Occupational Exposure to Dioxins by Thermal Oxygen Cutting, Welding, and Soldering of Metals

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This paper focuses on one aspect of occupational dioxin exposure that is novel and unexpected. Exposures in excess of the German threshold limit value of 50 pg international toxicity equivalent (I-TEQ)/m³ are very frequent, unpredictable, and sometimes very high—up to 6612 pg I-TEQ/m³—during thermal oxygen cutting at scrap metal and demolition sites. The same procedure involving virgin steel in steel trade and mass production of steel objects gave no such evidence, even though no final conclusions can be drawn because of the low number of samples analyzed. Low dioxin exposures during inert gas electric arc welding confirm previous literature findings, whereas soldering and thermal oxygen cutting in the presence of polyvinyl chloride give rise to concern. The consequences of occupational dioxin exposure were studied by analysis of the dioxin—blood concentration, the body burden, of men performing thermal oxygen cutting at scrap metal reclamation and demolition sites, in steel trade and producing plants as well as for industrial welders and white-collar workers. The results concerning body burdens are in excellent agreement with the dioxin exposure as characterized by dioxin air concentration in the workplace. The significant positive correlation between duration and frequency of performing thermal oxygen cutting at metal reclamation and demolition sites expressed in job-years and dioxin body burden speaks for the occupational origin of the observed overload after long times. The results reported here lead to consequences for occupational health, which are discussed and require immediate attention. — Environ Health Perspect 106(Suppl 2):715–722 (1998). http://ehpnet1.niehs.nih.gov/docs/1998/Suppl-2/715-722menzelabstract.html

Key words: dioxin, PCDD, PCDF, occupational exposure, thermal oxygen cutting, TRK—Wert, scrap metal reclamation sites, demolition sites, body burden, occupational health.

Introduction

Considering the extent of exposure and the number of papers dedicated to the impact of dioxins, it is impressive to note how much the environmental aspect outweighs the occupational point of view, even though the latter has added important knowledge about the adverse effects on human health (1–4).

Therefore, it might be appropriate to consider occupational health aspects of dioxins also in a journal dedicated to environmental health. In doing so, we will concentrate on one specific topic with very recent and rather unexpected findings as a result of our investigations.

In Germany 2,3,7,8-tetrachlorodibenzop-p-dioxin (2,3,7,8-TCDD) was classified in 1986 as a chemical known to induce cancer in animals (group III A2) (5) and in 1993 a legally executable threshold limit value at the workplace (TRK—Wert) of 50 pg/m³ international toxicity equivalent (I-TEQ) was established (6); at the same time the toxic potency of other members of the polychlorinated dibenzo-p-dioxin/poly-chlorinated dibenzofurans (PCDD/PCDF) family were taken into account by I-TEQ factors (7). The TRK—Wert is time weighed averaged over an 8-hr shift with a short-term exposure limit (STEL) 4 times higher for 15-min periods. Such short-term periods must not occur more often than 4 times per shift. Consequently, the TRK—Wert of 50 pg/m³ I-TEQ must also be met when the integration time of the measurement is 1 hr or longer. With this legal basis given, the occupational health authorities in Hessen felt compelled to check existing dioxin exposures by investigating all hazardous waste incineration (HWI) plants in the federal state of Hessen during routine operation (8, 9) in 1993. In contrast to our expectations, the exposure levels observed were low: always less than 8% of the TRK—Wert, which therefore can be lowered for such workplaces. For one employee, who was engaged in metal-repair work during the annual revisions of the plant, elevated PCDF blood values were observed. We therefore investigated the occupational exposure to dioxins during the annual revisions of HWI plants as well as thermal oxygen cutting at metal reclamation and demolition sites (10, 11).

The reason to investigate dioxin exposures at the workplaces where metals are welded, soldered, or thermally oxygen cut was the expectation that in all cases where traces of chlororganics such as polychlorinated biphenyls (PCBs) in old paint, oil, or the like are involved, the three criteria for dioxin formation are fulfilled: chlorinated compounds, elevated temperatures in the appropriate range, and heavy metal catalysis. To our knowledge we were the first to follow this line of evidence by checking the up-to-then unsuspected thermal oxygen cutting workplaces. In this paper we extend our previous findings (10, 11) about high dioxin exposures during thermal oxygen cutting at scrap metal reclamation and demolition sites and elevated dioxin body burdens in men performing such work for a long time.
**Materials and Methods**

