Modeling the Effects and Uncertainties of Contaminated Sediment Remediation Scenarios in a Norwegian Fjord by Markov Chain Monte Carlo Simulation

ARTICLE *in* ENVIRONMENTAL SCIENCE AND TECHNOLOGY · FEBRUARY 2008

Impact Factor: 5.33 · DOI: 10.1021/es070622l · Source: PubMed

Modeling the Effects and Uncertainties of Contaminated Sediment Remediation Scenarios in a Norwegian Fjord by Markov Chain Monte Carlo Simulation

TUOMO M. SALORANTA,*,† JAMES M. ARMITAGE,‡ HEIKKI HAARIO,§ KRISTOFFER NÆS,† IAN T. COUSINS,‡ AND DAVID N. BARTON†

Norwegian Institute for Water Research (NIVA) Gaustadalléen 21, N-0349 Oslo, Norway, Department of Applied Environmental Science (ITM), Stockholm University, SE-10691 Stockholm, Sweden, and Lappeenranta University of Technology, P.O. Box 20, FIN-53851 Lappeenranta, Finland

Received March 13, 2007. Revised manuscript received September 27, 2007. Accepted October 15, 2007.

Multimedia environmental fate models are useful tools to investigate the long-term impacts of remediation measures designed to alleviate potential ecological and human health concerns in contaminated areas. Estimating and communicating the uncertainties associated with the model simulations is a critical task for demonstrating the transparency and reliability of the results. The Extended Fourier Amplitude Sensitivity Test (Extended FAST) method for sensitivity analysis and Bayesian Markov chain Monte Carlo (MCMC) method for uncertainty analysis and model calibration have several advantages over methods typically applied for multimedia environmental fate models. Most importantly, the simulation results and their uncertainties can be anchored to the available observations and their uncertainties. We apply these techniques for simulating the historical fate of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) in the Grenland fjords, Norway, and for predicting the effects of different contaminated sediment remediation (capping) scenarios on the future levels of PCDD/Fs in cod and crab therein. The remediation scenario simulations show that a significant remediation effect can first be seen when significant portions of the contaminated sediment areas are cleaned up, and that increase in capping area leads to both earlier achievement of good fjord status and narrower uncertainty in the predicted timing for this.

1. Introduction

Numerous aquatic systems are contaminated with persistent organic pollutants (POPs) due to historic and present emissions from industry and other sources. At some of these sites remediation measures are planned aiming to reduce the impact and exposure of this pollution to the biota living in these waters. Models can be very valuable tools in helping the planning of such remediation measures as they enable the water managers and other stakeholders to holistically investigate the problems and seek potential solutions and remediation alternatives. Moreover, as models can synthesize scientific knowledge about the fjord or lake system, their use in environmental management planning can contribute to founding the management on a more scientific basis. One prominent example of the current initiative to address contamination issues in Norway is the effort to develop remediation plans for the Grenland fjords. The Grenland fjords (Figure 1) have some of the highest concentrations of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) in sediments of any Norwegian fjord. The main load of PCDD/Fs has come from a magnesium plant on Herøya in the Frierfjorden during the period 1951–2002. Since the 1960s dietary health advisories have been in place (first due to Hg-pollution), and since the 1980s commercialization bans on all seafood caught within the Frierfjorden area, as well as health advisories on selected commercial species such as cod and crab in the outer Grenland fjord areas have been in effect. Contaminated sediments currently constitute the only known significant source of PCDD/Fs causing high concentration levels in the biota of the Grenland fjords.

Here, we present an integrated modeling tool called the SF-tool (*1*), which is suitable for simulating the fate of POPs in aquatic systems. With this tool we simulate the effects of different contaminated sediment remediation scenarios on the future levels of PCDD/Fs in cod and crab in the Grenland fjords. These remediation scenarios consist of capping the contaminated fjord bottom with clean masses. The SF-tool also enables uncertainty and sensitivity analysis of the model results. In our current simulations, we apply the Extended Fourier Amplitude Sensitivity Test (Extended FAST) method for sensitivity analysis, and a Bayesian Markov chain Monte Carlo (MCMC) method for combined uncertainty analysis and model calibration. These methods have several advantages over methods typically applied for multimedia environmental fate models (*2, 3*). For example, the Extended FAST method reveals both the parameter's main effect on the model output and the sum of the effects due to its higher-order interactions with other parameters. More importantly, the MCMC method for uncertainty analysis can address some of the limitations inherent to basic Monte Carlo simulation (*4*), which rely on user-defined probability distributions for model input parameters. Because proper estimation of the correct distributions and the covariation of the model parameters is often difficult to determine due to limited data, inconsistencies in these estimates may easily lead to poor fit between the model results and observations when particular parameter combinations are sampled during the Monte Carlo simulation. As a result, the confidence bands in model predictions may be substantially overestimated giving a false impression of the reliability of model outcome (*5, 6*). However, in the MCMC method, input parameter distributions are updated during the procedure based on a comparison between the model results and observations. Consequently, improbable parameter combinations are disregarded as only the joint probability distribution of all the analyzed parameters which optimally fits the corresponding model results to the observations are considered in the final uncertainty analysis. Hence both model calibration and a proper uncertainty analysis can be gained from the same MCMC simulation and also the so-called parameter unidentifiability (or equifinality) problem (*7*), often met in manual model calibration, will be resolved.

