Hair chromium as an index of chromium exposure of tannery workers

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ABSTRACT The use of hair chromium (Cr) concentrations as an index of Cr exposure of tannery workers was investigated. As has been shown earlier, Cr from Cr III compounds used in the leather tanning industry is absorbed because concentrations of Cr in serum and urine of tannery workers are significantly increased compared with corresponding concentrations for unexposed controls. Hair samples were collected from 71 male tannery workers from four southern Ontario tanneries and from 53 male controls not exposed to Cr in the workplace. Subjects were matched for age, race, and socioeconomic status. Hair samples were washed, ashed in a low temperature ashers, and analysed by flameless atomic absorption. The median hair Cr concentrations for the tannery workers (551 ng/g) was significantly higher ($p = 0.0001$) than for the controls (123 ng/g). For the tannery workers, hair Cr concentrations were positively and significantly correlated with serum Cr ($r = 0.52$, $p < 0.01$) and with the preshift and postshift urinary Cr/creatinine ratios ($r = 0.43$, $p < 0.01$; $r = 0.64$, $p < 0.01$, respectively). These data indicate that trivalent Cr absorbed from leather tanning compounds results in raised concentrations of Cr in hair and that hair Cr concentrations may be used as an index of industrial Cr exposure.

Data on the use of hair chromium (Cr) concentrations in hair to monitor industrial exposure to Cr are limited.¹ Nevertheless, the use of hair to monitor environmental exposure to lead, mercury, cadmium, and arsenic is well documented.² Industrial exposure to Cr is usually monitored by analysis of air samples for total and hexavalent Cr.³ Some investigators have also examined Cr concentrations in urine,⁴⁻⁹ whole blood,^{5,10} and serum/plasma,¹¹ or red blood cells, or both,¹² as indices of industrial exposure. Measurements of Cr in all these biological samples have the potential to screen for industrial Cr exposure before the possible development of adverse health effects. Routine Cr analysis of such biological samples is difficult, however, because they normally contain concentrations of Cr that are less than 1 ppb, values well below the limits of detection for many analytical systems. By contrast, physiological concentrations of Cr in hair are up to 1000 times higher than those in the serum and urine, thus facilitating analysis. Hence, the

use of hair as a biopsy material for monitoring industrial exposure to Cr warrants further study.

We have investigated the use of hair Cr concentrations as an index of industrial exposure to trivalent Cr. We examined the relations between Cr concentrations in hair and corresponding Cr concentrations in the serum and urine of tannery workers exposed to industrial trivalent Cr and those unexposed to Cr in the workplace.

Methods

Details of the subjects recruited for this study have been published earlier.¹³ Samples were collected on a voluntary basis from 71 male tannery workers (mean age $\pm$ SD = 38 ± 11 years) from four southern Ontario tanneries and from 53 control subjects (40 ± 13 years) from the Guelph and Toronto areas. Subjects were matched for age, race, sex, and socioeconomic status. A questionnaire that included demographic and health data was completed by each subject. None of the subjects in this study had a history of coronary heart disease or of insulin or non-insulin dependent diabetes. Information on brands of shampoo and on the use of hair beauty treatments was also obtained.

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None of the subjects used bleaches, hair dyes, or other hair beauty treatments. The study was approved by the human ethics committee of the University of Guelph.

A small portion of hair (100–200 mg) was cut from the suboccipital portion of the scalp and the proximal 1.5 cm was placed in a plastic bag for later analysis. Hair samples were washed according to the method of Kumpulainen *et al.*¹⁴ The samples were rinsed with hexane, washed twice with 1% sodium lauryl sulphate solution, and subsequently rinsed six times in distilled deionised water. Wet hair samples were dried at 105°C in acid washed quartz glass boats to constant weight and then ashed in a low temperature asher (LTA 504, LFE Corporation, Waltham, MA) for 12–16 hours. The ash was dissolved in 4 ml of 0.1 N HCl (GFS Chemical Co, Cincinnati, OH) and subsequently analysed for Cr by flameless atomic absorption spectrophotometry (Varian Spectra 30, GTA 96 Furnace, Georgetown, Ontario).

Accuracy of the analytical method was checked by ashing and analysing a reference hair material, certified for Cr content.¹⁵ The mean $\pm$ SD ($n = 10$) was $1.3 \pm 0.2 \mu\text{g/g}$ compared with the certified value of $1.4 \pm 0.2 \mu\text{g/g}$. A pooled hair sample ($n = 68$) was also ashed and analysed in each run to check on the precision of the analysis. The mean $\pm$ SD of the pooled samples was $174 \pm 29 \text{ ng/g}$. In addition, a pooled ashed hair sample was analysed several times during each GFAAS analysis to check on the precision of the spectrophotometric analysis. Coefficients of variation within and between runs were 6% and 8%, respectively.

Area air samples were collected from three work areas in each tannery for three days as described previously.¹³ Total air Cr concentrations were determined by flame atomic absorption spectrophotometry according to the method outlined by the National Institution for Occupational Safety and Health.³

Fasted blood samples were collected from each subject in the sitting position and the serum was harvested. Spot urine samples were collected from each subject on a Friday afternoon (postshift). In addition, spot urine samples were collected from the tannery workers on the following Monday morning (preshift). Serum and urinary Cr concentrations were determined and have been reported previously.¹³

The hair Cr concentrations in the tannery workers and the control group were not normally distributed, therefore non-parametric statistics were used. The median was used to indicate central tendency and the first and third quartiles were used to measure dispersion. The Kruskal-Wallis test was used to test for differences in median hair Cr concentrations between the tannery workers and the control subjects. The Spearman rank correlation coefficient was used to test

for correlations between Cr concentrations in hair and corresponding values in serum and urine.

