A COUPLED FATE-TRANSPORT AND FOOD CHAIN MODEL FOR PBDES IN THE HIGH ARCTIC: APPLICATION TO LAKE ELLASJØEN, BEAR ISLAND, NORWAY

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INTRODUCTION

Polybrominated diphenyl ethers (PBDEs) are critical environmental contaminants since they have similar physical-chemical properties as PCBs and can be transported to the arctic[1] where they can be biomagnified to high concentrations in arctic food chains[2]. However, compared with PCBs, PBDEs are more highly influenced by biotransformation via debromination in both invertebrates and fish[3,4,5].

Arctic char from Lake Ellasjøen, located on Bear Island, Norway, contain among the highest concentrations of persistent organic pollutants (POPs), including PBDEs, ever reported in the arctic, and concentrations are significantly higher than nearby lakes[6,7]. Several hypotheses have been proposed to explain these high concentrations. First, it is suggested that fog, which blankets the lake roughly 75% of the year, increases loadings of POPs due to the ability of fog to scavenge POPs from the atmosphere. Second, seabirds that nest on cliffs at the extremity of the lake drainage basin and rest within the drainage basin and on the lake itself, increase loadings of POPs by depositing guano to the lake during the brief ice-free season. Third, increased lake productivity, resulting from the nutrient inputs (from guano), increases the opportunity for POPs to biomagnify up the food chain.

Mathematical modeling has been shown to be an important tool that can be used to tease out the factors responsible for contaminant accumulation in the abiotic and biotic compartments of aquatic systems[8,9]. However, most models have been developed and applied for PCBs in temperate lakes such as Lakes Ontario and Erie. Because arctic fish have physiologic adaptations that enable them to deal with harsh arctic conditions[10], these models need to be adapted if they are to be applied to arctic systems. In addition, rates of PBDE debromination need to be accounted for in the model equations.

The goal of this study is to improve our understanding of PBDE lake-wide dynamics, bioaccumulation, and biomagnification in a high arctic freshwater system. We hypothesize that the debromination of the higher brominated compounds plays an important role. We accomplish this goal by adapting and applying a coupled fate-transport and food chain model to PBDEs in the Lake Ellasjøen food web.

METHODS

Study Site

Lake Ellasjøen is located on Bear Island (74º30' N, 19º 0' E), which is approximately half way between the mainland of Norway and Spitsbergen. The island has an area of approximately 178 km^2 and measures 20 km from north to south. Lake Ellasjøen is the deepest lake on the island, with a maximum depth of about 40 m, situated in the southern, mountainous part of Bear Island. The lake has a surface area of 0.72 km^2 whereas the catchment area is estimated to be 6.1 km^2. It receives hydrological inputs from upstream, Lake Skutilen, and stream inflow during snowmelt. Snow melts within two weeks, which typically occurs in late June. The output of the lake flows into the Norwegian Sea.

A large breeding colony of little auk inhabits the southern catchment area of Lake Ellasjøen. Thousands of kittiwakes (*Rissa tridactyla*)[11] and hundreds of glaucous gulls use the lake as a resting area. The birds in the catchment area appear to have a large impact on the lake, as indicated by the growth of green algae on the shores directly below the little auk colony. There is minimal vegetation present in the catchment area, except for occasional submerged mosses. The lake has a very well developed profundal and pelagic zone, and is inhabited by Arctic Char (*Salvelinus alpinus*)[11].

Model Approach and Parameterization

The model consists of a sequentially linked whole lake fate and food-chain bioaccumulation models that estimate the behavior of PBDEs in Lake Ellasjøen. The linked model predicts the concentration of PBDE congeners in water, sediments, and biota resulting from loadings from inflow, snowmelt from mountains during spring run-off, atmospheric deposition, and guano deposition from the birds.

Fate and Transport Model

The fate and transport model is based on the QWASI (Quantitative Water Air Sediment Interaction) model developed by Mackay et al.[12]. The model uses fugacity (f, Pa), as an equilibrium criterion, which can be easily related to concentrations of contaminant in the respective phases. The model has been adapted to arctic lakes by Freitas et al.[13] and Helm et al.[14]. The lake is divided into three geographic compartments of defined volume and composition: water column (W), surficial sediment (Used) and deeper-lower sediment (LSed). Air is considered as a compartment with infinite volume and specified concentrations. We assume that these compartments are well mixed, i.e. there is no gradient in physical and chemical properties. Each bulk-compartment consists of sub-compartments (e.g., suspended solids and water). Physical-chemical properties for PBDE congeners are taken from Wania et al.[1].

