

Dioxin contamination of workers' blood and wastes at a chlorophenol manufacturing site in the UK

Stringer, R.L.^a, Ryan, J.J.^b & Howard, C.V.^c

^aEarth Resources Centre, University of Exeter, Laver Building, North Park Road, Exeter EX4 4QE, UK

^bHealth Canada, Tunney's Pasture, Ottawa, Canada, K1A 0L2

^cDepartment of Fetal and Infant Pathology, University of Liverpool, PO Box 147, Liverpool L69 3BX, UK

1. Introduction

Considerable research has been carried out on the environmental contamination surrounding the Coalite Chemicals Ltd site in Derbyshire, UK, since the discovery of severe contamination of adjacent farms in 1991. However the main focus of concern has been the contamination of farmland, foodstuffs and possible risk to the public via that route. No data were available regarding the exposure of the workers, some of whom were also exposed to 2,3,7,8-TCDD in

1968 as a result of an explosion in the 2,4,5-trichlorophenol manufacturing unit. This study was therefore initiated to provide clearer information on dioxin exposure of the workforce and data on some of the materials to which they may have been exposed.

2. Experimental

Blood samples were collected in 1993 from nine workers with at least ten years of employment at the plant. Five of these had been employed at the time of the Seveso-type accident at the plant in 1968 and four had participated in the subsequent cleanup. Samples were stored at -20°C and transported on dry ice. Analyses were carried out as described elsewhere¹⁾.

Samples of wastes were also obtained on two occasions and analysed according to method Verein Deutscher Ingenieure (VDI) 3499 by a laboratory accredited under Deutsches Akkreditierungssystem Prüfwesen (DAP) standards. These comprised one sample of organic waste and two samples of ash from the onsite incinerator which was widely regarded as the source of the local contamination, collected in 1991. Three further organic waste samples were collected in 1993.

3. Results

Blood dioxin concentrations ranged from 52 to 1166ppt ITEQ on a lipid basis with a mean of 286ppt. 2,3,7,8-TCDD ranged from 18 to 1080ppt (mean 214ppt). Coplanar PCBs (calculated according to ²⁾ ranged from 2.9 to 9ppt TEQ with a

mean of 5.7ppt.

Wastes varied considerably with respect to concentration of PCDD/Fs. The three wastes collected in 1993 contained levels from 0.034 μ g/kg ITEQ to 960 μ g/kg ITEQ. The waste collected in 1991 was exceptionally highly contaminated with 3040mg/kg ITEQ and 883mg/kg 2,3,7,8-TCDD. To the authors' knowledge, this is the highest industrially-related 2,3,7,8-TCDD level recorded in the literature. In comparison, the wastes used as a dust control spray in Times Beach and other parts of Missouri were reported to contain between 104 and 350mg/kg of 2,3,7,8-TCDD^{3,4,5}.

The two incinerator ashes were also unusually highly contaminated; 0.013 and 133mg/kg ITEQ respectively. The congener profiles of the ashes did not resemble the typical combustion pattern, being instead remarkably similar to that of the waste collected at the same time, with high concentrations of tetra- and pentachlorinated dioxins. The congener profiles of the waste and ashes collected in 1991 are shown in figure 1 below.

4. Discussion

The blood coplanar PCB results were similar to those reported previously in the UK⁶), indicating normal dietary exposure in these men. However, dioxins were substantially elevated. In all cases, 2,3,7,8-TCDD was higher than in the general population. This congener is particularly associated with the manufacture of 2,4,5-trichlorophenol which was produced at this facility from 1965 to 1976. The greatest exposure would be expected in those present at the time of the accident in 1968 and indeed there is a significant difference