**Sampling and Dioxin Analysis of Air**

Air samples were always taken by means of pumps and filters carried by the person performing the work. To characterize the environment, especially when the work was performed in open air, additional stationary samples were taken. In both cases particles were retained by glass fiber filters and gaseous dioxins were retained by polyurethane (PUR) foam (NILU Corp., Kjeller, Norway), since from our own observations (10) as well as from the literature (13) we know that 10 to 30% of total PCDD/PCDF in air can be found as vapor. For economic reasons PUR plugs and glass-fiber filters were extracted together. Personal samplers were operated at 3.3 liters/min by means of Alpha 1 pumps by Ametek (Ametek Testing Calibration Instruments, Largo, FL) and by Gilian (Gilian Instrument Corporation, Wayne, NJ), which were recalibrated before each use. The sampler head was the standard head for total dust (Gesamstaub/Gas [GGP]-Probenahmekopf, product of Gesellschaft für Schadstoffmeßtechnik GmbH Gutvellbrügen, Neuss-Norf, Germany) (14). The air volume taken varied according to the duration of the activities sampled and typically was around 1 m³. Prior to use, the glass-fiber filter was spiked with 250 pg 13C-half-labeled 2,3,7,8-TCDD. The working person was supervised with times and types of activities, and breaks recorded as well as the atmospheric parameters: temperature, air pressure, humidity, and wind velocity. Stationary samples of the environmental air were taken in accordance to immission measurements (15) by the PCDD/PCDF-immission sampler head developed by the Berufsgenossenschaftliches Institut für Arbeitssicherheit (BIA) (16), manufactured by Gesellschaft für Schadstoffmeßtechnik; the sampler head also accommodates two PUR plugs and was operated by use of a Gravicon PM4 pump (Gesellschaft für Schadstoffmeßtechnik). The air flow rate was exactly 4 m³/hr and the operation time was roughly the same as for the person who carried the sampler.

Total dust was determined gravimetrically. Prior to Soxhlet extraction with toluene, 14 I-TEQ congeners, fully 13C-labeled, were spiked on to the filter. The extracts were purified by use of a multi-column system including carbopack C on celite 545 (Supelco Corp., Bellefonte, PA). Identification was done by high resolution gas chromatography and high resolution mass spectrometry with an SP 2331 (Supelco) and a DB 5 spectrometer (J&W Scientific, Folsom, CA) or a VG Autospec (Micromass, Manchester, UK). Quantification was performed by isotope-dilution technique using the spiked standards added before extraction. Recovery rates are typically 65 to 115%, the detection limit for 2,3,7,8-TCDD is 0.2 to 1.0 pg/m³ for the person-carried sampler (depending on the air volume taken) and 0.03 pg/m³ for the stationary sampler.

**Sampling and Dioxin Analysis of Blood**

Between 60 and 80 ml whole blood was collected by free blood flow in a pre-cleaned, 2500 IU heparin-containing glass jar; the jar was closed by a Teflon-covered screw cap. Samples were transported frozen and stored at −20 to −30°C. While donating blood, the donor was questioned by the same interviewer, after a detailed questionnaire that covered nutritional and smoking habits, the dwelling environment, and details of type and duration of all occupational activities performed so far. For the present publication, this questionnaire was used to determine job-years of the occupation performed at the time of the investigation and to check for past occupational activities, as well as nutritional habits (e.g., catching and eating fish from local, possibly contaminated watersheds) and dwelling conditions (e.g., living in a flat with pentachlorophenol [PCP]-treated wood covers) which are indicative of nonoccupational exposure to PCDD/PCDF. A more detailed investigation concerning the correlation between the other parameters requested and PCDD/PCDF body burden will be the subject of a future paper.

For PCDD/PCDF analysis, 40 ml of the thawed blood was mixed with 35 ml water and spiked with 1000 pg octachlorodibenzo-p-dioxin (OCDD), respectively, 100 pg of all other 13C-labeled I-TEQ congeners. The PCDD/PCDF and all other fat-soluble compounds were adsorbed together with the blood fat onto modified silica (Chem-Un, Chemelut Hydromatrix; ICT, Bad Homburg, Germany) and eluted with hexan/isopropanol (3:2). Blood fat was determined gravimetrically and analysis of PCDD/PCDF together with coplanar PCBs followed the same regime as that described for the air samples. Recovery rates are 70 to 110% and the detection limit for 2,3,7,8-TCDD is 0.5 to 1.0 pg/g blood fat, which is equivalent to 5 fg/ml whole blood. For more detailed information on the analytical techniques we refer to previous publications (17–19).

During the investigations reported here, we also checked for overall reproducibility after long times by reanalysis of the same donors: one after 1 year, another after 2 years. The analyzing laboratory was blind to this fact and was informed only after delivery of the results. Differences for the I-TEQ values were +12% and −3%. The mean value of variation for the individual congeners analyzed was 16 ± 11% (n = 12) and 14 ± 10% (n = 11), when considering only results above the detection limit and without possible interferences. When all 17 congeners are considered, mean values of variation of 18 ± 15% and 20 ± 17%, respectively, were found (n = 17 in both cases). For the group parameters (sum of hexachlorodibenzo-p-dioxin [hexa-CCDD], sum of pentachlorodibenzofuran [penta-CCDF], etc., including I-TEQ values) mean values of 13 ± 9% and 12 ± 9% (n = 8 in both cases) was found for the two donors. We interpret these differences as analytical variations of the whole procedure and not as changes in the body burden of the person reanalyzed, which was taken to be constant. To us it appears that the long-term reproducibility with mean variations of less than 15% for the sum parameters including I-TEQ values is well acceptable, while individual components at very low concentrations may need more cautious interpretations.

