Nondetects and Their Use in the Determination of Toxic Equivalences (TEQs) for Livers of the Moose (Alces alces) from the Indian Township Zone, Maine USA

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Introduction

In the analysis of environmental samples collected from rural or isolated areas, the concentrations of persistent organic pollutants are often at or below the analytical method detection limit (DL). These concentrations are labeled as "non-detects". Long considered "censored data", these nondetects have complicated the computations of descriptive statistics, assessing differences among data groups, and the computation of regression models. The most common procedure for the treatment of this type of data is substitution. The common substitution value is ½ of the DL for the non-detects, although a maximum value could be assign at the DL and a minimum at zero.[1,2] However, statisticians are applying survival analysis to this type of data to reduce bias and improve accuracy and precision. These analyses include parametric methods based on maximum likelihood estimation (MLE) and non-parametric analyses based on Kapaln-Meier and related methods.[3,4]

Recently, the concentrations of dioxin-like compounds present in moose liver samples have been determined for twenty-one samples collected from zones in the Tribal traditional hunting grounds and shipped to the EPA Environmental Chemistry Laboratory, Stennis Space Center, Mississippi. The samples were selected for analyzed for the presence of the seventeen 2,3,7,8-Cl substituted polychlorinated dibenzo-*p*-dioxins, -furans and selected co-planar PCBs (77, 105, 118, 126, 156, 157, 169).[5]

The results from one of the three zones of the study were examined by the standard substitution procedure and survival analysis methods to determine the differences in the TEQ when applying the various techniques.

Materials and Methods

The liver samples were collected from adult moose (*Alcesalces*) from kills made on Tribal lands from September to November, 1999 from three geographically distinct Tribal areas: the Western Zone, the Mid-State Zone and the Indian Township Zone. The Appalachian Mountain Range and the Kennebec River were the boundaries for the purpose of this study. Of the three areas the data from the Indian Township Zone were examined. The results consisted of the mean lipid adjusted concentrations for each congener of the seven samples and the summary toxic equivalent (TEQ) concentrations for the PCBs and the PCDD/PCDFs and the overall summary TEQ concentration (PCBs+PCDD/PCDFs). The TEQs were determined from WHO 1998 toxic equivalent factors (TEFs).

Of the 168 individual congener concentrations measured in the seven samples, 47 were determined to be nondetects. In the case of substitution, the individual congener non-detects were replaced by zero, ½ of the detection limit, and the detection limit for each individual congener. The means of the individual congener concentrations were then determined together with the summary TEQs for PCBs and PCDD/PCDFs and the overall total.

In the case of the survival analysis, the methods for the estimation of summary statistics are the maximum likelihood estimate (MLE), and the regression on order statistics (ROS), and the non-parametric Kaplan-Meier (K-M) method. It is recommended that when the number of observations is less than 50 and the percent of censored data ranges from 50% – 80% that a robust maximum likelihood estimate (MLE) be applied. When the number of observations is less than 50 and the percent of censored data is greater than 80%, it is recommended that the value not be reported as the estimate is highly unreliable.[4] Given there qualifiers, the maximum likelihood estimate method was employed. Again the means of the individual congener concentrations were then determined together with the summary TEQs for PCBs and PCDD/PCDFs and the overall total.

Results and Discussion

The results from the analyses of the seven moose liver samples from the Indian Township Zone are presented in Table 1. With the use of the standard method of substitution, there are substantial differences among some of the individual congener concentrations calculated. Each of the substitution techniques is arguably as valid as the other and is used by different investigators depending on the intended use of the results (risk assessment, exposure evaluation, etc.). Hence, the summary statistics (standard deviation and variance) following substitution would be indeterminate estimates of their true values.