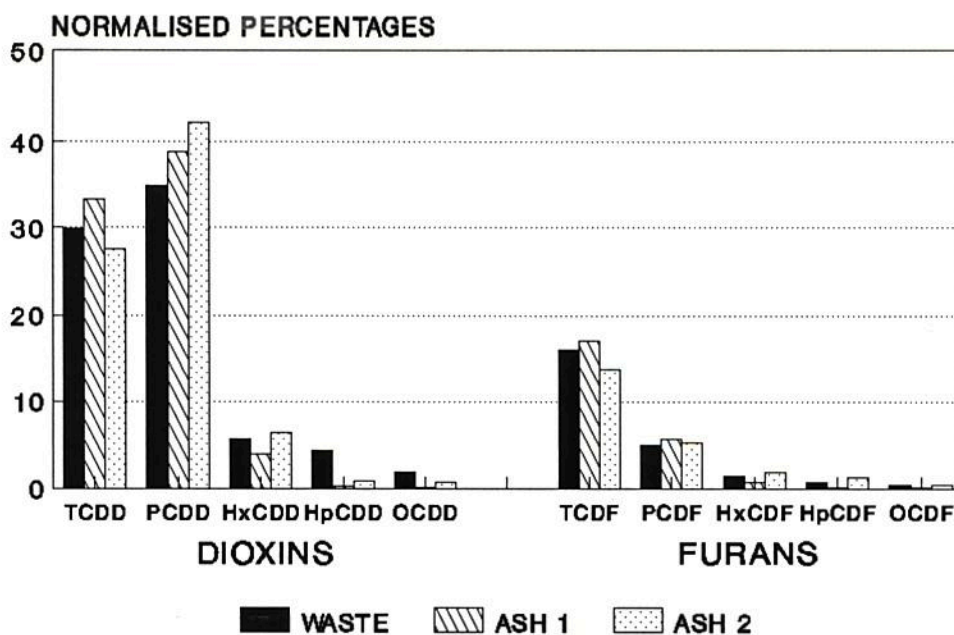


Figure 1: Congener profiles for wastes and ashes collected in 1991.

between 2,3,7,8-TCDD levels in those who participated in the cleanup after this incident and those who did not. The elevation of the blood levels in those workers not employed until after 1968 probably indicates both exposure to contamination of the site or process equipment and continued exposure to PCDD/F containing products and wastes. Back-calculations based on elimination half-lives of 5, 7 and 10 years were carried out for those workers involved in the 1968 accident. This gave estimated TCDD concentrations for that date in the lower range of those recorded at Seveso. Exposure of this magnitude has been associated with adverse health outcomes in other countries, and assessment of a number of immunological and other biochemical determinants is under way.

In 1991 the UK Ministry of Agriculture, Fisheries and Food published data showing unacceptable contamination of local farm produce, with the result that three farms were unable to sell their produce^{7,8)}. Blood samples were taken from residents on these farms to determine the extent to which they had been exposed. Three of the samples were in the normal range for the German population, but the rest were in the same range as has been encountered in industrially exposed workers elsewhere⁹⁾. The mean of the farmers concentrations is 173ppt, compared with 286ppt for the workers taking part in this study. However the workers' mean is strongly influenced by the extremely high maximum value. Apart from this one result, the farm residents and workers ITEQ levels are extremely similar.

The on-site incinerator was investigated in 1991 by Her Majesty's Inspectorate of Pollution (HMIP)¹⁰⁾ and concentrations of PCDD/Fs in ash can be calculated from their data to be in the same range as one of the ash samples analysed in this study. The other, however, taken from between the quench and the

scrubber, was between 1500 and 10000 times higher the HMIP samples at 133mg/kg.

This points to considerable variance in performance of the incinerator and emissions at times must therefore have been far higher than calculated by the regulatory authorities. From the similarity of the profiles of the 1991 ash and waste it is apparent that a proportion of the PCDD/Fs may have passed through the combustion system essentially unaltered. The incinerator was subsequently shut down.