**Quantitative Evaluation of PCDD and PCDF Toxicity**

PCDD and PCDF represent two families of closely related molecules, consisting of 135 and 75 members, respectively. These can be subdivided into different groups according to the number of chlorine atoms (four to eight) attached: tetra-, penta-, hexa-, hepta-, octa- chlorodibenzo-dioxins and furans (see "Appendix"). When analyzing for PCDDs or PCDFs, a single PCDD or PCDF is never found, but rather a large number of different ones are found, especially when they are formed de novo in combustion processes. To evaluate the toxic potency of such vast mixtures, the concept of toxicity equivalency factors (see "Appendix") has been established in the study (7) of the North Atlantic Treaty Organization–Committee on the Challenge of Modern Society (NATO-CCMS) and has gained both scientific and legislative (6) acceptance. The quantitative number of each factor is derived from experimental animals and from *in vitro* experiments (7). Essentially this concept provides factors to
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7 PCDDS and 10 PCDFs ranging between 0.001 and 1.0, which is given only to the most potent member, 2,3,7,8-TCDD. To obtain the quantitative number of the dioxin concentration representing the potency of the mixture analyzed, each concentration of the 17 PCDDS/PCDFs is multiplied with its appropriate toxicity factor and the results are totaled; this number is the concentration of 2,3,7,8-TCDD believed to have the same toxic potency as the mixture analyzed. The enormous advantage of this procedure is that it enables the investigator to make very complex mixtures comparable by use of a single number. For this reason, but also to conform to legal demands, PCDD/PCDF concentrations both in air and in blood are given in these 1-TEQ units throughout this paper.

Statistics

Statistical analysis of dioxin body burden of the different groups investigated here was performed by Kolmogorov-Smirnov 2-sample test. The dependence of dioxin body burden on duration of exposure was done by linear regression analysis.

Results and Discussion

Dioxin Concentration in Breathing Air Indicating Occupational Exposure

Table 1 summarizes relevant data concerning the dioxin exposure at workplaces where thermal oxygen cutting is performed. The first high exposure exceeding the TRK–Wert about 40-fold, was encountered during repair of the waste chute in an HWI plant. During the first two measurements listed, the double-walled, water-cooled chute, to which the solid hazardous waste is applied, was repaired by thermal oxygen cutting and fitting of new parts. The next four values refer to the same activities during the next revision of an HWI plant of identical design, although under very different conditions due to the knowledge obtained from the first measurements. On the one hand, ventilation was dramatically increased and on the other hand—and more importantly—the chute was pre-cleaned extensively before any repair work was started. As can be seen, these measures resulted in a dramatic, 10- to 100-fold, reduction of dioxin exposure, even though the TRK–Wert still is surpassed and respiratory protection remains necessary. To explain the results, it is reasonable to assume that during the operation of the HWI plant some of the dioxins formed in the off-gases may condense onto the water-cooled waste chute and be preserved there at relatively low temperatures. When the chute is heated again during repair, the dioxins present will be mobilized, unless they were removed before by intensive cleaning. Thus, precleaning of the waste chute reduces dioxin exposure during repair, but will mobilize dioxins as well, which requires protective measures.

The exposure to dioxins in HWI plants, especially during extensive repair, was to be expected, whereas the generation of dioxins during thermal oxygen cutting performed outside of HWI or MWI plants, was unreported. As can be seen in Table 1, six of seven person-specific air samples at three different demolition sites clearly exceed the 50 pg/m³ I-TEQ level, one of them 132-fold. For practical reasons demolition sites are excepted from TRK–Wert applications (see “TRK–Wert” in the “Appendix”), which does not affect the obligation to protect those exposed to dioxins here just as effectively as at every other workplace. Demolition site 1 was a coal-operated power plant; site 2 was an old gasometer; and site 3 was a crane. In no case were suspicious materials, like electric transformers or condensers, subject to thermal oxygen cutting, but rather steel constructions, high-pressure pipes, and boilers, mostly painted but free of grease and oil. In the case of the gasometer some black plastic material was present at a few spots, this material was

| Workplace | Dioxin concentration, pg/m³ I-TEQ | Total 2,3,7,8-PCDD, pg/m³ | Ratio PCDF / PCDD (2,3,7,8 congeners) | Multiple of occupational threshold limit TRK–Wert, 50 pg/m³ I-TEQ | Duration of sampling time, hr |
|-----------|-----------------------------------|---------------------------|--------------------------------------|---------------------------------|-----------------------------|
| HWI: waste chute | 1,830 | 21,678 | 1.5 | 36.6 | 2.1 |
| not precalined | 2,430 | 20,058 | 1.9 | 49.6 | 2.3 |
| HWI: waste chute | 90 | 6,911 | 1.2 | 1.6 | 3.7 |
| precalined | 20 | 354 | 1.2 | 0.4 | 3.9 |
| 33 | 794 | 1.1 | 0.6 | 3.5 |
| 140 | 2,680 | 1.1 | 2.8 | 3.3 |

Demolition site, plant no.

| Scrub metal reclamation site | 1a (same person 1b) | 98 | 227 | 3.4 | 2.0 | 0.4 |
|-----------------------------|---------------------|----|-----|----|----|----|
| 1b (same person 1a) | 858 | 1,266 | 17.2 | 3.8 | 4.5 |
| 2a | 348 | 95 | 24.5 | 7.0 | 2.6 |
| 2b | 1,183 | 300 | 26.0 | 23.7 | 3.1 |
| 3 | 19 | 96 | 2.1 | 0.4 | 3.9 |
| 4 | 17 | 25 | 5.1 | 0.3 | 1.2 |
| 5 | 15 | 118 | 0.8 | 0.3 | 4.0 |
| 6 | 20 | 37 | 3.4 | 0.4 | 4.1 |
| 7a | 18 | 30 | 3.9 | 0.4 | 4.1 |
| 7b | 8 | 46 | 1.1 | 0.2 | 4.7 |
| 8a | 77 | 86 | 5.8 | 1.5 | 7.4 |
| 8b | 137 | 116 | 5.1 | 2.7 | 5.0 |
| 9 | 23 | 26 | 5.0 | 0.5 | 5.6 |
| 10 | 93 | 25 | 27.3 | 1.9 | 4.2 |