* Corresponding author e-mail: tuomo.saloranta@niva.no.
† Norwegian Institute for Water Research (NIVA).
‡ Stockholm University.
§ Lappeenranta University of Technology.

10.1021/es070622l CCC: $40.75

Published on Web 11/20/2007

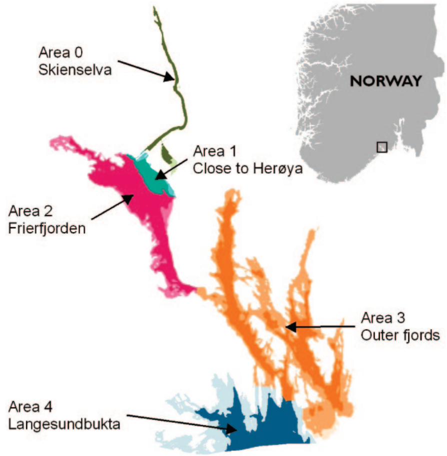

FIGURE 1. A bathymetric map showing the basis for horizontal compartment division in the model application for the Grenland fjords. The different colors show the horizontal division to five compartments, while the shading within a color indicates the different bottom depth intervals used in the vertical compartment division.

2. Materials and Methods

The main purpose of this modeling exercise was to simulate the long-term environmental fate of PCDD/Fs in the Grenland fjords following remediation of contaminated sediments and the subsequent impact on PCDD/F concentrations in biota. Simulations were also conducted using historical PCDD/F emission estimates and observed concentrations to calibrate the model and to estimate the prediction uncertainties with the MCMC method, as well as to evaluate the performance of the model. Model simulations were conducted iteratively to capitalize on the information gained first from the sensitivity analysis and then from the MCMC method. Throughout the paper we distinguish the terms “model (application)” and “model code” as in Refsgaard and Henriksen (*8*).

2.1. Monitoring Data. Time series of observed concentrations of PCDD/Fs ($C_{\mathrm{PCDD/F}}$) in water and sediment (particulate, organic carbon normalized data), as well as of $C_{\mathrm{PCDD/F}}$ in cod liver and crab hepatopancreas from different parts of Frierfjorden were compiled. This concentration data consisted of 15 water samples, 44 sediment samples, 43 individual or pooled cod liver samples, and 13 pooled crab hepatopancreas samples. In addition, four pooled cod liver samples from the open sea (Skagerrak) were included to represent the background $C_{\mathrm{PCDD/F}}$ in cod liver at an unpolluted site. These data originated from previous research projects and from long-term monitoring programmes (*9–11*). The concentrations in individual cod liver and crab hepatopancreas as well as in water and sediment samples were assumed to be log-normally distributed, as expressed in the likelihood function used in the MCMC simulation (see Supporting Information). In the MCMC simulation our model is calibrated against the yearly averages (medians) of these observations (Figure 2). The variances of these log-normal distributions both for the abiotic and biotic data were estimated as part of the MCMC simulation.

2.2. The SF-Tool. The SF-tool modeling package applied in our study consists of (i) a water−sediment fugacity model code (*12*) for simulating the sources, sinks and transports of POPs in a fjord, estuary or lake system, and (ii) a bioaccumulation rate constant model code (*13*) for simulating the intake and bioaccumulation of POPs in an aquatic food web. The modeled water column and sediment area, or food web are split into different compartments in the model, and these compartments make up the basic units (or resolution) in the model. Properties of these compartments, such as their size, concentration of various substances, interaction with other compartments, etc., make up most of the model parameters. The basic mass balance equation solved simultaneously for all compartments in the model code is

$$\frac{\mathrm{d}}{\mathrm{d}t}c(t) = Kc(t) + S(t) \qquad (1)$$

where $c(t)$ is a vector of $C_{\mathrm{PCDD/F}}$ in the model compartments at time t, $S(t)$ is a vector of PCDD/F sources (e.g., emissions) from outside into the model compartments at time t, and K is the specific process rate constant matrix. The biotic model code in the SF-tool is similar to that described in Saloranta et al. (*14*), while the abiotic code, of which application this paper mostly focuses on, is largely based on the model code formulation given in Persson et al. (*15*). The models can be executed both in dynamic and steady state modes and have been previously applied to several fjord systems in Norway (*1, 16, 17*). Both model codes are described in more details in Saloranta et al. (*1*). A model comparison exercise between our abiotic model and that of Persson et al. (*15*) with similar parametrization produced very similar results and thus increased our confidence on that our abiotic model code is correctly formulated.

