Heavy metal pollution among autoworkers. II. Cadmium, chromium, copper, manganese, and nickel

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ABSTRACT Garages and auto-repair workshops may be polluted with other heavy metals besides lead. Blood of autoworkers with high lead content was analysed for cadmium, chromium, copper, manganese, nickel, ALAD activity and carboxyhaemoglobin level. Cadmium and copper levels in blood of autoworkers were comparable with those of the control subjects while chromium and nickel levels were significantly higher ($P < 0.01$ for both metals), and scattered raised values of manganese were found. There was no significant mutual correlation between levels of various heavy metals determined in whole blood. High copper levels were slightly related to decreasing ALAD activity ($P < 0.1$). Nineteen per cent of autoworkers were found to have an abnormally high blood level of carboxyhaemoglobin. The amount of particulate heavy metal in autoworkshop air was not related to biochemical abnormalities found in the autoworkers. Various sources of pollution of these heavy metals in autoworkshops are discussed.

The toxicity of heavy metals such as cadmium, chromium, copper, manganese and nickel has recently been evaluated (Jonderko *et al.*, 1971; McNeely *et al.*, 1971; Tolonen, 1972; Albert *et al.*, 1973; Evans, 1973; Fleming *et al.*, 1974; Fleischer *et al.*, 1974; McHowell *et al.*, 1974; Ottolenghi *et al.*, 1974; Fassett, 1975; Royle, 1975 a, b; Samitz and Katz, 1975; Schoental, 1975). Sources of lead pollution in auto-repair shops have been described in Part I (Clausen and Rastogi, 1977). Analysis of motor exhausts has shown that besides various hydrocarbons, nitrogen oxides and lead, they often contain manganese, vanadium and boron. Information about heavy metal pollution in autoworkshops is, however, lacking (World Health Organization, 1969).

The fumes given off by metal-coated welding electrodes contain zinc, iron, chromium, copper, lead, titanium and vanadium (Sanderson, 1968; Steel, 1968). The use of chromium-pigment based paints, the addition of complex organometallic compounds to lubricants and oils and the use of compounds such as methylcyclopentadienyl manganese tricarbonyl as an additive to oils may also be

sources of heavy metal pollution in garages (Tolonen, 1972; Haar *et al.*, 1975). Finally, the steel used by such workers contains varying amounts of nickel and chromium which may cause pollution. Samitz and Katz (1975) have shown that nickel is released from prostheses by the action of sweat, blood and physiological saline.

This paper describes the determination of cadmium, chromium, copper, manganese and nickel levels in whole blood from autoworkers and the investigation of sources of pollution. The effect of automobile exhaust gases on carboxyhaemoglobin levels in autoworkers is also examined.

Material and methods

MATERIAL

The subjects and normal controls were those described in Part I (Clausen and Rastogi, 1977). Analysis for other heavy metals was carried out on autoworkers with high blood lead levels.

METHODS

Heavy metals in particulate air samples and in whole blood were determined by flameless atomic absorption spectrophotometry (Melgaard *et al.*, 1976a). Dust and oil samples treated with an acid mixture for analysis of lead were used for determination of the other heavy metals (Clausen and Rastogi, 1977). Standard curves were prepared by adding known amounts of each of the metals under investigation

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to a fixed amount of blood, dust or oil, with subsequent analysis to determine recovery of the metal. Cadmium was determined at 228.8 nm, chromium at 357.8 nm, copper at 324.7 nm, manganese at 279.5 nm and nickel at 232.0 nm using specific single-element hollow cathode lamps from Perkin-Elmer. ALAD activity in the blood of autoworkers has been described previously (Clausen and Rastogi, 1977). Carboxyhaemoglobin (COHb) in fresh blood samples was assayed by the classical method (Bauer *et al.*, 1974). Statistical analysis was as in Part I (Clausen and Rastogi, 1977). All data had mean and median values identical within the 5% limit.

Results

Heavy metal levels in whole blood from autoworkers and from control subjects are shown in Table 1. Heavy metal levels in individual control subjects have been reported previously (Melgaard *et al.*, 1976a).

Wilcoxon's test showed that levels of chromium and nickel were significantly higher in whole blood of autoworkers than of controls ($P < 0.01$ for both metals) while the levels of cadmium, copper and manganese were identical. The mean nickel content in whole blood of the autoworkers was three times higher than that of the controls. Forty per cent, 24% and 13% of autoworkers had levels of nickel,

chromium and manganese respectively that were higher than the upper range of the normal subjects.

If lead and other pollutant heavy metals have a common source, the individual blood levels of such metals may show a correlation. However, no significant correlation was observed between the levels of lead and of chromium, copper, manganese and nickel, but there was a slight correlation between copper and nickel (Spearman's rank correlation coefficient $r = 0.4681$, $P < 0.1$). Chromium and manganese levels did not correlate with those of nickel or with copper, and chromium levels did not correlate with manganese levels.