Results

The median hair Cr concentration for the tannery workers was significantly higher ($p = 0.0001$) than that of the controls (table).

Median hair chromium concentrations in tannery workers and controls

	Tannery workers ($n = 71$)	Control subjects ($n = 53$)	p^*
Hair Cr (ng/g)†	551 (310–1083)	123 (79–199)	0.0001

*Kruskal-Wallis test.

†1st–3rd quartiles.

Hair Cr concentrations for the tannery workers were significantly and positively correlated with corresponding concentrations of serum Cr ($r = 0.52$, $p = 0.0001$), postshift urinary Cr ($r = 0.71$, $p = 0.0001$), and with the postshift urinary Cr/Cr ratios ($r = 0.64$, $p = 0.0001$) (fig 1). The preshift urinary Cr concentrations and the Cr/Cr ratios were also correlated with hair Cr concentrations ($r = 0.45$, $p = 0.003$; $r = 0.43$, $p = 0.005$, respectively). Such relations were not found for the controls.

Hair Cr concentrations were also associated with the area of employment but not with duration of employment in the tanning industry. The median hair Cr concentration was significantly higher for workers handling wet hides in the chrome tan and wringing departments than for workers in other areas of the tanneries (fig 2a). Total air Cr concentrations did not significantly differ among work areas of the tanneries (fig 2b).

Hair Cr concentrations were not correlated with age, height, or weight in either group.

Discussion

The results of this study suggest that hair Cr concentrations may be used as indices of industrial exposure to trivalent Cr. For instance, tannery workers exposed to trivalent Cr had significantly higher median Cr concentrations in hair compared with unexposed controls. Concentrations of Cr in hair were associated with the area of work in the tannery.

To confirm the validity of hair Cr concentrations as a biological index of industrial Cr exposure, the relation between Cr concentrations in hair and body burden of Cr must be established.^{16,17} At present, comparable data exist for mercury, arsenic, and lead but not for Cr.^{2,17} Nevertheless, the significant positive

Fig 1 Scatter plot of $\log_{10}$ hair chromium concentrations and (a) $\log_{10}$ serum chromium concentrations, (b) $\log_{10}$ postshift urinary chromium concentrations, and (c) $\log_{10}$ postshift urinary Cr/CrE ratios.

correlations observed here among three independent indices of Cr exposure for the tannery workers (concentrations of Cr in hair, serum, and urine) indicate that hair is a valid measure of industrial exposure to Cr.

There are several advantages of using hair analysis to assess industrial exposure to Cr compared with the analysis of Cr in serum or urine. No special equipment is required for collecting or storing hair for Cr analysis, whereas trace element free equipment and clean room conditions are essential for collecting serum and urine.¹⁸ Indeed, the wide range (1000-fold) of physiological Cr concentrations reported for serum and urine compared with hair^{18,19} may arise in part from failure to include such precautions. In addition, Cr concentrations in hair are much higher than those

in serum or urine so that accuracy and precision during analysis are more easily achieved.

Any exogenous contamination must be removed by a standardised washing procedure before hair Cr concentrations may be used as an index of industrial exposure to Cr. Several washing methods for hair analysis have been described.^{14,20,21} The results of this study suggest that the washing procedure of Kumpulainen *et al*, used here, effectively removed any exogenous Cr contamination from the hair of the tannery workers.¹⁴ Positive correlations were noted between the hair Cr concentrations and corresponding serum and urine Cr concentrations. Saner *et al* also observed a significant positive correlation between hair Cr concentrations and urinary Cr/CrE ratios in Turkish tannery workers.¹

Fig 2 (a and b) Total air chromium concentrations and hair chromium concentrations in three work areas of tanneries.

Biological monitoring for industrial Cr is not routinely performed, especially if the exposure is to trivalent Cr which is considered to be poorly absorbed.²² Instead, concentrations of total Cr and Cr VI in air samples are conventionally measured. This approach can, however, produce misleading results. For example, in our study total and hexavalent air Cr concentrations in all areas of the tanneries studied were well below the maximum allowable time weighted average exposure as proposed by the Ontario Ministry of Labour.²³ Concentrations of Cr in hair, serum, and urine, however, were considerably raised, especially in those tannery workers working in the chrome tan and wringing departments. These results are not surprising because the Cr content of these biological samples represents that which is absorbed not only through the respiratory tract but also through the skin and the gastrointestinal tract. Other investigators have also reported no correlation between air Cr (total and Cr VI) and urinary Cr in workers exposed to Cr VI^{11, 24} and Cr III.^{25, 26} Hence, our findings indicate that trivalent Cr was indeed absorbed by the tannery workers and emphasise the importance of biological monitoring.

The absence of any significant correlations between hair Cr concentrations and those of serum Cr, urinary Cr, or urinary Cr/Cr ratios for the controls is not unexpected. Other investigators have failed to observe consistent correlations in normal unexposed individuals between hair trace element concentrations and corresponding concentrations in other tissues, fluids, or organs.¹¹ To our knowledge, no comparable data for Cr exist at present.

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