A New Method to Quantitatively Estimate Biomagnification in Food-Chains.

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Objectives

The objective of the investigation was to develop a method by which biomagnification of potentially persistent chloro-organic substances can be estimated quantitatively from field data in an aquatic food-chain. Biomagnification is defined as an increasing concentration of a substance from food (lower trophic level) to consumer (higher trophic level) in a food-chain. A number of substances (e.g. PCBs, DDT, Hg and Cd) have been shown to occur in concentrations that are considerably higher in top consumers than in primary producers [1]. The magnitude of relative biomagnification per trophic step has however been difficult to estimate quantitatively since there has been no method by which the trophic distance between two organisms can be numerically estimated by a measurable quantity. Persistent environmental pollutants are likely to have long residence times in biota and their negative effects in nature are likely to be substantial. Biomagnifying substances have in general caught interest by causing negative effects in a top predator population. For the future this seems an unthinkable way of detecting harmful substances in the environment.

In recent years biological interpretations of changes in the relative abundances of naturally occurring stable isotopes of nitrogen and carbon have provided a method to characterize food web dynamics and quantify trophic levels [2]. The new method presented in this abstract utilizes fractionation of stable isotopes of nitrogen and carbon as a quantitative estimate of trophic distance between organisms and relates the concentrations of chloro-organic substances in different organisms to this fractionation. The approach makes it possible to identify biomagnifying pollutants and estimate the magnitude of their tendency to be biomagnified. In this abstract the method has been applied to PCDD/F data from two characteristic Baltic food-chains. One food-chain is pelagic (phytoplankton → zooplankton → herring → cod) and the other is littoral (phytoplankton and sediment trap collected material → blue mussel → juvenile eider duck).

Approach and methods

The metabolic processes of animals enrich the heavy isotopes of C and N (^{13}C ,^{15}N) in relation to the lighter (^{12}C ,^{14}N) in a predictable way and consumers thus become enriched in the heavier isotopes in relation to their foods. The enrichment of the heavier isotopes can be attributed either to fractionation in assimilation or in excretion. The $^{13}C/^{12}C$ ratio has been found to generally increase by 1 ‰ and the $^{15}N/^{14}N$ ratio by 3-5 ‰ per trophic transfer (i.e. trophic level)[2]. Stable carbon and nitrogen isotopes are therefore useful to characterize

the trophic level of an organism.

Changes in isotopic composition are expressed in relation to a standard substance. For C the standard used is the carbon in a well defined limestone and for N it is the atmospheric N_2 composition. The trophic levels are expressed as δ-values, which are given in ‰, and calculated as for example $\delta^{15}N$:

$$(1) \qquad \delta^{15}N = \frac{(^{15}N/^{14}N)_{sample} - (^{15}N/^{14}N)_{air}}{(^{15}N/^{14}N)_{air}} \cdot 1000$$

Enrichment of the heavy isotope (i.e. increasing trophic level) is thus expressed as an increase in the δ-value. If the difference between $\delta^{15}N$ of two different organisms from the same habitat is more than 3 ‰ they are generally considered to belong to different trophic levels. The δ-value can be treated mathematically as a continuous variable and used to estimate the numeric distance between the trophic levels of two organisms. By relating the pollutant concentration in organisms in a food-chain to the δ-values of the same organisms, biomagnification can be quantitatively estimated.

To estimate biomagnification from field data an applicable mathematical model most be chosen. If a theoretical food-chain is considered where a constant proportion of food from one trophic level is converted to biomass in the next trophic level and all of a given pollutant present in that food is absorbed and none is metabolized (i.e. complete biomagnification), the concentration of the pollutant will increase exponentially upwards in the food-chain. The concentration of the pollutant (C) can then be expressed by the exponential model $C=A \cdot e^{B \cdot \delta^{15}N}$ where $\delta^{15}N$ is a measurement of trophic level and A and B are constants. The constant A will be dependent on the background concentration in the base of the food-chain (e.g. phytoplankton), whereas the constant B will be a measurement of the degree of biomagnification. A value of B around zero indicates that a substance is flowing through the food-chain without being biomagnified, whereas a B value greater than zero indicates that a substance is biomagnified. Negative values indicate that the substance is not taken up, or is metabolized. Since $\delta^{15}N$ is known to be more affected by trophic transfers than is $\delta^{13}C$ it is the most suitable variable to describe the food-chain dynamics.

