A chain model for dioxins: from emission to cow's milk

Slob, W., Van Jaarsveld, J.A.
National Institute of Public Health and Environmental Protection (RIVM), P.O.Box 1, 3720 BA Bilthoven, The Netherlands

In 1989 elevated levels of dioxins were found in Dutch cow's milk originating from areas near municipal solid waste (MSW) incinerators[1]. These levels exceeded in some cases the Dutch milk standard of 6 pg (i)-TEQ/g milk fat, a value that was founded in an exposure analysis for the Dutch population[2]. These findings triggered an extensive research programme in the Netherlands, including emission measurements at all Dutch MSW incinerators, analyses of soil samples and analyses of a large number of milk samples from several areas surrounding an MSW incinerator[3]. At the same time a mathematical chain model giving a quantitative relation between these measurements was developed[4]. The calibration and validation of this model will be discussed.

Model description

The chain model consists of an atmospheric model (OPS model[5,6]), a pasture model and a toxicokinetic (PBPK) model of the cow. The OPS model is a universal model for atmospheric transport and deposition of material (gases or particles). When source characteristics and weather conditions are specified, the model predicts both dry and wet deposition at a particular location for a given time period. Deposition calculations were carried out separately for the local and for the background sources (all others including foreign ones) for both short and long-term weather conditions.

The pasture model calculates the dioxin concentration in soil at a given location from long-term deposition (i.e. based on average weather conditions), as predicted by the OPS model. Short-term deposition (i.e. based on the actual weather conditions), both dry and wet, is used to calculate the amount of dioxins on grass. These amounts are assumed to be dependent on the amount of rain in the relevant period due to wash-off.

The dioxin intake by the cow from soil and grass consumption serves as the input for the toxicokinetic model to predict the concentration in milk. An extensive description of the chain model is given elsewhere[4].

Uncertain model parameters

The OPS model has been validated on a regional scale (SO_2, NO_x, Pb measurements)[5], and, to some extent, for long-range transport[6]. Its validity for predicting deposition of dioxins on a local scale was supported by dioxin measurements in soil[1]. We therefore assumed all parameters of the OPS model to be accurate.

The pasture model contains two parameters for which no quantitative information exists. They both relate to the amount of deposited dioxins that are washed-off from the grass by rain. The pasture model assumes that, in a given month, the fraction of dry deposition remaining on the grass equals $\exp(-\theta_d\ mm)$ and, similarly, for wet deposition $\exp(-\theta_w\ mm)$, where *mm* denotes the amount of rain in the relevant month. Since no measurements exist to determine θ_d and θ_w, these parameters have to be estimated by calibrating the concentrations predicted by the chain model to the measured concentrations in milk. The other parameters of the pasture model, which could be quantified from existing data, were considered beyond dispute.

The parameters of the toxicokinetic model were obtained from several kinetic studies in cows[7]. In a toxicokinetic study in which two cows received a single dose of contaminated fly ashes by gavage, the bioavailability of dioxins in fly ashes was found to be approximately 1%[8]. However, the applicability of this value to field conditions is uncertain. The other parameters of the toxicokinetic model were considered to be accurate.

Model calibration

Since both wash-off parameters are unknown, they have to be estimated by calibration of the model. To that end we selected a set of 69 analysed milk samples originating from four different areas close to an MSW incinerator, at several periods of time in 1989 and 1990. Two of the four relevant incinerators were closed down in April 1990. All milk samples constitute bulk samples over a one-month period. Apart from minimising the deviations between predicted and measured milk levels, two other criteria were considered to be relevant for calibration of the model, viz.:

(1) there should be no systematic relation between model residuals and sampling period;

(2) where the incinerators were closed down, predicted concentrations in milk minus the short-term contribution from the local source should agree with concentrations in local milk as measured some time after closure of the incinerator.

As a first step, model predictions of the chain model were compared to measured concentrations in milk, by setting both wash-off parameters equal to zero (i.e. no wash-off). This resulted in an overall underestimation of the measurements. In addition, both criteria (1) and (2) were not satisfied. Since bioavailability is considered to be an uncertain parameter as well, this parameter was estimated along with the wash-off parameters by calibrating the model to the measurements. This resulted in a satisfactory agreement between predicted and measured milk levels (average deviation 20%; see Fig. 1) at an estimated bioavailability of 4.5%. Since bioavailability is strongly correlated with the two wash-off parameters, calibration of the model with bioavailability fixed at other values also results in reasonable fits. However, the value of approximately 4%, that resulted from calibration, was optimal with respect to criteria (1) and (2) as well.

Model validation

The calibrated model was used to predict another set of analysed milk samples relating to other areas or to other periods. The five milk samples from Alkmaar, all taken in October 1989, were consistently underestimated by the model. It might be that the emission of the relevant incinerator was at that time lower than in the period the emission was measured (March 1990). For the other samples, agreement between predicted and

measured values was good (see Fig. 2).

The chain model quite accurately describes the spatial variation in dioxin concentrations in cow's milk. This can be seen most clearly from the 1990 data originating from the area near AVR (the largest installation in the Netherlands), which have a wide range because of the divergent locations that were sampled (see Fig. 1).