2.3. Model Application. For the Grenland fjords model application, the fjords were divided horizontally to five areas (Figure 1) and vertically to 2–3 layers (surface, intermediate, deep) which resulted in a total of 13 water compartments. As each water compartment is associated with a sediment compartment, defined by the corresponding water−sediment interface area, the total number of model compartments was 26. All the model compartment areas and volumes were calculated by using digital bathymetric maps. The water flow matrix was adopted from Persson et al. (*15*) and adjusted according to the geometry of the model domain. In addition, the atmosphere over the Grenland fjords, as well as the upper river Skienselva and open sea at Skagerrak acted as a source and/or sink for the PCDD/Fs at the model boundaries. Data and nominal values for the abiotic model parameters and for the PCDD/F water background concentrations at model boundaries C_{bg} and emission rate time series E in 1951–2002 (see Supporting Information, Figure S1) were adopted primarily from Persson et al. (*15*). The nominal values of the fraction of resuspension rate R of the gross sedimentation rate, sediment organic carbon mineralization rate M, and the thickness of the active bioturbated sediment layer H (dry particles) were the same as in Persson et al. (*15*), except for H and M in the surface compartments where an order of magnitude smaller values were assumed due to the steepness and wave-exposure of these sediment areas, especially in the Frierfjorden. The nominal values of the sediment permanent burial rates B in Frierfjorden were assumed to be 650, 1500, and 1800 g dry sediment $\mathrm{m}^{-2}\,\mathrm{yr}^{-1}$ in the surface, intermediate and deep compartments of Area 1 and 2, respectively. These values were based on the observed range of 638–1942 g dry sediment $\mathrm{m}^{-2}\,\mathrm{yr}^{-2}$ from dated sediment cores (*15*). For other nominal model parameter values, see Saloranta et al. (*1*). Abiotic simulations were conducted from 1950–2100 and incorporated the historical emissions and the remediation scenarios to be discussed below.

2.4. Remediation Scenarios. Long-term simulations were conducted for a series of remediation scenarios, listed in Table 1, assumed to take place in 2010. Although the model application covers the whole Grenland fjord system, our main focus for the remediation scenarios is the innermost Frierfjorden basin, which is separated from the outer fjords by a shallow sill (24 m). In a previous investigation, Saloranta et al. (*1, 18*) concluded that capping of contaminated sediments in Frierfjorden will have no significant effect on the future evolution of the $C_{\mathrm{PCDD/F}}$ in sediment in the outer fjords (Areas

