Impact of PCDD/PCDF Emissions of a Copper Reclamation plant: Five Years of Experience with Environmental Monitoring

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Introduction

Copper reclamation is one of the industrial processes known for its PCDD/PCDF emission potential. For this reason, the vicinity of the only Austrian copper reclamation plant, situated in Brixlegg (Tyrol), was investigated for evidence of contamination by these in part highly toxic compounds. In terms of risk assessment, particular attention was paid to the food chain "grass – cow's milk – man" since this area, lying in an inner alpine valley, is mostly exploited for dairy farming. Since 1987, the aims of the investigations have been to determine the contamination of the environs of the plant by PCDD/PCDFs, to provide the basis for emission–reduction measures, to determine the latter's effectiveness and to take precautionary and corrective action. The paper at hand presents an overview of the results obtained so far. All PCDD/PCDF values are given in International Toxicity Equivalents (TE). For lack of space there will be no isomer specific consideration of the topic.

Investigations of 1987/88

In 1987/88 PCDD/PCDFs in different media were investigated in order to assess the contamination situation. Table 1 summarises the then obtained results.

Tab. 1: Levels of PCDD/PCDF in different media 1987/88 (in TE)

	level	remark	ref.
Emissions: concentr.	155 and 46 ng/Nm³	2 sources (shaft furnace)	8, 2
load	26 g/a		2
Ambient air	1.2–2.3 pg/m³	4 periods 11–15 d, 300 m	3, 5
Spruce needles 10/87	51; 55; 75; 86 ng/kg	age 0.5, 1.5, 2.5, 3.5 a	1, 2
Soil	0.0–332 ng/kg	n =20, 230–4600 m	1, 5
Hay (1987)	18–36 ng/kg dw.	n = 3, 1000–2200 m	2
Fodder grass (5/88)	13–23 ng/kg dw.	n = 5, 280–2900 m	2, 5
Cow's milk, farms (2/88)	20.1–69.5 ng/kg fat	n = 6	2, 6
Cow's milk, farms (4/88)	14.0–28.3 ng/kg fat	n = 4	4
Human blood	152; 946 ng/kg fat	2 farmers	1
	41; 66; 77 ng/kg fat	3 family members	unpubl.
Mother's milk	9.3–45.9 ng/kg fat	n = 5	unpubl.

Compared to reported data, emission concentrations, annual loads, concentrations in the ambient air, spruce needles, hay or fodder grass and in cow's milk were comparably high at that time. The soil samples exhibited strikingly higher levels depending on the distance from the copper plant and the prevailing wind directions. Contamination of the soil, however, was not as high as comparable cases that have been reported. Two blood samples from farmers living in the area which is influenced by the copper reclamation plant showed conspicuously high levels. The other three blood samples taken from members of their families lay within the normal range. In the five samples of mother's milk investigated no conspicuously high concentrations were detected.

Emission reduction measures

On account of the – in part – extremely high measured values, the use of plastic–containing materials in the shaft furnace of the copper reclamation plant was banned. The later

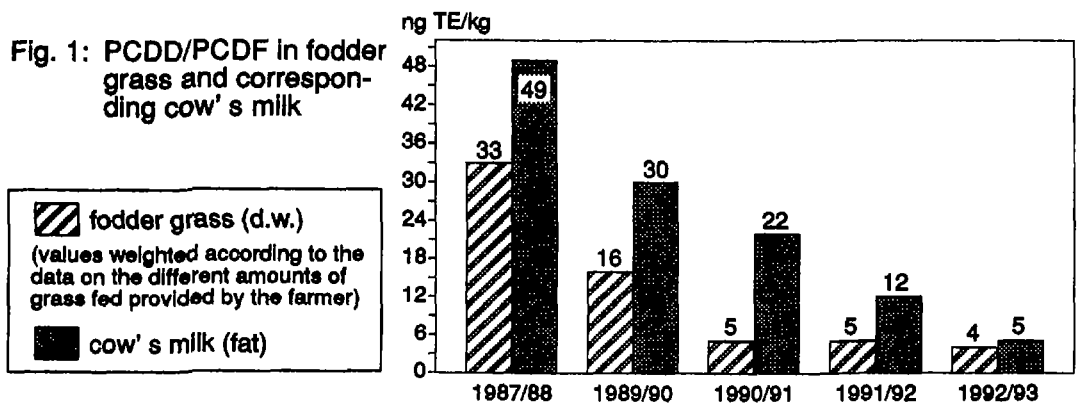
installation of an afterburner onto the shaft furnace – after initial technical problems – drastically reduced the emissions from an annual load of 26 g TE to less than 1 g TE (calculated from measurements at defined sources) since 1989. The standard for the PCDD/PCDF emissions from the shaft furnace has been set at 0,9 ng TE/Nm^3 by the authorities. But as a rule, the actual measurements lay even clearly below this level. Emissions were further reduced by other measures, such as stabilising the entire plant area, the regular use of a sweeping machine and, finally, the filtering of exhaust air from the plant building.