Production plants and steel trading

| 1 | 1 | 62 | 0.27 | 0.02 | 2.9 |
| 2a | 1.7 | 1,655 | 0.0008 | 0.03 | 6.0 |
| 2b | 0.07 | 11 | 0.13 | 0.001 | 6.0 |
| 3a | 0.8 | 9 | 0.20 | 0.016 | 4.6 |
| 3b | 3.0 | 539 | 0.34 | 0.06 | 4.6 |
| 3c | 0.3 | 11 | 0.7 | 0.005 | 4.6 |

*Numbers refer to different plants; letters refer to different determinations.
positive for chlorine components, as determined by a quick test. The most surprising result is that of demolition site 1d, which had the highest dioxin exposure ever encountered in our studies, since in this case a neat steel rotor of a steam turbine was cut. While in the case of the HWI samples the ratio of PCDF/PCDD (taking into account only 2,3,7,8 congeners) is rather constant between sites 1 and 2, irrespective of the dioxin I-TEQ concentration, this ratio varies much for the samples taken from the demolition sites. In addition, this ratio appears to be higher when the dioxin I-TEQ concentration is high.

Other workplaces where old material is subject to thermal oxygen cutting are scrap metal reclamation sites. Of the 14 person-related air samples from 10 sites, half of them clearly exceed the TRK-Wert, one more than 20-fold. This is—as in the case of the demolition sites—the more surprising, since all the operations monitored were performed in the open air, often at considerable wind speeds. The material worked on was typical for metal reclamation sites: big containers, bulky steel constructions, heavy-duty machines, and so on. The material was always paint coated, and often greasy and oily. Of the paint samples collected and analyzed by a quick test for organohalides, about 25% were positive and there was no obvious correlation between positive results and dioxin I-TEQ concentrations at the respective workplaces. With respect to the ratio PCDF/PCDD (2,3,7,8 congeners only) a picture emerges that is similar to the case of the demolition sites, although both the ratio and the dioxin I-TEQ concentrations are lower, but they parallel each other.

As can be seen from Table 2, the ambient dioxin I-TEQ concentrations in the vicinity of the open-air thermal oxygen cutting, as determined by stationary sampling, is much lower than for the person-related air samples, but much higher than ambient open air values (20). At metal reclamation site 2 this emission value reaches two-thirds of the occupationally defined TRK-Wert, which is impressive, since the cutting operations were performed 5 to 10 m apart in the open air and indicates that we deal here with an environmental problem as well.

From these results it is obvious that thermal oxygen cutting outside of incinerators is also a highly relevant activity with respect to occupational dioxin exposure. At metal reclamation sites as well as at demolition sites, such exposures are very frequent, sometimes very high, and in no way pre-dictable. The necessity for prompt protective measures at scrap metal reclamation and demolition sites does not require—and cannot wait for—detailed models explaining dioxin generation at such places. In contrast, as we can in no way assume that at these working places dioxin exposure is well below the TRK-Wert at all times, we must do what can be done immediately: using personal respiratory protection.

The validity of this conclusion strongly depends on how well our results represent the work shift of a person performing thermal cutting of metals, especially with respect to the percentage of the shift covered. As can be seen from the last column in Table 1, the duration of personal sampling is, with one exception, always longer than 1.2 hr. This exception, determination 1a, represents the attempt to trace the source of dioxin exposure during thermal cutting by operating the person-carried pump only when cables attached to the scrap metal were burned, while determination 1b averages over the whole shift of this same person. The results show that burning cables is not an important contributor to dioxin exposure during thermal oxygen cutting, as exposure during this activity is lower than the exposure averaged over the whole shift (1b). Calculating the median of the duration of our exposure assessments at HWI plants, scrap metal plants, and demolition plants yields the value of 4 hr ($n = 27$), that is more than half the 8-hr shift. In addition, all determinations—with the exception of 1a, which served other purposes—meet the criterion to represent the TRK-Wert, as they all lasted longer than 1 hr (see "Introduction" and "Appendix"), which even holds true for the 5th percentile (1.4 hr), while the 95th percentile (6.3 hr) is in excess to 75% of the 8-hr work shift.