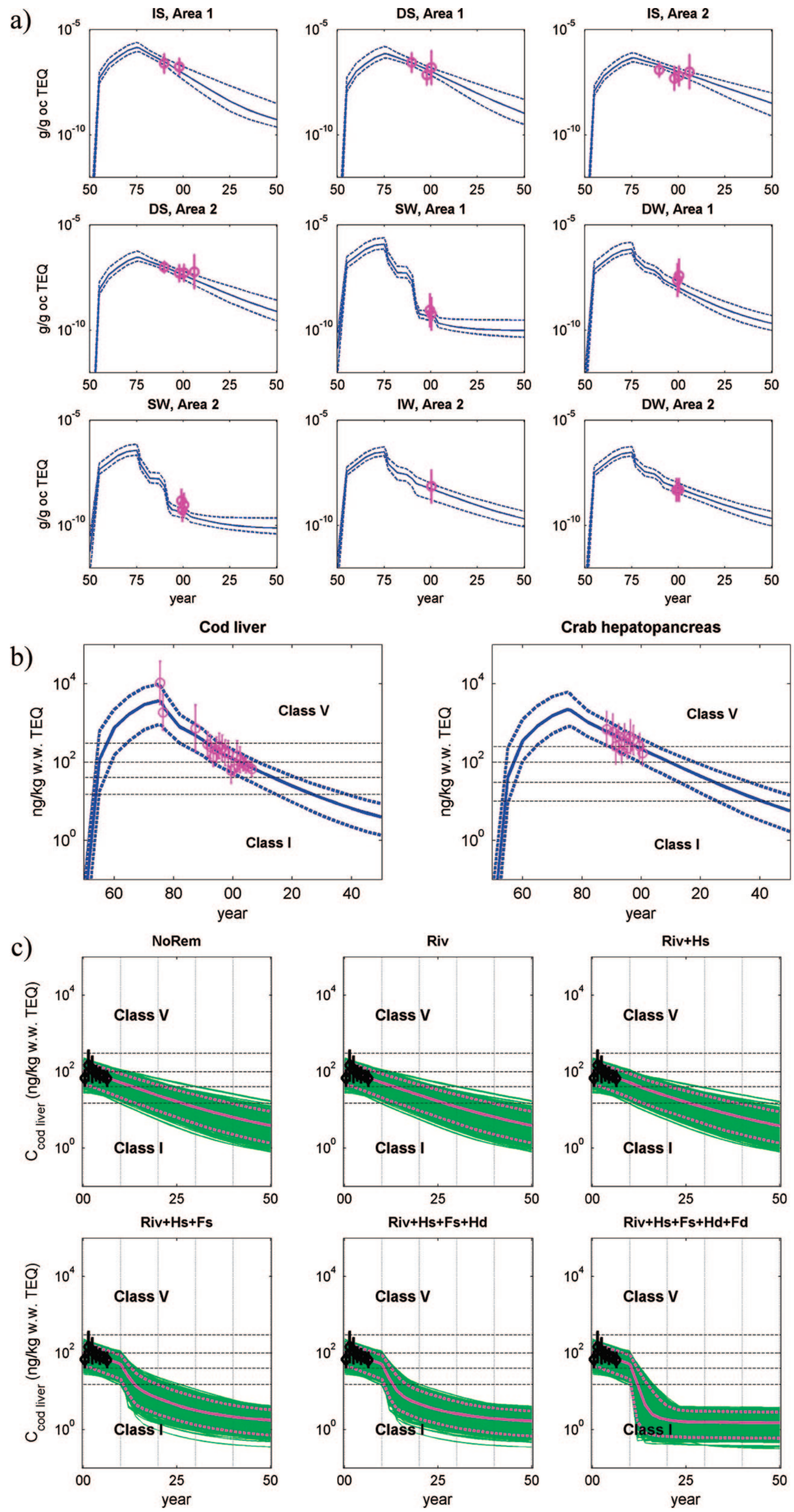

FIGURE 2. (a) Time evolution (1950–2050) of the median $C_{PCDD/F}$ in two intermediate (IS) and two deep sediment (DS) compartments as well as in two surface (SW), one intermediate (IW), and two deep water (DW) compartments in Frierfjorden (Areas 1 and 2; see Figure 1). (b) Time evolution (1950–2050) of the median $C_{PCDD/F}$ in cod liver and crab hepatopancreas in Frierfjorden. (c) Time evolution (2000–2050) of the median $C_{PCDD/F}$ in cod liver in Frierfjorden in six different remediation scenarios (see Table 1). The solid lines denote the median, and dashed lines the 2.5th and 97.5th percentiles of the 2000 model simulations (all shown by the green lines in (c)) run with parameter values resampled from the chain resulting from the MCMC simulation. Corresponding median yearly observations and their 95% confidence bands are shown (calculated using median values of σ_{abio} and σ_{bio}). In (a) the concentrations represent the sum of the three simulated PCDD/F congeners in toxicity equivalents (TEQ) and "oc" denotes organic carbon. In (b) and (c) the concentrations represent the sum of 17 PCDD/F congeners in toxicity equivalents, "w.w." denotes wet weight, and the horizontal dashed lines denote the limit values for the five Norwegian pollution status classes (I−V) defined for PCDD/F concentration in cod liver and crab hepatopancreas.

TABLE 1. Sediment Remediation (Capping) Scenarios in the SF-Tool Application for the Grenland Fjords. For Area Definition, See Figure 1

scenario name	description of (incremental) capping area	capped area (% of total area of Frierfjorden and Skienselva)
NoRem	none	0 km^2 (0%)
Riv	River Skienselva (Area 0)	2.8 km^2 (12%)
Riv+Hs	+ shallow areas (<24 m) close to Herøya (Area 1)	3.4 km^2 (14%)
Riv+Hs+Fs	+ shallow areas (<24 m) in Frierfjorden (Area 2)	8.9 km^2 (38%)
Riv+Hs+Fs+Hd	+ deep areas (>24 m) close to Herøya (Area 1)	11.2 km^2 (47%)
Riv+Hs+Fs+Hd+Fd	+ deep areas (>24 m) in Frierfjorden (Area 2)	23.8 km^2 (100%)

3 and 4 in Figure 1), or vice versa, owing to the slowness and ineffectiveness of the transport processes between the sediments of different fjord areas, especially since they are separated by a shallow sill. Furthermore, cod tracking studies (*19*) have indicated that a local cod population is confined to Frierfjorden. The remediation scenarios for this area simply represent incremental increases in the proportion of the total area of the Frierfjorden and River Skienselva (see Figure 1) subject to capping with clean material and range from no-action (i.e., 0% capped) to complete 100% capping of the contaminated sediments. Note that the capping material was assumed to have the same physical properties (e.g., organic carbon content) as the contaminated sediments themselves.

2.5. Modeling Bioaccumulation. To transfer the simulated abiotic $C_{PCDD/F}$ time series to $C_{PCDD/F}$ in cod and crab, we used a modified version of the methodology and model results described in Saloranta et al. (*14*). They simulated the intake and bioaccumulation of PCDD/Fs in the Frierfjorden food web consisting of 12 species or species groups with a similar model code as contained in the SF-tool. This abiotic-to-biotic transformation is based on the linearity of the steady state version of our biotic model ((*14*); i.e. $\mathrm{d}c(t)/\mathrm{d}t = 0$ in eq 2), which means that, e.g., a 20% reduction in the dissolved PCDD/F concentration in water C_w and sediment pore water C_{pw} (term S in eq 2) will eventually lead to a similar reduction in the simulated $C_{PCDD/F}$ of all the organisms in the food web (term c in eq 2). The time it takes for such reduction is dependent on the response time T_r of the organism to changes in its abiotic forcing (after N response times the system has covered $(1–1/e^N) \times 100\%$ of its way toward the new (quasi) steady state). This method gives us a rather robust modeling strategy for the biotic system, in which we use the biotic model only to calculate what fraction β of the $C_{PCDD/F}$ in the organisms is caused by C_{pw} when $C_{pw} = C_w$, and to estimate T_r for the organisms on the basis of the eigenvalues of the rate constant matrix and the model output (*14*). In addition, we use a bioaccumulation factor K_{BAF} to relate the dissolved $C_{PCDD/F}$ to $C_{PCDD/F}$ in the biota. The conversion from abiotic to biotic concentrations is thus $C_b = K_{BAF}(\beta C_{pw} + (1 - \beta)C_w)$, and area and volume weighted averages of the simulated time series of C_{pw} and C_w in the six sediment and six model compartments in the Frierfjorden (Areas 1 and 2 in Figure 1) were used as the PCDD/F forcing for cod and crab. In addition, the simulated time series of C_b were "delayed" in the model according to T_r both for cod and crab. Cod were assumed to stay in the top 0–50 m of the water column and crab on the corresponding sediment bottom area in the Frierfjorden, and be exposed to the $C_{PCDD/F}$ there either directly or via their prey. Areally and volumetrically, cod and crab were exposed mostly to the intermediate and deep water compartments in Area 2 (Figure 1), and to the corresponding sediment compartments, which comprised 75 and 78% of the total exposure area and volume, respectively.