Monitoring investigations 1987–1993

For the monitoring investigations a farm whose premises of 20 ha lie, at a distance of 1400–2200 km, within the prevailing wind direction from the copper reclamation plant was chosen. The fodder grass is cut three times a year. Every day the approximately 20 milk cows are each fed with about 15 kg (d.w.) fodder grass taken from the farm premises plus about 2 kg of (uncontaminated) grain. In winter hay from the three cuts is equally drawn upon. The annual milk yield amounts on average to about 4000 kg per cow. On the farm premises PCDD/PCDF in soil amounts to 21 ng TE/kg.

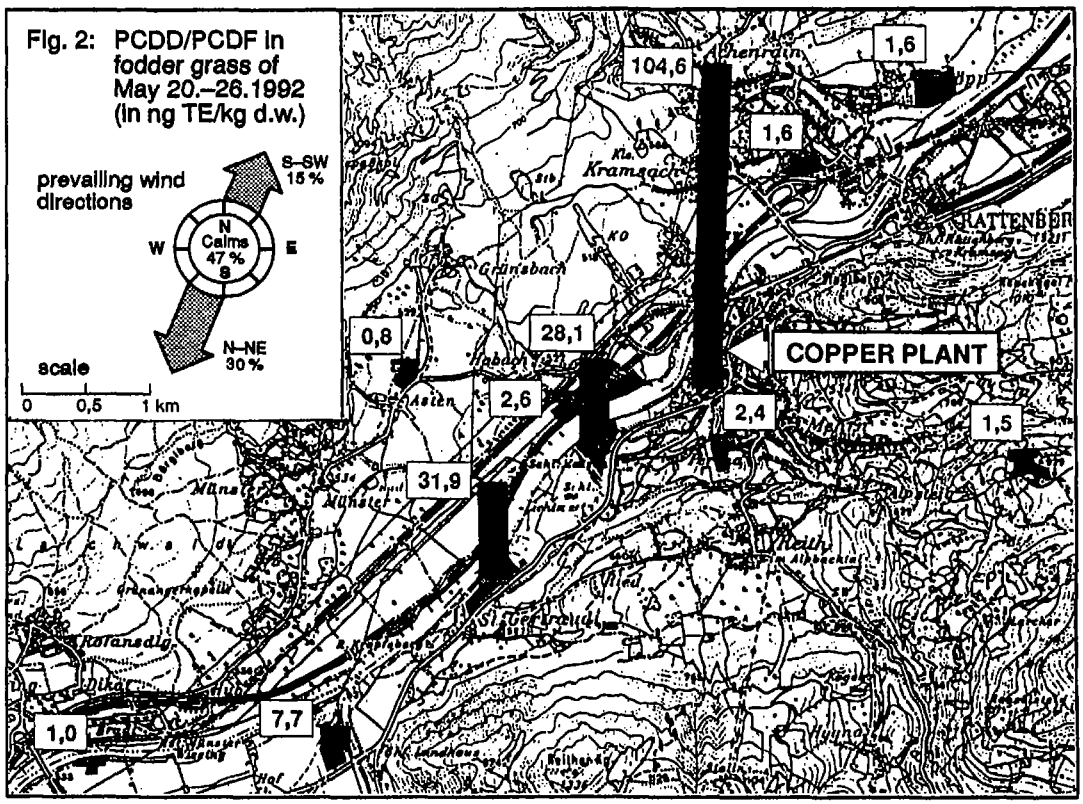
Representative grass samples from the whole farm area were taken at the times when the fodder grass was cut. Milk samples were usually taken at the end of the winter feeding period from the collecting tank of the farm because it is assumed that by then the equilibrium between fodder and milk has been established (6,7). Figure 1 summarises the results from the winter feeding periods 1987/88 until 1992/93.