The high dioxin exposures at thermal oxygen cutting sites prompted us also to look into workplaces where steel is welded, even though Linde et al. (12) reported low exposures. As can be seen from Table 3, electric welding within an HWI plant leads to exposures close to the TRK-Wert, whether it is done in the boiler or at the precleaned waste chute. This, however, we associate with the liberation of preformed dioxins and not as a consequence of the welding process itself. In accordance with Linde et al. (12) we find low dioxin exposures on inert gas electric arc welding when construction elements for a bridge were mass produced in an industrial workshop. Although it should be worthwhile to scan additional welding workplaces, we do not see a high priority for the surveillance of workplaces dealing with virgin steel. We should respond differently to the repair welding of

### Table 2. Environmental PCDD/PCDF air concentrations near thermal oxygen cutting of metals in the open air as determined by stationary sampling

| Workplace | Dioxin concentration, pg/m³ I-TEQ | Total concentration, 23,7,8-PCDD, pg/m³ | Ratio PCDF/PCDD (2,3,7,8 congeners) | Multiple of occupational threshold limit TRK-Wert 50, pg/m³ I-TEQ | Duration of sampling time, hr |
|-----------|-----------------------------------|--------------------------------------|---------------------------------|-----------------------------|------------------------------|
| Demolition site 1d | 1.45 | 4.8 | 1.5 | 0.03 | 4.8 |
| Metal reclamation site | 2 | 39 | 12.3 | 23.5 | 0.78 | 4.4 |
| | 3 | 4 | 8.1 | 3.0 | 0.08 | 4.2 |
| | 4 | 0.18 | 1.7 | 1.9 | 0.004 | 1.5 |
| | 5 | 0.15 | 56.5 | 0.02 | 0.003 | 2.1 |
| | 6 | 0.35 | 6.5 | 3.1 | 0.07 | 2.3 |
| | 7 | 2.1 | 15.2 | 0.95 | 0.04 | 2.6 |
| | 8 | 3.8 | 27.1 | 1.1 | 0.08 | 1.0 |

*Numbers refer to different plants; letters refer to different determinations.*
old constructions, in which we see a close relationship to thermal oxygen cutting and which should be investigated.

Because we started our search for dioxin exposures outside of HWI plants with the hypothesis that such exposure is due to chlororganics present when the metals are heat stressed, we specifically looked at two workplaces where the presence of chlororganics during heating of metals is known. One is the soldering of polyvinyl chloride (PVC)-insulated copper plumbing (WiCu-Rohr), which leads—depending on the extent of removal of the PVC insulation from the spot to be soldered—to more or less pyrolysis of PVC. As seen in Table 4, the TRK-Wert was not surpassed in our measurements, and accordingly, the PCDF/PCDD ratio is on the low side. The results nevertheless indicate that such work is to be performed under very good ventilation only, especially in narrow rooms, and that it is essential to remove the PVC insulation generously by mechanical cutting and never by burning.

Another example of involvement of PVC in the heat treatment of metals is its recent use as a component in anticorrosive paints. As seen in Table 4, thermal oxygen cutting of steel plates treated with such paint leads to dioxin exposures well in excess of the TRK-Wert. The discontinuation of the use of PVC as a component in anticorrosive paint is the solution to this problem, which is the only example of the dioxin exposure during thermal oxygen cutting for which we can identify the source and which therefore should be eliminated.

### Dioxin Body Burden of Occupationally Exposed and Unexposed Men

Considering both the frequent and high dioxin exposures during thermal oxygen cutting at scrap metal reclamation and demolition sites it is of interest to investigate whether the dioxins have reached the men performing such work, enhancing their body burden. Although exposure to dioxins via respiration is of minor importance for the population at large [1.2% of total intake according to Travis (20), 0.01%, respectively, for people living near contaminated sites (21)], this is expected to be different for men performing thermal oxygen cutting at scrap metal reclamation and demolition sites. Since the TRK-Wert is $2.5 \times 10^3$-fold (20), respectively $10^2$-fold (21) higher than the ambient dioxin air concentrations assumed in these studies, exceeding the TRK-Wert frequently and drastically should increase the body burden of those affected.

### Table 4. Occupational PCDD/PCDF exposure during soldering and thermal oxygen cutting of metals involving PVC pyrolysis as determined by personal air sampling.

| Workplace                  | Dioxin concentration, pg/m³ I-TEQ | Total 2,3,7,8-PCDD, pg/m³ | Ratio PCDF/PCDD (2,3,7,8 congeners) | Multiple of occupational threshold limit TRK-Wert 50, pg/m³ I-TEQ | Duration of sampling time, hr |
|----------------------------|-----------------------------------|--------------------------|-------------------------------------|---------------------------------------------------------------|-------------------------------|
| PVC pyrolysis              |                                   |                          |                                     |                                                               |                               |
| Thermal cutting of steel coated with PVC paint | 80                               | 118                      | 5.6                                 | 1.6                                                          | 2.1                           |
| Soldering of PVC insulated copper pipes (WiCu) | 77                               | 160                      | 5.2                                 | 0.2                                                          | 0.5                           |
|                            | 9                                 | 38                       | 2.8                                 | 0.2                                                          | 0.5                           |
|                            | 21                                | 136                      | 3.3                                 | 0.4                                                          | 0.4                           |

As seen in Figure 1, the dioxin body burden of the German population at large in 1994 ($n = 134$, median body burden 17.3 I-TEQ pg/g blood fat) (19) does not differ from our local control group of male white-collar workers ($n = 16$, median body burden 18.5 I-TEQ pg/g blood fat), while men currently performing thermal oxygen cutting in production plants or steel trade are higher ($n = 7$, median 25.1 I-TEQ pg/g blood fat) and industrial welders still somewhat more increased ($n = 9$, median 29.9 I-TEQ pg/g bloodfat). At first sight 21 men currently performing thermal oxygen cutting at scrap metal and demolition sites appear not to differ from the latter two groups, since the median is 26.9 I-TEQ pg/g blood fat. This figure distorts the facts indeed, since 20% of the 21 men had less than 1 job-year, while all members of the other groups had job-years above 1. Using the cut-off criterion of equal to or larger than 1 job-year brings the number for men at scrap metal reclamation and demolition sites to 17 and the median of dioxin body burden to 44.4 I-TEQ pg/g blood fat (Figure 1), which differs from all other groups and indicates the occurrence of enhanced body burden. The statistical analysis of this group as compared to our local reference group yields a statistically significant difference at $p < 0.05$.

