Environ. Health, 1994, 66, 23-31.

11 S.F. Ho, C.T. Sam and G.B. Embi, Occup. Med., 1998, 48, 369-373.

12 R. Dykeman, G. Aquilar-Madrid, T. Smith, C.A. Juárez-Pérez, G. Piacitelli, H. Hu and M. Hernandez-Avila, *Amer. J. Indust. Med.*, 2002, **41**, 179-187.

13 D-U. Park and N-W. Paik, Ann. Occup. Hyg., 2002, 46(2), 237-243.

14 D.G. Hodgkins, T.G. Robins, D.L. Hinkamp, M.A. Schork and W.H. Krebs, *Br. J. Indus. Med.*, 1992, **49**, 241-248.

15 D.G. Hodgkins, T.G. Robins, D. L. Hinkamp, A.M. Schork, S.P. Levine and W.H. Krebs, *J. Occup. Med.*, 1991, **33(12)**, 1265-1273.

16 D. Barltrop and F. Meek, Arch. Environ. Health, 1979, 34(4), 280-285.

17 M.W. Ruby, A. Davis, T.E. Link, R. Schoof, R.L. Chaney, G.B. Freeman and P. Bergstrom, *Environ. Sci. Technol.*, 1993, **27**, 2870-2877.

18 S.C. Hamel, K.M. Ellickson and P.J. Lioy, Sci. Total Environ., 1999, 243/244, 273-283.

19 K.M. Ellickson, R.J. Meeker, M.A. Gallo, B.T. Buckley and P.J. Lioy, *Arch. Environ. Contam. Toxicol.*, 2001, 40, 128-135.

B. Berlinger, D.G. Ellingsen, M. Náray, G. Záray and Y. Thomassen, J. Environ. Monit., 2008, 10, 1448-1453.

21 G. Uzu, J.J. Sauvain, A. Baeza-Squiban, M. Riediker, M.S.S. Hohl, S. Val, K. Tack, S. Denys and P. Pradere, C. Dumat, *Environ. Sci. Technol.*, 2011, **45**, 7888-7895.

22 D.G. Ellingsen, E. Zibarev, Z. Kusraeva, B. Berlinger, M. Chashchin, R. Bast-Pettersen, V. Chashchin and Y. Thomassen, *Environ. Sci. Processes Impacts*, 2013, 15, 357-365.

- G.E. Hatch, In: Parent R.A., editor, *Comparative biology of the normal lung*. Boca Raton, CRC Press, 1992, 617-632, ISBN 0-8493-8839-2.
- 24 S.C. Hamel, B. Buckley and P.J. Lioy, *Environ. Sci. Technol.*, 1998, 32, 358-362.
- Y. Thomassen, E. Nieboer, D. Ellingsen, S. Hetland, T. Norseth, J.O. Odland, N. Romanova,
 S. Chernova and V.P. Tchachtine, *J. Environ. Monit.*, 1999, 1, 15-22.
- 26 D.R. Helsel, NJ, USA: Wiley, 2nd ed., 2012, ISBN 978-0-470-47988-9.
- 27 B.K. Lee, Br. J. Indust. Med., 1982, 39, 283-289.
- 28 S. Bruce, B. Noller, V. Matanitobua and J. Ng, *J. Toxicol. Environ. Health*, 2007, 70, 1700-1711.
- 29 H.N. Jaggard, Master Thesis, Dept. of Geological Sciences and Geological Engineering, Queen's University, Kingston, Ontario, Canada, 2012, 177
- 30 H. Roussel, C. Waterlot, A. Pelfrêne, C. Pruvot, M. Mazzuca and F. Douay, Arch. Environ. Contam. Toxicol., 2010, 58, 945-954.
- 31 M.R. Cave, J. Wragg and S. Chenery, EGU General Assembly, Vienna, Austria, Geophysical Research Abstracts, 2013, 15, EGU2013-1440-1.
- 32 A.L. Juhasz, J. Weber and E. Smith, J. Hazard. Mater., 2011, 186, 1870-1879.
- 33 C.H. Yu, L.M. Yiin and P.J. Lioy, Risk Analysis, 2006, 26, 125-134.
- 34 M.W. Ruby, R. Schoof, W. Brattin, M. Goldage, G. Post, M. Harnois, D.E. Mosby, S.W. Casteel, W. Berti, M. Carpenter, D. Edwards, D. Cragin and W. Chappell, *Environ. Sci. Technol.*, 1999, 33, 3697-3705.