The total snowpack runoff contribution to loadings is calculated as a product of snowpack volume and the measured melt-water concentration. Measurements of snow accumulation across the watershed were collected in advance of snowmelt and the Geographic Information System (GIS) – ArcView was used to calculate total snowpack volume throughout the catchment. We assumed an average water content of the snowpack and further assumed that the average

measured melt water concentrations represent concentrations of PBDEs after post-depositional changes in the snowpack.

Air–water exchange could be a key contributor of PBDE loading to the arctic lakes. PBDEs in the particulate and gas-phases are transported from air to water via wet and dry deposition of particles, rain dissolution, snow and fog deposition in addition to adsorption (diffusive transfer). The model quantifies rates of rain dissolution (dissolution of total gas-phase chemical in precipitation) and atmospheric deposition (wet and dry) using measured concentrations and deposition rates.

Fog, because of its occurrence at ground level, could conveniently transfer contaminants from air to the water surface or the catchment area. Fog droplets are efficient collectors of particulate and gas-phase pollutants by the process of nucleation and collision scavenging. The fate of chemicals in fog is particularly interesting for Lake Ellasjøen where summer fog occurs frequently (visibility is less than 1000m for about 130 days/yr). For Lake Ellasjøen, we calculate the deposition rate of fog as[15]:

[1] $$G_{Fog} = \frac{F_c * r_w}{A_c * E}$$

where G_{Fog} is the fog deposition rate ($g/m^2/d$), Fc is the measured fog water collection rate (m^3/d), A_c is the cross-sectional area of the collector (m^2), ?$_w$ density of water (g/m^3), and E the collector efficiency, which is typically 50% for planner fog collectors.

The total loading of contaminants through fog deposition (g/d) is calculated as

[2] Fog deposition = $G_{Fog} * C_{Fog} * A_{Fog}$

where C_{Fog} is the average measured concentration of PBDE congeners in the fog water samples (g/g) and A_{Fog} the area of the fog covered over the lake surface and its surroundings (m^2).

The exchange of chemicals between the upper sediment layer and water column occurs through the diffusion and advective movement of particles. Particle transport rates, sedimentation and resuspension, are highly site specific and require measurements using sediment traps deployed in the lake. In absence of sediment trap data, we use particle transport rates reported for arctic oligotrophic lakes. The diffusive flux between water and sediments is based on Fick's first law. The mass transfer coefficient for this exchange is taken from Freitas et al.[13] and Helm et al.[14] and applies to all chemicals.

The model considers average summer conditions for the steady-state calculations. The fate model was parameterized and calibrated using field measurements of hydrology and PCB concentrations measured between 1996 and 2001.

Food Chain Model

The food web model is based on the models of Campfens and Mackay[16] and Morrison et al.[17] which were originally developed for PCBs in Lake Ontario. Our adapted model accounts for cold temperature organism physiology in all trophic levels so that it can be applied to arctic systems. The food web of Lake Ellasjøen consists of four classes of organisms. These classes are phytoplankton, zooplankton, benthic invertebrates, and arctic char. Fish may feed on all organisms including their own class. The dietary preference of each species is expressed in the

form of a predator/prey matrix that was constructed using the measured gut contents of each organism class (unpublished data). The model estimates the intake of PBDEs from the gills and the diet and the rate of elimination via gills, feces, growth and metabolic transformation of each species. Significant debromination of highly brominated congeners, e.g. BDE-99, into lower congeners, e.g. BDE-47, has been reported to increase the bioaccumulation of their metabolites[3,4]. Food web debromination rates of PBDEs are estimated by modifying metabolism/degradation rates to maximize the correspondence between modelled and measured concentrations of each PBDE congener.

RESULTS

The model was used to estimate rates of PBDE debromination. After accounting for these rates, we found comparable biomagnification and bioaccumulation relative to PCBs of similar hydrophobicity.

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