CONCENTRATIONS OF PCDDs AND PCDFs IN COW'S MILK COLLECTED FROM FARMS NEAR MUNICIPAL INCINERATORS IN NEW YORK STATE

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Introduction

Before use of modern emission control systems a significant atmospheric source of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDDs/Fs) was incineration of municipal waste. Studies conducted in Europe have shown that PCDD/F concentrations can be elevated in cow's milk samples from farms near municipal incinerators[1]. In the USA, the potential for municipal incinerator emissions to impact PCDD/F concentrations in cow's milk has been evaluated by collecting milk samples before and after startup of incinerators located near farms in Connecticut and Vermont[2,3]. In each study, no significant differences were found between the PCDD/F concentrations in pre- and post-operational samples. However, the Connecticut incinerator was a state-of-the art facility from which any PCDD/F emissions probably contributed minimally to the ambient PCDD/F depositional flux. In the Vermont study, farms may not have been optimally located relative to the predominant wind direction. In the current study, one group of cow's milk samples (study samples) was collected in 1991 from farms within a range of 3.2 to 15 km of four municipal solid waste incinerators (MSWIs) in upstate New York and another group from farms within a range of 26 to 56 km from the MSWIs (control samples). The control farms were located in areas where there was no identifiable industrial activity. Statistical comparisons were made between mean PCDD/F concentrations in milk samples from control farms and study farms and, using measured PCDD/F emissions data from stack tests, relationships between modeled deposition rates and PCDD/F milk concentrations were determined by linear regression. Finally, measured PCDD/F cow's milk concentrations were compared to PCDD/F milk concentrations predicted using exposure modeling. A comprehensive description of this study, that also evaluated other chemicals in other media, is in a NYS DOH report[4].

Experimental Methods

MSWIs: The largest of the four incinerators (Incinerator A) could burn 2400 tons of shredded waste per day; several other combustion sources were in the surrounding area including chemical manufacturing plants and a hazardous waste incinerator. The other three incinerators had lower capacities. The smallest (Incinerator D) had a capacity of 120 tons/day. The other two plants, Incinerators B and C, had waste capacities of 200 tons/day. While these three incinerators were in smaller population areas than Incinerator A, industrial facilities with combustion emissions were within 5 km of each plant. All incinerators were designed for energy recovery and, except for Incinerator D which had no air pollution controls, they were equipped with electrostatic precipitators. MSWIs B and D are no longer operating and the other two MSWIs have been upgraded with advanced air pollution control equipment.

Sampling and Analytical Methods: Cow's milk samples were collected from bulk tanks at each farm and refrigerated at 4°C for transportation to the laboratory where they were stored at 20°C prior to analysis. The proteins in a 400 ml volume of milk were denatured with H_2SO_4 and then the lipid was extracted with iso-octane. A fraction representing 2% of the extracts was set aside for lipid analysis and the remaining extract was mixed with an equal volume of CH_2CL_2 prior to cleanup. Additional details on cleanup and extraction are described elsewhere[5]. The gas chromatography (GC)/ high resolution mass spectrometry (MS) system used to analyze sample extracts for PCDDs and PCDFs was a Hewlett-Packard 5890A GC with a 50 m x 0.25 mm i.d. DB5 (J & W Scientific, Palo Alta, CA) fused silica capillary column interfaced directly to the ion source of a FISONS/VG AUTOSPEC Q MS, operated at 10,000 resolution.

Data Analysis: Using the t-test, three comparisons were made between mean study and control milk concentrations for each congener/congener group: (1) mean for all study farms vs. mean for all control farms (2) mean for study farms near a single incinerator vs. mean for all control farms and (3) mean for study farms near a single incinerator vs. mean for control farms near a single incinerator. Where the combined number of study and control samples was less than ten, the Mann-Whitney rank order test was used.

Modeling Analysis: Dispersion modeling used the COMPDEP (Version 93340) model. Deposition rates were calculated using a unit emission rate. Congener-specific deposition rates were estimated by multiplying the unit deposition rates by the number of stacks at each facility and by measured stack emission rates. PCDD/F concentrations in cow's milk were predicted using a model developed by NYSDOH[6]. The International Toxic Equivalency Factors were used to express the total PCDD/F concentrations in terms of 2378–TCDD equivalents (TEQs)[7].

Results and Discussion

Milk samples were collected from 28 farms (15 study farms and 13 control farms). There was one non-2378–substituted HpCDF congener that in some of the milk samples constituted 50% of the total HpCDF concentration. This was the only major non-2378–substituted congener found in any of the milk samples and therefore this presentation is restricted to consideration of results for 2378–substituted congeners. Since signals for several analytes were close to their limits of detection (LODs), rigorous quality control was undertaken by analyzing twelve laboratory method blanks and seven milk samples in duplicate. The range of the background signals for OCDD and OCDF (1.4-6.8 and 0.2-1.2 pg/g fat respectively, based on a 400 ml milk sample) suggested that background contamination could have made a significant contribution to the milk samples (2.4–58 pg/g fat for OCDD and 0.4–6.1 pg/g fat for OCDF). Therefore, OCDD and OCDF were eliminated from the statistical comparisons. In the case of the other 2378-substituted PCDDs/Fs, the LODs were in the range 0.01-0.1 pg/g fat and, with the exception of 2378-TCDF, a maximum of two samples had background signals which in every case were close to the LOD. However, 9 of the 12 method blanks had 2378-TCDF signals in the range of 0.02–0.05 pg/g fat with a mean value of 0.03 pg/g fat. Since the mean values of 2378–TCDF in the study and control milk samples were only 0.06 and 0.05 pg/g fat respectively, results for this analyte were also excluded from the calculations. Finally, results for 12378–PeCDF, 123789–HxCDF and 1234789–HpCDF were eliminated from consideration, as these analytes were not detected in the majority of the milk samples. For the eleven remaining 2378–substituted PCDDs/Fs there were several comparisons

where mean concentrations in study samples were statistically ($p<0.05$) higher than mean concentrations in control samples. Data from these comparisons are shown in Table 1.