The ALAD activity in blood was depressed by lead but a corresponding effect was not observed with other heavy metals with the exception of copper (Spearman's rank correlation coefficient $r = 0.4423$, $P \leq 0.1$).

Analysis of air samples showed that air in all types of workshops was contaminated with the heavy metals under investigation compared to ambient air outside the workshops (Table 2). The heavy metal concentration in workshop air samples did not exceed the TLV (0.1 mg Cd, 0.1 mg CrO₃, 5.0 mg Mn and 1.0 mg Ni/m³) or MAC values (0.1 mg Cd oxide, 0.01 mg CrO₃, 0.3 mg Mn and 0.5 mg Ni/m³).

As oil is a possible source of contamination, the heavy metal content in various oils (used and unused) commonly employed in this industry was examined

Table 1 Heavy metal content of whole blood of autoworkers

Subjects	Cd ($\mu\text{g}/100\text{ ml}$)($\mu\text{mol/l}$)		Ni ($\mu\text{g}/100\text{ ml}$)($\mu\text{mol/l}$)		Mn ($\mu\text{g}/100\text{ ml}$)($\mu\text{mol/l}$)		Cu ($\mu\text{g}/100\text{ ml}$)($\mu\text{mol/l}$)		Cr ($\mu\text{g}/100\text{ ml}$)($\mu\text{mol/l}$)	
Controls:										
Mean	1.64	0.15	1.7	0.29	5.7	1.0	83	13.1	4.5	0.86
SD	± 0.85	± 0.08	± 1.5	± 0.26	± 2.6	± 0.5	± 26	± 4.1	± 2.9	± 0.55
Range	0.3-4.8	0.03-0.43	0.4-5.4	0.07-0.92	0.5-9.8	0.1-1.8	45-162	71-25.5	0.8-8.4	0.2-1.6
Autoworkers:										
Mean	1.56	0.14	5.3	0.90	5.6	1.0	82	12.9	5.7	1.10
SD	± 0.84	± 0.08	± 4.8	± 0.82	± 4.7	± 0.9	± 46	± 7.2	± 3.9	± 0.75
			$P < 0.01$						$P < 0.01$	

Table 2 Heavy metal content of workshop air*

Workshop	No. of samples	Cd $\mu\text{g}/\text{m}^3$ air	Cr $\mu\text{g}/\text{m}^3$ air	Cu $\mu\text{g}/\text{m}^3$ air	Mn $\mu\text{g}/\text{m}^3$ air	Ni $\mu\text{g}/\text{m}^3$ air
Autoworkshop	17	0.05 $\pm$ 0.04 (0.01-0.23)	0.14 $\pm$ 0.13 (0.01-0.4)	0.32 $\pm$ 0.12 (0.03-0.76)	0.19 $\pm$ 0.11 (0.04-0.44)	0.13 $\pm$ 0.11 (0.02-0.49)
Plate workshop	4	0.07 $\pm$ 0.06 (0.025-0.20)	1.2 $\pm$ 1.05 (0.06-3.75)	0.57 $\pm$ 0.22 (0.30-0.84)	0.55 $\pm$ 0.33 (0.06-0.87)	0.15 $\pm$ 0.09 (0.08-0.31)
Paint workshop	3	0.066 0.067 0.01	0.51 5.45 0.35	0.60 0.30 0.08	0.12 0.99 0.05	0.23 0.26 0.14
Outside the workshop	8	0.007 $\pm$ 0.000 (0.0-0.02)	0.05 $\pm$ 0.04 (0.0-0.22)	0.03 $\pm$ 0.02 (0.01-0.35)	0.08 $\pm$ 0.05 (0.01-0.16)	0.08 $\pm$ 0.06 (0.02-0.22)

*Range in parentheses

Table 3 Heavy metal* content of used motor oils

Car type	Oil	Motor driven (km)	Parts per million Cd	Cu	Cr	Ni	Mn
Ford Cortina 1969	Gulf Multi-G 20-50	1700	1.01	18.22	23.49	30.35	10.15
Renault 4, 1973	Chevron (type ?)	2600	1.16	25.24	14.09	17.83	8.63
Mascot 1965	Mobil Special SAE 10 W 50	4000	0.66	19.58	12.36	12.24	3.94
Datsun 1973	Mobil Special SAE 10 W 50	1600	0.94	7.52	15.55	25.82	2.57
Ford Taunus 1300, 1971	Esso Uniflow SAE 10 W 50	4500	0.69	5.11	26.45	12.22	5.93
Volvo 142, 1973	Shell Spirax Gear Oil HD 80	5500	0.54	11.19	19.01	16.45	2.87