It was found that model predictions followed temporal variation as well, though somewhat less accurate that spatial variation. This is probably due to the fact that emissions fluctuate with time. Since the emission measurements were done on three consecutive days at each incinerator, no information is available on the magnitude of such fluctuations. With respect to mechanisms underlying emission fluctuations, knowledge is still largely speculative.

Although the model contains three correlated parameters that were estimated by calibration, the validation study showed that the model has predictive power for new data. Presently, a field study will be carried out to assess the bioavailability of dioxins in cows under field conditions and to estimate both wash-off parameters. This should reveal if the values of these parameters as obtained by calibration, are realistic.

Model applications

The chain model served several purposes. First, the relative contribution of local incinerators to dioxin concentrations in cow's milk could be quantified. Second, the model could be used as a guideline in choosing suspect locations for sampling cow's milk, which is particularly useful in view of the high costs of the chemical analysis of dioxins. Third, the scarce measurements could be completed to give a more comprehensive (spatial and temporal) picture. And fourth, effects of proposed measures could be evaluated. For example, decision makers were dissuaded from the idea of soil clean-up in a particular area as the model showed that this would not reduce the dioxin levels in milk sufficiently to comply with the milk standard. Evaluating the effect of emission reduction would be another example. Thus, it was shown that an emission of 0.1 ng/m^3 flue gas, which all MSW incinerators in the Netherlands must satisfy after 30 november 1993, would make a negligible contribution to the dioxin level in local cow's milk.

References

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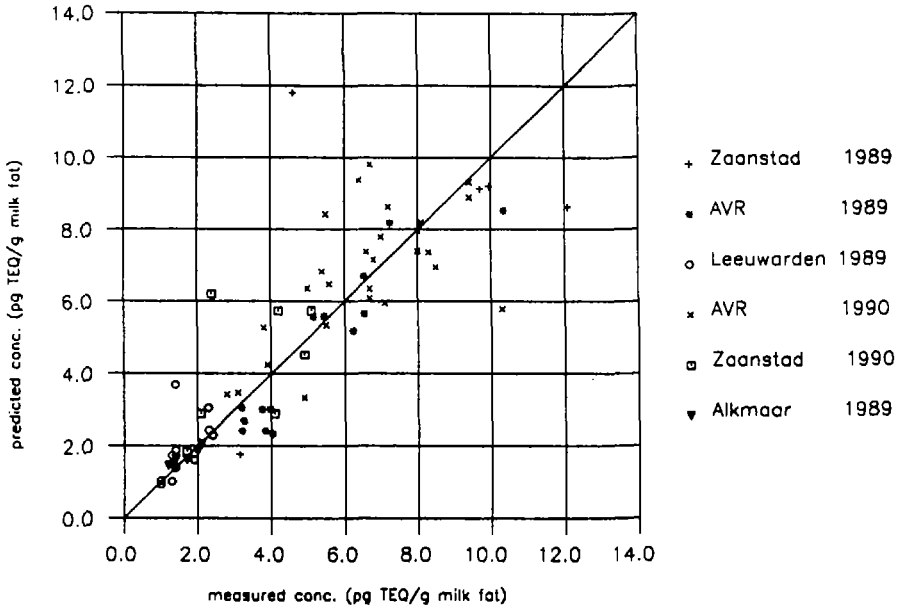

Fig. 1. Predicted and measured dioxin concentrations in monthly bulk samples of cow's milk after calibrating the model to the measurements. Milk samples originate from several areas and periods.

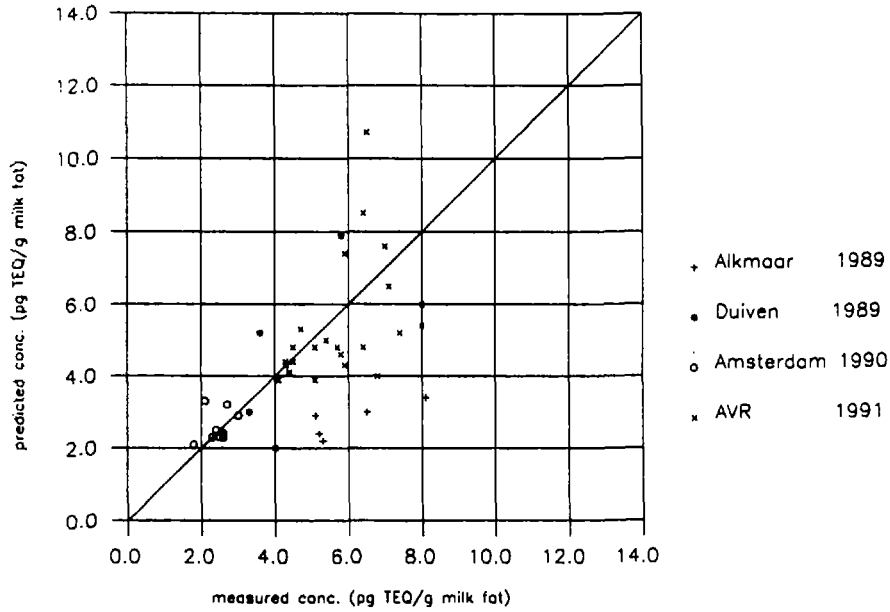

Fig. 2. Predictions of the calibrated chain model for a new set of data. Monthly bulk samples from several sites and periods.