Assuming that dioxin body burden is a consequence of occupational exposure, then the former should be a function of the...
extent of exposure. This is expressed best in terms of job-years, which is the time in years spent in the profession multiplied by the fraction of time spent with performing the activity in question, that is welding or thermal oxygen cutting, while for white collar workers this fraction is set to one. Plotting dioxin body burden for each of the four groups as a function of job-years should make any causal relationship between occupational exposure and dioxin body burden obvious and at the same time should control for artefacts, as for instance the confounding of age, using the white collar group as a reference without occupational exposure.

As shown in Figure 2, no dependence of dioxin body burden from job-years can be found for the white collar workers, the industrial welders or the thermal oxygen cutters working in steel trade or industrial workshops. The results shown in Figure 3 are very different; the figure shows the increase of dioxin body burden with the duration of thermal oxygen cutting at scrap metal and demolition sites ($r=0.79$ at $p<0.001$), correlating body burden and duration of dioxin exposure with high statistical significance. After very long times the body burden can rise to more than 10-fold of the typical body burden of the population at large.

Figure 3 also indicates that the use of respiratory protection by four men cutting high-grade steel brings about a reduction of dioxin body burden. Furthermore, one person in Figure 3 differs from all others (solid dot), as determined by use of the questionnaire. While for all other persons no indications of additional dioxin exposure from nutritional habits, dwelling conditions, or previous occupational activities were found, he is the only one whose past occupation is likely to have contributed to his present dioxin body burden more than his present one, since he worked 14 years as a mechanic in a paper-producing factory and only 1 year at a scrap metal reclamation site where he performed oxygen cutting. This previous occupational activity is considered a confounder with respect to dioxin body burden. Since the calculated line in Figure 3 is not visibly affected by inclusion or exclusion of this data point and the correlation coefficient $r$ is unchanged, we did not exclude this data point.

**Conclusion**

Our first reports on novel occupational dioxin exposures outside of incinerators and chemical plants, that is, thermal oxygen cutting at scrap metal reclamation and demolition sites, have been verified by the results reported here to the extent that requires immediate response (22). The exposure in excess to the TRK–Wert at these sites is so frequent and consistent that these workplaces can no longer be considered safe from overexposure to dioxins and therefore protective actions must be taken. The exposures can be high and are not predictable at all. The excessive dioxin body burden of people performing such work for more than 1 job-year in addition to the clearcut time dependence of the increase of body burden with job-years leaves no doubt about the causal relationship to the workplace, thermal oxygen cutting at scrap metal reclamation and demolition sites. The mechanism of dioxin formation at these places remains unresolved and requires additional efforts to exclude such exposures for the future.

Thermal oxygen cutting of virgin steel in the steel trade and mass production of steel items was found inconspicuous in our investigations, a result that also correlates well with the moderate dioxin body burden, not differing from the population at large and the lack of its increase with job-years for the men performing such work. However, both numbers of blood and air samples are low and reconfirmation of this first, desirable, result is required before these workplaces can be definitely excapulated.

Of concern is the use of PVC as a component in anticorrosive paints, which leads to exposures well in excess of the TRK–Wert when steel thus preserved is cut thermally. Since in this case the cause of dioxin exposure is obvious and known, it is necessary to exclude such exposure in the future by banning PVC as a component of anticorrosive paint.

From these results we draw the following conclusions:

- Thermal oxygen cutting at scrap metal reclamation and demolition sites must be replaced by mechanical cutting whenever possible.
- If unavoidable, such work must be performed with respiratory protection, which covers both particulates and organic vapors (in Germany: P3/A2 filters).
- The causes of dioxin exposure in these workplaces must be identified by more detailed investigations to replace personal protective measures with actions that prevent the formation of dioxins under these circumstances.
- Repair welding might be of concern and should be investigated, while welding of virgin steel gives no reason for concern.
- Thermal oxygen cutting of virgin steel in an industrial setting may not be a cause for concern but should be investigated further.

**Appendix**

**Abbreviations and Glossary**

2,3,7,8-PCDD (polychlorinated dibenzo-p-dioxin): sum of the concentrations of all PCDDs carrying a chlorine atom in the 2,3,7, and 8 position. The corresponding sum for the 2,3,7,8-PCDF can be calculated from this number and the ratio PCDD/PCDF in Tables 1 to 4.