Table 1. Statistically Significant Differences in Mean PCDD/F Concentrations in Cow's Milk (pg/g milk fat)

Comparison Groups			Study Farms	Control Farms
Study (n)	Control (n)	Analyte	Mean ± SD	Mean ± SD
All (15)	All (13)	2378 - TCDD	0.09 ± 0.06	0.04 ± 0.02
		23478 - PeCDF	0.46 ± 0.30	0.25 ± 0.13
B (4)	B (3)	2378 - TCDD	0.13 ± 0.06	0.04 ± 0.0009
		23478 - PeCDF	0.63 ± 0.15	0.25 ± 0.04
		12378 - PeCDD	0.58 ± 0.19	0.19 ± 0.08
		123478 - HxCDF	0.35 ± 0.04	0.16 ± 0.08
		234678 - HxCDF	0.36 ± 0.11	0.12 ± 0.07
		EPA TEQ	1.1 ± 0.19	0.45 ± 0.18
B (4)	All (13)	2378 - TCDD	0.13 ± 0.06	0.04 ± 0.02
		23478 - PeCDF	0.63 ± 0.15	0.25 ± 0.13
		12378 - PeCDD	0.58 ± 0.19	0.28 ± 0.44
		123478 - HxCDF	0.35 ± 0.04	0.28 ± 0.42
		123678 - HxCDF	0.35 ± 0.06	0.26 ± 0.38
		234678 - HxCDF	0.36 ± 0.11	0.16 ± 0.19
		EPA TEQ	1.1 ± 0.19	0.73 ± 1.0
A (3)	All (13)	2378 - TCDD	0.13 ± 0.06	0.04 ± 0.02
		23478 - PeCDF	0.80 ± 0.44	0.25 ± 0.13
		123678 - HxCDF	0.46 ± 0.21	0.26 ± 0.38
		234678 - HxCDF	0.40 ± 0.14	0.16 ± 0.19
C (2)	All (13)	2378 - TCDD	0.06 ± 0.007	0.04 ± 0.02

As shown in Table 1, MSWI B was the only facility for which mean concentrations of certain congeners from study samples were significantly greater than control samples for that incinerator and all control samples. MSWI B also was the facility for which there was the greatest number of congeners with significant differences between study and control farm milk samples. Concentrations of certain congeners from the A and C study samples were significantly greater than concentrations of the corresponding congeners in all control samples (four congeners for A and one congener for C) but not significantly different from their own control samples. There were no significant differences in PCDD/F concentrations for study samples compared to any control samples for MSWI D. However, one control milk sample from MSWI D had the highest PCDD/F concentrations found in the entire study (TEQ concentration of 4.1 pg/g milk fat). No obvious source of PCDDs/Fs was identified for this farm. Statistical tests repeated without this farm in the data set did not change the results. These analyses suggest that MSWIs A and B may have an association with concentrations of certain congeners in milk samples from study farms, while such

an association was not apparent for MSWIs C and D. This may be explained by the fact that the A and B study farms were located in the predominant downwind direction from their local incinerators while the C and D study farms were not. Also, MSWI A had the largest capacity of any of the MSWIs studied and the B study farms were the closest of all study farms to an incinerator.

In the modeling analysis, linear regression was used to test the hypothesis that there was a relationship between modeled PCDD/F deposition rates and measured PCDD/F concentrations in milk. The results of these analyses showed that variations in milk concentrations were significantly correlated with the variations in modeled deposition rates for five congeners for MSWI A (23478-PeCDF, 123478-HxCDF, 123678-HxCDF, 234678-HxCDF, and 123478-HxCDD); five for MSWI B (2378-TCDD, 23478-PeCDF, 123678-HxCDF, 234678-HxCDF, and 123478-HxCDD); one for MSWI C (2378-TCDD); and none for MSWI D. These results are generally consistent with the results of the previously described statistical analyses (Table 1). For the congeners for which modeled deposition rate and measured milk concentration correlated significantly, exposure modeling was used to predict congener concentrations in milk. The results of the exposure model (which assumes a linear relationship between milk concentration and deposition rate) were plotted, as were the lines of best fit for the regression analyses. When the slopes of these lines were compared using the t-test, no significant differences were found for two congeners each for MSWIs A and B, indicating that while the model is not a reliable quantitative predictor, it may provide order-of-magnitude estimates for farms with the greatest likelihood of impact.

The results of this study suggest, but do not prove, that emissions from some of the incinerators may have contributed to the presence of certain PCDD/F congeners in milk from some farms. However, the mean EPA TEQs from all the study samples (0.8 pg/g milk fat) and controls (0.73 pg/g milk fat) were at the lower end of the range of TEQs reported in the literature for milk (0.52 to 6.7 pg/g milk fat)[4]. Other chemicals in other media did not show consistent differences between study and control farms [4].

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