2.6. Model Sensitivity Analysis: Extended FAST. The sensitivity of the results from the SF-tool abiotic model application in the Grenland fjords was analyzed by the Extended FAST global sensitivity analysis method (*20, 21*). In this method values for the model parameters that are included in the analysis are sampled in a wave-like form, so that the amplitude of the particular wave is equal to the parameter's predefined variation range (e.g., minimum−maximum), and so that none of the frequencies of the waves can be constructed as a linear combination of the other waves using integer coefficients up to a specific value. Each parameter is thus "marked" with a particular frequency. The model is then run numerous times choosing at each run a new set of parameter values from the wave-like parameter samples, covering well the whole multidimensional parameter space, and the model output is monitored. Finally, contributions of the different parameters on the model output variance can be identified from the periodogram based on the discrete Fourier transformation of the model output. The resulting sensitivity indices reflect both the parameters' role in the model code and our knowledge of their possible value ranges. The 17 model parameters analyzed using this technique are presented in Supporting Information, Table S1 along with the range of possible values considered. The model was run from 1950 to 2100 for a total of 70000 simulations. The model outputs for which the parameters' sensitivity was monitored included log-transformed values of C_w and C_{pw} and the change in their predicted concentrations over various time periods (e.g., 1975–2000, 2000–2100). To shorten the total model simulation time, both in Extended FAST and MCMC simulation, only three PCDD/F congeners were simulated. These were 23478-PeCDF, 123478/123479-HxCDF, and 123678-HxCDF, the three congeners contributing the most to the total toxicity equivalent $C_{PCDD/F}$ (*22*) in the biota of the Grenland fjords (65% together) (*10*).

2.7. Model Uncertainty Analysis and Calibration: MCMC Method. We applied a MCMC simulation method (*23, 24*), based on Bayesian inference, for automatic model calibration and estimation of proper parameter and prediction uncertainties in our current model application. The use of MCMC methods in numerical water quality modeling is still rather limited but is anticipated to increase due to the significant advantages of the method for certain applications (*5, 6, 24–26*). The Metropolis−Hastings algorithm (*23*) and the adaptive version of it (*26, 27*) which we use in the MCMC simulation, are based on "guided" random walk in the parameter space. After the chain of these random "steps" in the parameter space has properly converged, the chain represents a sample from the correct and complete posterior joint probability distribution of all the analyzed parameters which optimally fits the corresponding model results to the uncertain observations used in the analysis in a probabilistic sense. More details on the adaptive Metropolis-Hastings sampling scheme used in our MCMC simulation are described in the Supporting Information.

In the MCMC simulation of our model application, we estimated values of 15 calibration coefficients ($a_1 - a_{15}$) as well as standard deviations (σ_{abio}, σ_{bio}) of the individual $\log_{10}$-transformed abiotic and biotic observations on the basis of our prior knowledge of the parameter values and the observations of $C_{PCDD/F}$ in water, sediment and biota described in section 2.1. The calibration coefficients were used in the MCMC simulation to directly represent model parameter values or to scale the nominal parameter values or parameter values from another compartment. The selection of the abiotic model parameters to be estimated in the MCMC simulation (B, R, C_{bg}, E and the organic carbon settling rate U_{poc}) was based primarily on the results of the model sensitivity analysis (see section 3.1). In addition, all the parameters used to relate the abiotic $C_{PCDD/F}$ to biotic $C_{PCDD/F}$ (i.e., T_r, K_{BAF}, β) were estimated in the MCMC simulation. The prior distributions of the calibration coefficients were based on expert judgment and some previous observations and model results (*14*), and they were set to be statistically independent marginal distributions, spanning a relatively wide range. The values of the rest of the model parameters, not estimated with the MCMC method, were fixed to their nominal values. Details on the prior distributions and the relations of the 15 calibration coefficients to the corresponding model parameters are given in Supporting Information, Table S2 and Figure S3.