- 35 C. Julien, P. Esperanza, M. Bruno and L.Y. Alleman, J. Environ. Monit., 2011, 13, 621-630.
- 36 J. Niu, P.E. Rasmussen, N.M. Hassan and R. Vincent, *Water Air Soil Pollut.*, 2010, 213, 211-225.
- 37 H.Y. Chuang, M.L.T. Lee, K.Y. Chao, J.D. Wang and H. Hu, *Amer. J. Indust. Med.*, 1999, 35, 595-603.
- **38** T.M. Spear, M.A. Werner, J. Bootland, A. Harbour, E.P. Murray, R. Rossi and J.H. Vincent *Am. Ind. Hyg. Assoc. J.*, 1997, **58**, 893-899.
- **39** D-UK. Park and N-W. Paik, Am. Occup. Hyg., 2002, **46**, 237-243.
- 40 C. Chavalitnitikul, L. Levin and L-C. Chen, Am. Ind. Hyg. Assoc. J., 1984, 45(12), 802-808.
- 41 T. Sanders, Y. Liu, V. Buchner and P.B. Tchounwou, Rev. Environ. Health, 2009, 24, 15-45.
- 42 K. Murata, T. Iwata, M. Dakeishi and K. Karita, J. Occup. Health, 2009, 51, 1-12.

Tables

Table 1: Composition and pH of Hatch extraction fluid per litre DI water. Calcium chloride (0.2251 g) Magnesium chloride hexahydrate (0.21 g)Magnesium sulfate (0.0342 g)Potassium chloride (0.37 g)Potassium dihydrogen phosphate (0.03g) Sodium bicarbonate (2.27 g)Sodium chloride (7.0 g) Dibasic sodium phosphate (0.1196 g)D-glucose (1.0 g)Phosphatidylcholine (10 g) α -tocopherol (0.001 g) Uric acid (0.025 g)Serum albumin (10 g) Lysosyme (2.5 g) Apo-transferrin (0.2 g)Ascorbate (0.05 g)Glutathione (0.05 g)pH =7.4

| | BAT (site A) | CBAT (site A) | BBAT (site B) | CBBAT (site B) |
|--------------------------|----------------|----------------|----------------|-----------------|
| Exposure status | exposed | controls | exposed | controls |
| Number of workers | 32 | 17 | 32 | 16 |
| Age [years]* | 32.7 ± 8.1 | 31.5 ± 8.8 | 30.4 ± 7.9 | 34.6 ± 10.2 |
| Body mass index* | 23.9 ± 3.0 | 24.9 ± 3.1 | 22.6 ± 2.3 | 22.0 ± 2.8 |
| Smokers [number] | 2 | 1 | 0 | 0 |
| Employment [years]* | 11.8 ± 7.6 | 9.1 ± 7.0 | 10.7 ± 7.4 | 14.7 ± 9.5 |
| Protective equipment [%] | 0 | 0 | 0 | 0 |
| Hand washing | 43.8 | 47.1 | 40.6 | 31.3 |
| before meals [%] | | | | |

Table 2: Characteristics of the workers investigated (all male).

*arithmetic mean ± standard deviation

| | Site A (BAT) | Site B (BBAT) | |
|-----------------------------|--------------|---------------|--|
| Minimum | < 0.25 | < 0.23 | |
| Lower quartile [*] | 0.55 | 0.41 | |
| Median [*] | 1.5 | 0.70 | |
| Upper quartile [*] | 5.7 | 1.5 | |
| Maximum | 74 | 52 | |
| | | | |

Table 3: Total Pb air concentration $(\mu g/m^3)$.

*estimated with censoring at the highest detection limit (0.25 μ g/m³)

| | Gastric juice | | Hatch solution | |
|----------------|---------------|------|----------------|------|
| Sample | BAT | BBAT | BAT | BBAT |
| Minimum | 59.6 | 65.0 | 2.0 | 2.8 |
| Lower quartile | 85.8 | 84.9 | 2.5 | 4.2 |
| Median | 88.8 | 92.0 | 4.9 | 5.6 |
| Upper quartile | 91.3 | 94.9 | 7.1 | 7.9 |
| Maximum | 97.4 | 99.1 | 18.4 | 11.6 |
| Ν | 16 | 14 | 14 | 13 |

Table 4: Solubility (%) of Pb in gastric juice and Hatch solution.*

*all parameters estimated without samples with one or both fractions below detection limit (see chapter data analysis for details)

Figures



Figure 1: Boxplot of Pb concentrations [µg/l] in blood of exposed (BAT) and controls (CBAT) at site A, and exposed (BBAT) and controls (CBBAT) at site B.



Figure 2: Censored boxplot of Pb concentrations $(\mu g/m^3)$ in air at site A and site B. The horizontal line denotes censoring at the highest detection limit (0.25 $\mu g/m^3$).



Figure 3: B-Pb $[\mu g/L]$ versus A-Pb $[\mu g/m^3]$. Two data points with high A-Pb concentrations not shown).

ENVIRONMENTAL IMPACT STATEMENT

Pb-acid battery recovery operation is expected to emit particles to the workroom atmosphere containing predominately Pb in the metallic form, as PbO, PbO₂ or as PbSO₄. In addition, Pb-acid battery water which contains high Pb levels as soluble ions and particulates forms might form dust with high concentration of Pb after contaminating the dusty floors. As part of a larger exposure assessment study of Pb among car battery repair workers, the present study employed simulated lung fluid and gastro-intestinal juice to investigate the respiratory and gastric bioaccessibility of Pb in particulate matter collected among battery repair workers.