By August 1992 the situation on the neighbouring farms had improved to the extent that the milk from only one exceeded the Maximum Tolerable Concentration (MTC) which was set at 17.5 ng ITEQ/kg fat. It is suggested that the source of the high levels of contamination have now ceased⁸⁾. The massive contamination of one of the samples of the incinerator ash certainly suggests that the incinerator could have been emitting high concentrations of PCDD/Fs while it was in operation and the coincidence of its closure with the drop in milk concentrations would appear to confirm this.

However, the analysis of the waste present at the site in 1993 certainly demonstrates that substantial dioxin generation continued in production processes and probably still occurs at present. Given the results obtained here it would seem advisable to extend research efforts to ascertain the exposure status of the remainder of the workforce and identify sources and routes of contamination. Current processes should be examined to ensure that PCDD/Fs are no longer being synthesised. At the same time, historical contamination of the site and equipment should be examined and further cleanup may be required.

5. References

- 1) Ryan, J.J., Lau, B.P-Y. & Boyle, M.J. (1994) Dioxin-like compounds in human blood. In: Biological Mass Spectrometry: Present and Future. Eds. Matsuo, Caprioli, Gross & Setama, John Wiley & Sons, Chp 3.16, pp 583-602
- 2) Ahlborg, U.G., Becking, G.C., Birnbaum, L.S., Brouwer, A., Derks, H.J.G.M., Feeley, M., Golor, G., Hanberg, A., Larsen, Liem, A.K.D., Safe, S.H., Schlatter, C., Waern, Younes, M. & Yrjänheikki, E. (1994) Toxic Equivalency factors for dioxin-like PCBs. Chemosphere 28(6): 1049-1067
- 3) Sun, M. (1983) Missouri's costly dioxin lesson. Science 219: 367-369
- 4) Freeman, R.A., Schroy, J.M., Hileman, F.D. & Noble, R.W. (1986) Environmental mobility of 2,3,7,8-TCDD and companion chemicals in a roadway soil matrix. In: Chlorinated dioxins and dibenzofurans in perspective. Eds. Rappe, Choudhary & Keith, Publ: Lewis Publishers Inc, pp 171-183
- 5) Arthur, M.F. & Frea, J.I. (1989) 2,3,7,8-Tetrachlorodibenzo-p-dioxin: Aspects of its important properties and its potential biodegradation in soils. J. Environ. Qual. 18(1): 1-11
- 6) Duarte-Davidson, R., Harrad, S.J., Allen, S., Sewart, S. & Jones, K.C. (1993) The relative contribution of polychlorinated biphenyls (PCBs), polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) to toxic equivalent values derived for bulked human adipose tissue samples from Wales, United Kingdom. Arch. Environ. Contam. Toxicol. 24:100-107
- 7) MAFF (1992) Third report of studies on dioxins in Derbyshire carried out by the Ministry of Agriculture, Fisheries and Food. Publ: Food Safety Directorate, 31pp
- 8) Harrison, N., de M. Gem, M.G. & Startin, J.R. (1994) Dioxins in milk: a case study of localised contamination. Organohalogen Compounds Vol 20. Proceedings of the 14th International Symposium on Chlorinated Dioxins, PCB and Related Compounds, November 21-25, 1994, Kyoto, Japan. pp 73-76
- 9) Startin, J.R., Wright, C., Kelly, M. & Charlesworth, E.A. (1994) Dioxin concentrations in the blood of individuals on farms near Bolsover, U.K. Organohalogen Compounds Vol 21. Proceedings of the 14th International Symposium on Chlorinated Dioxins, PCB and Related Compounds, November 21-25, 1994, Kyoto, Japan. pp 117-120
- 10) Berryman, R.J., Bennett, S.L., Ambidge, P.F., Lee, D.S. & McCrorie, S.K.C. (1991) Investigations into the emissions of dioxins and furans from the smokeless fuel plant and chemical waste incinerator at the Coalite works, Nr Bolsover, Derbyshire. Publ: DoE report no. DoE/HMIP/RR/91/066.