The total length of our final parameter chain (i.e., the number of model runs in the MCMC simulation) was 10^5. Due to the adaptive MCMC method and the preliminary simulations made prior to the simulation of the final chain, the convergence of the final chain (judged by visual inspection) was rapid. To further ensure proper convergence, the first 20000 runs of the chain were discarded in further use of the chain (the so-called burn-in period, see the Supporting Information). The final model simulations and uncertainty analysis essentially represent the results generated by randomly drawing samples of parameter sets from this chain and conducting simulations over the time period under consideration.

3. Results and Discussion

3.1. Model Sensitivity Analysis. The results from the sensitivity analysis of the abiotic model vary according to the type and time of the output variable. For example, many different parameters, such as B, U_{poc}, E, and the observed organic carbon–water PCDD/F partitioning parameter K_{oc} were found influential for C_{pw} in the intermediate and deep sediment compartments in 1975 when the PCDD/F emissions from the magnesium plant were at their highest level. For our main output variable of interest in the model calibration, the change in predicted C_w and C_{pw} in Frierfjorden between 1975 and 2000, the model results were clearly most sensitive to parameters B, R, and H (shown in Supporting Information, Figure S2 for C_{pw} in the intermediate and deep compartments). Although H was identified as an influential parameter, it only plays a role in scaling the rate coefficients in the model (the so-called D-values), and can thus be fixed to its nominal value in the compartments, bearing in mind that all the sediment-related rate parameters, such as B and R, are related to this specific value of H. When the change in predicted C_w and C_{pw} was taken between 2000 and 2100, i.e., for the hundred year period after the closure of the magnesium plant, the parameter C_{bg} was also identified as somewhat influential.

3.2. MCMC-Calibrated Model Simulations of PCDD/Fs in the Grenland Fjords. After the MCMC simulation the resulting (marginalized) posterior distributions of the calibration coefficients a_1–a_{15} were compared to their prior distributions (details are shown in Supporting Information, Section 2.3 and Figure S3). Posterior distributions related to parameters T_r, β for crab, as well as B and R in the shallow and deep compartments resembled much their prior distributions, indicating that a wide range of values (though within the prior distributions) could give adequate fit between the model results and observations, while the distributions related to parameters C_{bg}, E, K_{BAF}, U_{poc}, β for cod, and B and R in the intermediate compartments were well refined in the MCMC simulation. For example, the estimated posterior distribution of E was on average a factor 4 lower than the nominal emission estimate (*15*), and the posterior distribution of β for cod indicated a larger influence of the water column than estimated in the prior distribution. The medians of the distributions estimated for σ_{abio} and σ_{bio} were 0.40 and 0.73, respectively.

Figures 2a–b show simulation results from the calibrated model compared to the corresponding observations over the period 1950–2050 in the absence of any remediation measures. To produce the results presented in Figure 2 the model was run 2000 times and parameter value sets were on each simulation round randomly resampled from the parameter chain that resulted from the MCMC simulation. The calibrated model generally fits well with yearly medians of observations of $C_{PCDD/F}$ in sediment and water compartments, as well as in cod liver and crab hepatopancreas. The model bias (MB), i.e the factor by which the predictions tend to under- (MB < 1) or overestimate (MB > 1) the yearly medians of observations (*15*), was 1.02, 0.58, and 0.94 for sediment, water and biota, respectively (median bias of the 2000 simulations). The spread in the observations is a result of both spatial and temporal variability within the abiotic model compartments and within the cod and crab populations. By using the estimated distributions of σ_{abio} and σ_{bio} the calibrated model can also be used to simulate individual observations, and thus e.g. the 90th percentile of the $C_{PCDD/F}$ in the cod (liver) population.

Simulation results (Figure 2c) on the effect of the six different remediation scenario alternatives (Table 1) on $C_{PCDD/F}$ in cod liver show that a significantly different reduction in $C_{PCDD/F}$ in cod after the remediation measures have taken place in 2010 can first be seen when large areas of the Frierfjorden are capped (i.e., in scenario Riv+Hs+Fs), and thus significant portions of the contaminated sediment areas are cleaned up. The propagation of model parameter uncertainties onto the predicted date when the Frierfjorden can be considered to be in good status again can be represented, e.g., by the year when the 2.5th ("best case"), 50th ("median case"), and 97.5th ("worst case") percentiles of the simulations of $C_{PCDD/F}$ in cod liver (representing median of the population) fall below the limit value of the national pollution status class I "insignificantly polluted" (<15 ng kg^{-1} wet weight). The model predicts these years to be 2014, 2026, and 2039 in the "NoRem" scenario, 2011, 2014, and 2020 in the "Riv+Hs+Fs" scenario, and 2010, 2012, and 2015 in the whole fjord capping scenario "Riv+Hs+Fs+Hd+Fd" (Figure 2c). The increase in capping area in these scenarios thus leads to both earlier achievement of good fjord status and narrower uncertainty in the predicted timing for this.

Combining probability distributions of remediation costs and the predicted number of years it takes to achieve a limit value concentration, e.g., in cod liver (the remediation effect) can be used as a basis for priority-setting of remediation alternatives based on expected effect-to-cost ratio and its variance (*28*). Furthermore, adding distributions of valuation of remediation benefits to households to this analysis can provide a first cut benefit-cost analysis of whether large scale remediation is economically desirable (*28*).