Analysis of PCDD/F and isotopic composition of the samples was made by high-resolution mass-spectrometry [3].

Results

The nitrogen isotope data gave food-chain descriptions that were qualitatively consistent with previous conceptions of the trophic arrangements in the two food-chains. The $\delta^{13}C$ values in the study were strongly correlated to $\delta^{15}N$ indicating that the material in different organisms had a common source, i.e. phytoplankton production[3].

The exponential model $C=A \cdot e^{B \cdot \delta^{15}N}$ was fitted to dry weight concentrations (dw) of four different combinations of 2,3,7,8-substituted PCDD/Fs, and the constants A and B were estimated (Figure 1). The summed concentration of **total PCDD/Fs** (i.e. the sum of all 2,3,7,8-substituted isomers) was found to decrease exponentially with increasing trophic level ($B \sim -0.15$) indicating that as a group the 2,3,7,8-substituted PCDD/Fs were not biomagnified. The summed 2,3,7,8-TCDD **toxic equivalents** (pg TEQ/g dw, Nordic system) of the same isomers was however found to be greater in the organisms at the higher trophic levels ($B \sim +0.12$) but the fit of the exponential model to TEQ versus $\delta^{15}N$ was not

strong. It can be concluded that the total concentrations of 2,3,7,8-substituted PCDD/Fs decreased with increasing trophic level, whereas the toxic content of the 2,3,7,8-substituted PCDD/Fs in the organisms tended to increase. The result implies a selective enrichment of 2,3,7,8-substituted isomers with high toxic equivalens factors (TEF).