*Assayed in triplicate

Table 4 Heavy metal* content of unused oils

Oil type	Parts per million Cd	Cu	Cr	Ni	Mn
Mobil Oil 46-SAE-90 Gear Oil	0.16	2.50	2.38	25.76	0.76
Mobil Oil Motor cleaner	0.09	5.38	8.27	1.98	0.34
Mobil Oil FK Tyre cleaner	0.30	4.57	5.44	6.05	2.13
Mobil Oil Super 10 W 50	0.20	2.31	7.17	34.55	1.46
Mobil Oil Special Oil 10 SAE 40	0.23	1.95	3.74	2.76	1.99
Mobil Oil code no. 80-90	0.01	1.69	6.54	3.93	1.15
Mobil Oil code no. 20-30	0.07	1.37	0.54	1.77	1.55
Melkylen cleaner Perfection A/S	0.36	32.67	1.76	92.94	3.42
Brake-washing oil	0.06	2.05	2.05	7.23	0.52
Hydraulic Oil (Mobil Oil)					
Lockheed Brake Oil Univs. Series 329*	87	3.34	3.13	14.95	1.05

*Assayed in triplicate

(Tables 3 and 4). Some unused oils had a high nickel content, but all the used oils were contaminated with heavy metals.

The cumulative toxic effect (TS) of lead, cadmium, chromium, copper, manganese and nickel pollution in the air together:

$$TS = \frac{C_{\text{dust}}}{\text{HGV}_{\text{dust}}} + \frac{C_{\text{Pb}}}{\text{HGV}_{\text{Pb}}} + \frac{C_{\text{Cd}}}{\text{HGV}_{\text{Cd}}} + \frac{C_{\text{Cr}}}{\text{HGV}_{\text{Cr}}} + \frac{C_{\text{Cu}}}{\text{HGV}_{\text{Cu}}} + \frac{C_{\text{Mn}}}{\text{HGV}_{\text{Mn}}} + \frac{C_{\text{Ni}}}{\text{HGV}_{\text{Ni}}}$$

where C represents the concentration of a metal and HGV the threshold limit value, was below the acceptable limit according to the Danish (1.0) or Swedish standard (1.14).

Nineteen per cent of the autoworkers had carboxy-haemoglobin levels of 12% or more. This may represent a pathological level (Moeschlin, 1972). Seventy-one per cent of the workers with carboxy-haemoglobin values above 12% complained of dizziness and headache.

No signs of heavy metal pollution other than those described previously (Clausen and Rastogi, 1977) were found in blood samples of the group being studied.

Discussion

The heavy metal content of whole blood of the control subjects was comparable with those found

by Butt *et al.* (1964), Delves *et al.* (1971) and Hecker *et al.* (1974). The group mean of the cadmium and copper content in whole blood from the autoworkers was normal. However, 15% of the autoworkers had significantly increased levels of manganese. Welding fume is a possible source of this pollution as manganese may be released from metal-coated electrodes during welding. Another source may be the use of methylcyclopentadienyl manganese tricarbonyl used as an additive in machine, diesel and fuel oils (Tolonen, 1972). It may be argued that organic manganese may affect the autoworkers in a way similar to organic lead.

One of the major sources of cadmium pollution may be the burning of crude oil (Fancher, 1973). However, it was not possible to trace any major source of cadmium pollution during the present study and cadmium levels in the whole blood of autoworkers were normal, making it impossible to correlate the high percentage of autoworkers having high blood pressure (Clausen and Rastogi, 1977) with cadmium levels (Carrol, 1966). The level of copper was found to be normal but very variable in the exposed group.

The levels of chromium and nickel in the whole blood of autoworkers were significantly higher than those of the controls. The sources of these metals are not clear. Chromium derivatives are known to be used as pigments in corrosion-protective

paints and welding of old metal plates coated with such paint may release chromium to the air. Chromium and nickel may also be given off during welding with metal-coated electrodes. When automobile engines are hot it is also possible that lead from leaded motor oils (lead naphthenate) and lubricants may be exchanged with nickel and chromium in steel (from cylinders and other mechanical parts). A release of chromium and nickel into the engine oil may account for the increase in chromium and nickel content of many oils after use. Finally, nickel may be eluted from steel parts by the action of sweat (Samitz and Katz, 1975) and thus be a source of intake for autoworkers.

Knowledge of the toxic effects of heavy metals other than lead is scanty (Albert *et al.*, 1973). Manganese and nickel can, like lead, give rise to peripheral neuropathy and brain damage (Tolonen, 1972). Our recent electrophysiological investigation (Melgaard *et al.*, 1976b) showed peripheral nerve abnormalities in autoworkers with high heavy metal levels. The high levels of nickel, chromium and manganese among the autoworkers underlines the need for scrupulous hygiene in autoworkshops.

Carbon monoxide pollution in the autoworkshops was not abnormally high as indicated by the carboxyhaemoglobin levels in autoworkers. This finding is in agreement with the results obtained by Ljungström (1972) who found that carbon monoxide pollution in autoworkshops (35 ppm) was not above the Swedish TLV. However, 19% of the autoworkers had carboxyhaemoglobin values of over 12%, the limit which Moeschlin (1972) found to be pathological for smokers. The group of autoworkers included both smokers and non-smokers and there was no correlation between the level of carboxyhaemoglobin and tobacco consumption.

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