3.3. Further Discussion. The MCMC simulation technique, which is still a novel and little used technique in the field of chemical fate modeling, has shown in our study to be well suited for combined model calibration and uncertainty analysis of the relatively simple rate constant based mass-balance models used for predicting the fate of POP in the abiotic and biotic environment (*12*). This technique can resolve the major problems of estimation of model parameter distributions, correlations and unidentifiability encountered with the more frequently used basic Monte Carlo simulation techniques.

With 26 model compartments the total number of parameters in the whole Grenland fjords model application becomes a few hundred. However, as the sensitivity analysis indicated, only a small fraction of these seem to be influential for a given model output (although not every parameter in every compartment can be included in the sensitivity analysis due to computational limitations). Thus fixing most of the model parameters to their nominal values seem to be well-justified for our particular application.

In our SF-tool model application in the Grenland fjords the use of the MCMC method to estimate the parameter distributions has led to narrower uncertainty estimates in the model predictions than estimated previously (*1, 18*). The overall impact of the different remediation scenarios has remained quite similar though. However, the simulation results and their uncertainties are now also well-anchored to the available observations and to their uncertainties. The coarse depth resolution in the model should be borne in mind and taken as approximate if planning real capping measures. Moreover, we have simulated ideal 100% effective capping and have not yet considered any uncertainties, technicalities or ecological effects of a possible capping operation.

The use of the SF-tool for holistic simulation of the Grenland fjords abiotic and biotic system as well as the inclusion and propagation of model parameter value uncertainties in the model results, and thus their presentation as probability distributions instead of single values, has already provided a unique and valuable knowledge input for the local environmental managers and other stakeholders in the Grenland fjords PCDD/F pollution problem. This model-based knowledge of the probabilistic future evolution of $C_{PCDD/F}$ in cod and crab, when combined with the estimates of consequences, i.e., the estimated costs of the particular capping operation and its expected benefits, provides a basis for a complete risk assessment. In this assessment we can evaluate whether the huge costs of an apparently extensive as well as expensive (costs estimated to be up to 10–100 million $ (*28*)) capping operation are justified by the achieved benefits, or whether just waiting for the slower natural recovery to remedy the pollution problem would be the preferred way to go.

Acknowledgments

We warmly thank the two reviewers for their comments on the manuscript and Roar Brænden and Birger Bjerkeng for technical help. The work in this study was funded by the Research Council of Norway (contracts 159214/S30 and 172708/S30), Norwegian Institute for Water Research (NIVA), Department of Applied Environmental Science at Stockholm University (ITM), Norsk Hydro, and the County Governor of Telemark.

Supporting Information Available

Additional details on the theory and application of the MCMC simulation method, the models in the SF-tool, the prior and posterior distributions of the calibration coefficients and their relation to model parameters, as well as the setup and results of the sensitivity analysis. This material is available free of charge via the Internet at http://pubs.acs.org.

Literature Cited

(1) Saloranta, T. M.; Armitage, J.; Næs, K.; Cousins, I.; Barton, D. N. *SF-Tool Multimedia Model Package: Model Code Description and Application Examples from the Grenland Fjords. NIVA-report 5216*; Norwegian Institute for Water Research: Oslo, Norway, 2006.

(2) MacLeod, M.; Fraser, A. J.; Mackay, D. Evaluating and expressing the propagation of uncertainty in chemical fate and bioaccumulation models. *Environ. Toxicol. Chem.* **2002**, *21*, 700–709.

(3) Luo, Y.; Yang, X. A multimedia environmental model of chemical distribution: Fate, transport, and uncertainty analysis. *Chemosphere* **2007**, *66*, 1396–1407.

(4) Cullen, A. C.; Frey, H. C. *Probabilistic Techniques in Exposure Assessment*. Plenum press; NY, 1999.

(5) Lin, H.-I.; Berzins, D. W.; Myers, L.; George, W. J.; Abdelghani, A.; Watanabe, K. H. A Bayesian approach to parameter estimation for a crayfish (*procambarus* spp.) bioaccumulation model. *Environ. Toxicol. Chem.* **2004**, *23*, 2259–2266.

(6) Weber, C. L.; Vanbriesen, J. M.; Small, M. S. A stochastic regression approach to analyzing thermodynamic uncertainty in chemical speciation modelling. *Environ. Sci. Technol.* **2006**, *40*, 3872–3878.

(7) Beven, K. A manifesto for the equifinality thesis. *J. Hydrol.* **2006**, *320*, 18–36.

(8) Refsgaard, J. C.; Henriksen, H. J. Modelling guidelines - terminology and guiding principles. *Adv. Water Resour.* **2004**, *27*, 71–82.

(9) Persson, N. J.; Gustafsson, Ö.; Bucheli, T. D.; Ishaq, R.; Næs, K.; Broman, D. Soot-carbon influenced distribution of PCDD/Fs in the marine environment of Grenlandsfjords, Norway. *Environ. Sci. Technol.* **2002**, *36*, 4968–4974.