Fig. 1: PCDD/PCDF in fodder grass and corresponding cow' s milk



Since 1987/88 contamination of both fodder grass and cow's milk has continously decreased. Until July 1992, however, the decrease remained below the expectations. It had been expected that given a soil contamination of 21 ng/kg TE in the investigated area grass contamination would decrease approximately to background values following the retrofitting of the shaft furnace (reduction of the overall load of 26 g TE/year until 1988 to less than 1 g per year after 1989 from all measured sources). This shows that the retrofitting of the shaft furnace initially did not bring the expected success. PCDD/PCDF contamination of the milk corresponded to fodder contamination, thus confirming the results obtained from other investigations.

Given the rather slow decrease in grass contamination the question of the general contamination situation presented itself again for consideration. This is why in May 1992 again grass samples were taken from ten areas in the vicinity of the copper reclamation plant and investigated for their PCDD/PCDF levels. The results are given in figure 2.



Up to a distance of 4.5 km in the prevailing wind direction from the copper reclamation plant the grass samples investigated in May 1992 showed unexpectedly high PCDD/PCDF levels. At a distance of 6 km and outside the prevailing wind direction almost background concentrations were measured.

Another astonishing aspect of the results was that ten days before the grass of the area situated between the areas exhibiting a contamination of about 30 ng TE/kg (see fig. 2) showed a contamination of only 4 ng TE/kg, which corresponded to the general trend since 1987.

The unique, exceptionally high level of grass contamination is probably due to an abnormal situation in the copper reclamation plant, but conclusive explanations could never be provided.

In spring 1993 after the highly contaminated grass had been fed, cow's milk from another five farms whose grazing areas are influenced by the copper plant were investigated. The values obtained lay between 1.0 and 2.1 ng TE/kg fat, i.e. within the normal range. Therefore it can be concluded that in the case at hand measured grass contaminations had no long–term effects. Probably airborne PCDD/PCDF contamination is strongly influenced by the weather (wash–off by the rain).

Follow–up investigations of grass carried out in August 1992 and May 1993 at the control farm yielded values of 2.9 and 1.6 ng TE/kg, respectively. The latter value corresponds to the values which are usually obtained when the influence of airborne PCDD/PCDFs lies within the normal range.

RISK

Regulations for cow's milk and fodder for dairy cattle

In 1988, on account of the Brixlegg case, the Federal Ministry for Health set the maximum PCDD/PCDF concentration in cow's milk at about 35 ng TE/kg fat. The Federal Environmental Agency has recommended, however, to use the Dutch limit values (6 ng TE/kg fat) for cow's milk. In Germany a similar value of 5 ng TE/kg milk fat is being recommended.

For the dairy cows' fodder the Federal Environmental Agency recommended a maximum value of 3 ng TE/kg dry weight. This value was derived from the results given in fig.1 and was assumed to guarantee that a value of 6 ng/kg TE is not exceeded in cow's milk.

Conclusions

- Copper reclamation can be an important source of PCDD/PCDF emissions.
- Grassland farming is particularly sensitive to PCDD/PCDF contamination.
- In the case at hand airborne PCDD/PCDF do exert a greater influence on fodder contamination than the impact of the soil and the contaminated environs.
- Single emission measurements carried out at defined sources and at set times do not necessarily represent the total amount of emissions.
- Diffuse sources (like f.e. the exhaust air from plant buildings, raised dust from the plant premises or technical irregularities within the plant) may have a strong influence on ambient air concentrations.
- Therefore an extensive, permanent control monitoring would be necessary for plants with a high PCDD/PCDF emission potential.
- Threshold values especially for milk and fodder are important as they provide the basis for administrative measures to be taken in cases of contamination.

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