2,3,7,8-TCDD (2,3,7,8-tetrachlorodibenzo-p-dioxin): the most potent, toxic member of the 210 individual chemicals that form the PCDD/PCDF (dioxin) family. This chemical was released in kilogram quantities at the accident in Seveso.
HRGC (high resolution gas chromatography).
HRMS (high resolution mass spectrometry).
HxCDD, HxCDF (hexachlorodibenzo-dioxins, hexachlorodibenzofurans): these compounds carry six chlorine atoms in the dibenzodioxin (=furan) molecule.
HWI (hazardous waste incineration plant).
I-TEF (international toxicity equivalence factors): PCDD/PCDF congener-specific factors ranging between 1.0 for the most potent 2,3,7,8-TCDD and 0.001 for the least potent congeners like OCDD or OCDF (6,7,22).
I-TEQ (international toxicity equivalents): calculated by multiplying the concentration of each PCDD/PCDF congener with its specific I-TEF (see above) and summing these numbers (6,7,22). The result has the dimension of the concentrations used in the calculations and represents the concentration of 2,3,7,8-TCDD that would have the same toxic potency as that specific complex mixture of PCDD/PCDF. This procedure permits the expression of the toxic potency of very complex mixtures with a single number, which is important in the quantitative comparison of mixtures needed in developing regulations. This concept has been extended to other chemicals and complex mixtures such as PCBs (22).
I-TEQ congener: a member of the dioxin family for which an I-TEF has been assigned. It carries a chlorine atom in the 2,3,7, and 8 position of the dibenzo-p-dioxin-, the dibenzo-p-furan molecule, respectively.
NATO–CCMS (North Atlantic Treaty Organization–Committee on the Challenge of Modern Society).
OCDD (octachlorodibenzo-p-dioxin): the dibenzo(dioxin molecule carrying the highest possible number—eight—of chlorine atoms.
OCDF (octachlorodibenzofuran): the dibenzofuran molecule carrying eight chlorine atoms, the highest possible number.
PCB (polychlorobiphenyl): two coavally bound benzene rings (biphenyl) carrying varying numbers of chlorine atoms, up to ten.
PCDD/PCDF (polychlorodibenzo-p-dioxins/polychlorodibenzofurans): dibenzo-p-dioxin and dibenzofuran molecules carrying varying numbers of chlorine atoms at different places within the molecule, colloquially abbreviated as dioxins or the dioxin family.
PCP (pentachlorophenol): used as a wood preservative in the past and contaminated by PCDDs to varying degrees.
PUR (polyurethane): a plastic that forms foams with large surfaces capable of adsorbing all types of gases, including gaseous dioxins.
PVC (polyvinyl chloride): chlorine-containing plastic that is mass produced.
STEL (short-term exposure limit): concentration of a chemical at the workplace elevated above the time-weighted, averaged exposure limit and tolerated only if it does not surpass a given multiple of the exposure limit and if such episodes do not occur more often than a given number per shift and do not last longer than a given time, typically 15 min.
TRK-Wert German: (Technische Richt Konzentration): a threshold limit value at the workplace for cancer causing chemicals. In contrast to the MAK-Wert (German: Maximale Arbeitsplatz Konzentrationen) the TRK-Wert is defined by technical feasibility and not by scientific deduction of a limiting value which, if not surpassed, is assumed not to harm the health of humans at the workplace. As a consequence, TRK-Werte must be lowered whenever technically possible, thereby reducing the probability of causing cancer in people. The TRK-Wert is time-weighted averaged over an 8-hr shift; short-term levels over a period of up to 15 min may surpass the TRK-Wert not more than 4-fold. The sum over such peak times must be less than 1 hr per shift with the consequence that determinations averaging over 1 hr and more must keep within the 50 pg/m³ I-TEQ limit or otherwise the TRK-Wert is surpassed. With respect to demolition sites, there is a legal peculiarity because these are excepted from the TRK-Wert application (6). This exception requires legal clarification, but even now it does not in any way interfere with actions to be taken to protect thermal oxygen cutters at demolition sites from overt dioxin exposure as well as at any other workplace, which on the contrary is required immediately.
WICu-Rohr (German: warme [heat] insulated copper pluming): the insulating material is typically made from PVC.

REFERENCES AND NOTES

1. Manz A, Berger J, Dwyer JH, Fliesch-Janys D, Nagel S, Waldgott H. Cancer mortality among workers in a chemical plant contaminated with dioxin. Lancet 338:959–964 (1991).
2. Fliesch-Janys D. Preliminary results on the exposure to polychlorinated dioxins and furans and mortality in a cohort of workers of a herbicide producing plant in Hamburg, Germany. In: Current Views on the Impact of Dioxins and Furans on Human Health and the Environment. Proceedings of The Toxicology Forum, 9–11 November 1992, Berlin: The Toxicology Forum, eds. The Toxicology Forum:Washington, 1992:207–217.
3. Fingerhut MA, Halperin W, Marlow D. Mortality among U.S. workers employed in the production of chemicals contaminated with 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD). In: NIOSH Final Rpt PB 91125971. Springfield, VA:National Technical Information Service, 1990.
4. Zober MA, Messerer P, Huber P. Thirty-four-year mortality follow-up of BASF employees exposed to 2,3,7,8-TCDD after the 1953 accident. Int Arch Occup Environ Health 62:139–157 (1990).
5. Deutsche Forschungsgemeinschaft. List of MAK and BAT values.