(10) Bjerkeng, B. *Statistisk Vurdering av Overvåking av Dioksiner i Organismer. NIVA-rapport 5123*; Norwegian Institute for Water Research, Oslo, Norway (in Norwegian), 2005.

(11) Bakke, T.; Ruus, A.; Bjerkeng, B.; Knudsen, J. A.; Schlabach, M.; Skaare, J. U.; Berg, V. *Overvåking av Miljøgifter i Fisk og Skalldyr fra Grenlandsfjordene 2001–2002, NIVA-rapport 4702*; Norwegian Institute for Water Research, Oslo, Norway (in Norwegian), 2003.

(12) Mackay, D. *Multimedia Environmental Models: The fugacity approach*; 2nd ed.; Lewis Publishers: Boca Raton, FL, 2001.

(13) Gobas, F. A. P. C. A model for predicting the bioaccumulation of hydrophobic organic chemicals in aquatic food webs: application to Lake Ontario. *Ecol. Modell.* **1993**, *69*, 1–17.

(14) Saloranta, T. M.; Andersen, T.; Næs, K. Flows of dioxins and furans in coastal food webs: Inverse modelling, sensitivity analysis, and applications of linear system theory. *Environ. Toxicol. Chem.* **2006**, *25*, 253–264.

(15) Persson, N. J.; Cousins, I. T.; Molvær, J.; Broman, D.; Næs, K. Modeling the long-term fate of polychlorinated dibenzo-p-dioxins and furans (PCDD/Fs) in the Grenland fjords, Norway. *Sci. Total Environ.* **2006**, *369*, 188–202.

(16) Armitage, J.; Saloranta, T. M. *Simulating the Fate of Polycyclic Aromatic Hydrocarbons (PAHs) in the Sunndalsfjord, NIVA-report 5113*; Norwegian Institute for Water Research: Oslo, Norway, 2005.

(17) Saloranta, T. M. *Simuleringer av Polysykliske Aromatiske Hydrokarboner (PAH) i Ranfjorden, NIVA-rapport 5172 (in Norwegian)*; Norwegian Institute for Water Research: Oslo, Norway, 2006.

(18) Saloranta, T. M.; Barton, D. N.; Armitage, J.; Næs, K.; Cousins, I. Modelling the effects and uncertainties of different sediment remediation scenarios in the Grenland fjords, Norway. *Organohalogen Compd.* **2006**, *68*, 452–455.

(19) Næs, K.; Persson, J.; Saloranta, T.; Andersen T.; Berge J. A.; Hylland, K.; Ruus, A.; Tobiesen, A.; Bergstad, O. A.; Knutzen, J. A. *Dioxins in the Grenland fjords-DIG: Summary of the Research Project, NIVA-rapport 4876 (in Norwegian)*; Norwegian Institute for Water Research: Oslo, Norway, 2004.

(20) Saltelli, A.; Tarantola, S.; Chan, K. P.-S.; Scott, E. M. A quantitative model-independent method for global sensitivity analysis of model output. *Technometrics* **1999**, *41*, 39–56.

(21) Saltelli, A.; Chan, K.; Scott, E. M. *Sensitivity Analysis*; Wiley; New York, 2000.

(22) Van den Berg, M.; Birnbaum, L.; Bosveld, A. T. C.; Brunström, B.; Cook, P.; Feeley, M.; Giesy, J. P.; Hanberg, A.; Hasegawa, R.; Kennedy, S. W.; Kubiak, T.; Larsen, J. C.; van Leeuwen, F. X. R.; Liem, A. K. D.; Nolt, C.; Peterson, R. E.; Poellinger, L.; Safe, S.; Schrenk, D.; Tillitt, D.; Tysklind, M.; Younes, M.; Wærn, F.; Zacharewski, T. Toxic Equivalency Factors (TEFs) for PCBs, PCDDs, PCDFs for humans and wildlife. *Environ. Health Perspect.* **1998**, *106*, 775–792.

(23) Gamerman, D. *Markov Chain Monte Carlo: Stochastic Simulation for Bayesian Inference*; Chapman & Hall: London, UK, 1999.

(24) Larssen, T.; Huseby, R. B.; Cosby, B. J.; Høst, G.; Høgåsen, T.; Aldrin, M. Forecasting acidification effects using a Bayesian calibration and uncertainty propagation approach. *Environ. Sci. Technol.* **2006**, *40*, 7841–7847.

(25) Kuczera, G.; Parent, E. Monte Carlo assessment of parameter uncertainty in conceptual catchment models: The Metropolis algorithm. *J. Hydrol.* **1998**, *211*, 69–85.
(26) Malve, O.; Laine, M.; Haario, H. Estimation of winter respiration rates and prediction of oxygen regime in a lake using Bayesian inference. *Ecol. Modell.* **2005**, *182*, 183–197.
(27) Haario, H.; Saksman, E.; Tamminen, J. An adaptive Metropolis algorithm. *Bernoulli* **2001**, *7*, 223–242.
(28) Barton, D. N. *Uncertainty Analysis of Remediation Costs for Contaminated Marine Sediments, NIVA-Report 5320*;Norwegian Institute for Water Research: Oslo, Norway, 2007.

ES070622L