In the use of the standard analysis of substitution, the overall total mean TEQ for ½ DL [12.4 pg/g] is bounded by the overall total mean TEQ for zero [11.617 pg/g], the lower bound, and the overall total mean TEQ for DL [13.157 pg/g], the upper bound of the range for the zone. The percent difference between 0 and ½ DL and ½ DL and DL are 1.6% and 1.5%, respectively, and the percent difference between zero and DL is 3.1%. The differences among the various substitution values are minimal. However, this would not be unexpected with data from isolated, background areas.

In the use of survival statistics analysis, specifically the maximum likelihood estimate (MLE) technique chosen for this case, the overall total mean TEQ for MLE [11.705 pg/g] fell within the upper and lower bounds of the substitution TEQs. The value represents a better approximation of the true TEQ value. Based on a lognormal distribution, which is frequently encountered in environmental data, MLE solves a likelihood equation to determine the mean and standard deviation that provided the observed data, for both nondetects and detected values.

Although the results for both methods of analyses are comparable in this case, often results can be extremely different, depending on which method of substitution is used. This can cause divergent summary toxic equivalent (TEQs) values, changing risk assessments and altering environmental decisions. The underlying basis for estimation of the true value for environmental analyses favors the increasing use of survival analysis.

Acknowledgements
We thank John Warren, EPA/QAS for his comments on the paper.

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Table 1. Analysis of Moose Livers (pg/g, lipid adjusted) and (pg/g, TEQ)

Location	**Indian Township Zone**	**Indian Township Zone**	**Indian Township Zone**	**Indian Township Zone**
Classification	**Sub**	**Sub**	**Sub**	**MLE**
ND Value	**0**	**½ DL**	**DL**	**Estimate**
Concentration	**pg/g**	**pg/g**	**pg/g**	**pg/g**
PCBs:				
PCB 77	12.826	12.826	12.826	12.826
PCB 118	893.015	893.015	893.015	893.015
PCB 105	423.403	423.403	423.403	423.403
PCB 126	65.553	65.553	65.553	65.553
PCB 156	59.592	59.592	59.592	59.592
PCB 157	20.687	20.687	20.687	20.687
PCB 169	**1.226**	**1.359**	**1.394**	**1.320**
PCB TEQ SUM	6.742	6.742	6.742	6.742
PCDDs/PCDFs:				
2,3,7,8-TCDF	**0.808**	**0.873**	**0.938**	**0.869**
1,2,3,7,8-PeCDF	**0.082**	**0.520**	**0.958**	**n/a**
2,3,4,7,8-PeCDF	5.359	5.359	5.359	5.359
1,2,3,4,7,8-HxCDF	2.525	2.525	2.525	2.525
1,2,3,6,7,8-HxCDF	2.512	2.512	2.512	2.512
2,3,4,6,7,8-HxCDF	4.037	4.037	4.037	4.037
1,2,3,7,8,9-HxCDF	**0.008**	**0.533**	**1.059**	**n/a**
1,2,3,4,6,7,8-HpCDF	2.452	2.452	2.452	2.452
1,2,3,4,7,8,9-HpCDF	**0.313**	**1.067**	**1.822**	**0.785**
OCDF	**1.636**	**2.170**	**2.704**	**2.090**
2,3,7,8-TCDD	**0.121**	**0.313**	**0.505**	**0.299**
1,2,3,7,8-PeCDD	**0.711**	**1.079**	**1.447**	**0.948**
1,2,3,4,7,8-HxCDD	**1.054**	**1.422**	**1.790**	**1.260**
1,2,3,6,7,8-HxCDD	**0.772**	**1.140**	**1.508**	**1.022**
1,2,3,7,8,9-HxCDD	**0.660**	**1.257**	**1.594**	**0.852**
1,2,3,4,6,7,8-HpCDD	9.442	9.442	9.442	9.442
OCDD	14.513	14.513	14.513	14.513
PCDD/F TEQ	4.877	5.658	6.414	5.363
TOTAL TEQ	11.617	12.400	13.157	11.705

Note: Bold indicates the presence of nondetects.