Appendix IIIA2: 2,3,7,8-Tetrachlorodibenzo-p-dioxin. Mitteilung XXII der Senatskommission zur Prüfung gesundheitsschädlicher Arbeitsstoffe. Weinheim:VCH Verlagsgesellschaft, 1986
6. Technische Regel für Gefahrstoffe TRGS 901 Nr. 42. TRK-Wert für chlorierte Dibenzoxydine und -furane. Bundesarbeitsblatt. (Bundesministerium für Arbeit und Sozialordnung, ed.) Köln, Germany:W Kohlhammer Verlag, 1993:71–73.
7. NATO. Pilot Study on International Information Exchange on Dioxins and Related Compounds. Scientific Basis for the Development of the International Equivalency Factors (I-TEF) Method of Risk Assessment for Complex Mixtures of Dioxins and Related Compounds. Rpt No 178. North Atlantic Treaty Organisation, December 1988.
8. Bolm-Audorff U, Menzel HM, Murzen R, Päpke O, Turcer E, Vater U. Dioxin- and Furanelastations von Beschäftigten in Sondermüllverbrennungsanlagen. In: Verhandlungen der Deutschen Gesellschaft für Arbeitsmedizin und Umweltmedizin e.V. (Kessel R, ed). Fulda, Germany:Rindt Druckerei, 1993:105–108.
9. Päpke O, Ball M, LisZA, Menzel HM, Turcer E, Bolm-Audorff U. Occupational exposure of chemical waste incinerator workers to PCDD/PCDF. Organohalogen Compounds 21:105-110 (1994).
10. Menzel HM, Turcer E, Bienfait HG, Albracht G, Päpke O, Bolm-Audorff U. Dioxinexposition beim Brennen, Trennen und Schweßen von Metallen. In: Verhandlungen der Deutschen Gesellschaft für Arbeitsmedizin und Umweltmedizin e.V. (Munzberger E, ed). Fulda, Germany:Rindt Druckerei, 1996;323–327.
11. Menzel HM., Turcer E, Bienfait HG, Albracht G, Päpke O, Ball M, Bolm-Audorff U. Exposure to PCDD’s and PCDF’s during welding, cutting and burning of metals. Organohalogen Compounds 30:70–75 (1996).
12. Linde H, Striess B, Stüber H. Polychlorierte Dibenzodioxine und -furane an MAG-Schweißplätzen. Staub, Reinhalung der Luft 55:179–182 (1995).
13. Stockmann R, Hahn JU, Lichtenstein N, Neumann H-D, Schick W. Polychlorierte Dibenzodioxine und -furane an Arbeitsplätzen, In: Messungen von Gefahrstoffen BIA Arbeitsmappe Nr 7552, Gesamtstaub. Bielefeld, Germany:Erich Schmitt Verlag, 1993.
14. Berufsgenossenschaftliches Institut für Arbeitssicherheit. BIA Arbeitsmappe Nr 7552, Gesamtstaub. Bielefeld, Germany:Erich Schmitt Verlag, 1989.
15. Verein Deutscher Ingenieure. Handbuch Reinhalung der Luft, VDI Richtlinie 3499 Blatt 2, Messen von Polychlorierten Dibenzop(dioxinen und Dibenzofurannen. Verein Deutscher Ingenieure, ed. Berlin:Beuth Verlag, 1993.
16. Berufsgenossenschaftliches Institut für Arbeitssicherheit. BIA Arbeitsmappe Nr 6880 Gesamtstaub. Bielefeld, Germany:Erich Schmitt Verlag, 1989.
17. Päpke O, Ball M, LisZA, Scheuert K. PCDD/PCDF in whole blood samples of unexposed persons. Chemosphere 19(1-6):941–948 (1989).
18. Päpke O, Ball M, Lis A. PCDD/PCDF in humans—an update of background data. Organohalogen Compounds 13:81–84 (1993).
19. Päpke O, Ball M, Lis A. PCDD/PCDF und coplanare PCB in Humanproben; Aktualisierung der Hintergrundbelastung, Deutschland 1994. Organohalogen Compounds 22:275–279 (1995).
20. Travis CC, Hattemayer-Frey HA. Human exposure to dioxin. Sci Total Environ 104:97–127 (1991).
21. U.S. EPA. Estimating Exposure to Dioxinlike Compounds. Chapt 9–34. EPA/600/6-88/005B. Washington:U.S. Environmental Protection Agency, 1992.
22. Menzel HM, Albracht G, Bienfait HG, Turcer E, Walter D, Emmel C, Knecht U, Päpke O, Bolm-Audorff U. Dioxinexpositionen und Biomonitoring an Schneidbrenn- arbeitsplätzen auf Schrottplätzen, Abbruchbaustellen und bei industrieller Fertigung. Dokumentationsband über die 37. Jahrestagung der Deutschen Gesellschaft für Arbeitsmedizin und Umweltmedizin e.V. in Weibaden. (Borsch-Galetke E, ed). Fulda, Germany:Rindt Druck, 1977; 497–499.
23. Safe S. Polychlorinated Biphenyls (PCBs), dibenz-p-dioxins (PCDDs), Dibenzofurans (PCDFs) and Related Compounds: Environmental and Mechanistic Considerations Which Support the Development of Toxic Equivalency Factors (TEFs). Critical Review in Toxicology. Vol 21 (McClellan RO, ed). Boca Raton, FL:CRC Press, 1990;51–88.