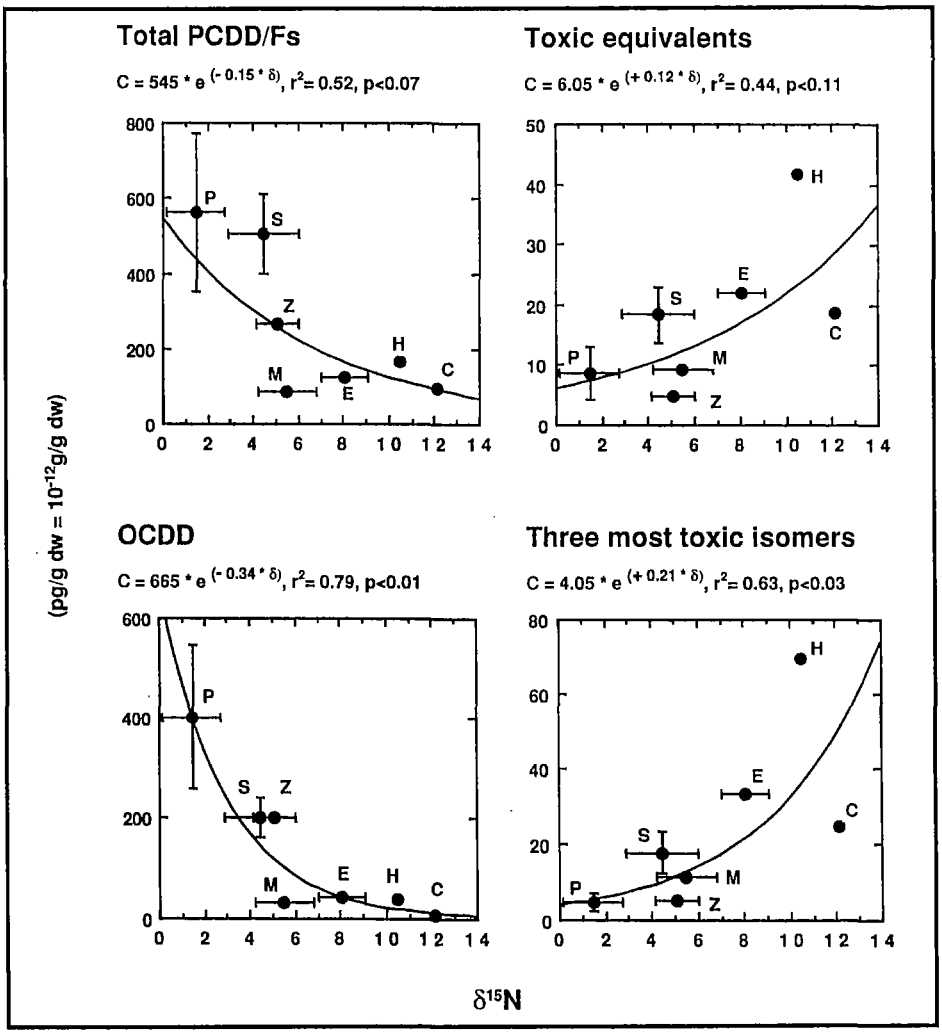

Fig 1.Concentration of PCDD/Fs as function of trophic level $\delta^{15}N$ in samples from two food-chains in the Baltic. (P=phytoplankton, S=sediment trap material, Z=zooplankton, M=mussels, E=eider, H=herring, C=cod) see text for further information.

The concentration of **OCDD** was high at the lower trophic levels but decreased with increasing $\delta^{15}N$ (B~-0.34). OCDD/F has a small TEF (0.001) and contributed little to TEQ, particularly at the higher trophic levels, but it contributed substantially to the mass of total 2,3,7,8-substituted PCDD/Fs. The trend of decreasing total 2,3,7,8-substituted PCDD/Fs with increasing $\delta^{15}N$ could thus largely be explained by an exponential decrease in

OCDD/F. The observed trophic level dependent increase in TEQ must then by explained by specific accumulation of highly toxic isomers. The **three most toxic isomers** of PCDD/F (i.e., 2,3,7,8-TCDD, 2,3,4,7,8-PnCDF and 1,2,3,7,8-PnCDD) all have a TEF greater or equal to 0.5. The summed concentration of these three isomers increased slightly with increasing δ^{15}N-value (B=+0.21) . The trend of decreasing concentrations of total PCDD/F and increasing values of TEQ with increasing δ^{15}N can thus be largely explained by by the decreasing concentrations of OCDD and a selective accumulation of the three most toxic isomers.

The results can be explained by two alternative hypotheses: either there was a less efficient uptake of OCDD compared to the other isomers, or a lower metabolization/excretion rate of the highly toxic isomers.

Conclusions

This new method makes it possible to identify and quantitatively estimate the tendency of food-chain biomagnification for potentially persistent substances in complex environmental samples. The method has been applied to PCDD/F data from two food-chains in the Baltic and indicated a selective enrichment of toxic PCDD/F- isomers in the upper levels of the food-chains and a rapid concentration decrease of OCDD with increasing trophic level. The data material is however limited and the emphasis of the abstract is therefore focussed on the method as such.

The estimation of the bioaccumulation power B gives an ecological estimate of the tendency of biomagnification for a given pollutant. This parameter can for ecological risk assessment be considered in relation to traditional toxicological information since a high value of B may indicate long residence time in biota and high concentrations in top-predators. The present possibilities of isomerspecific detection of organic pollutants in minute concentrations (femtogram levels) by mass-spectrometry makes the stable isotope method a potentially powerful tool for early identification of future priority pollutants and assessment of their ecological impact at low environmental concentrations.

Further research is however required to fully assess the applicability of the method. The generality of food-chain enrichment of heavy stable isotopes and the statistically required numbers of isomerspecifically analysed environmental samples have to be investigated further to judge the generality of the method.

References

1 Thomann RV. Bioaccumulation model of organic chemical distribution in aquatic food chains. Env. Sci. Tech. 1989; 23:699-707

2 Peterson BJ, Fry B. Stable isotopes in ecosystem studies. Ann. Rev. Ecol. Syst. 1987; 18:293-320

3 Broman D, Näf C, Rolff C, Zebühr Y, Fry B, Hobbie J. Using ratios of stable nitrogen isotopes to estimate bioaccumulation and flux of polychlorinated polychlorinated dibenzo-p-dioxins (PCDDs) and dibenzofurans (PCDFs) in two food chains from the northern Baltic. *Environ Toxicol Chem* 1992;11:331-345