

German Federal Environmental Specimen Bank: Retrospective Monitoring of Organotin-Compounds in Marine Samples and Evaluation of Results

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Within the framework of the Federal Environmental Specimen Bank-Program, the German Federal Environmental Agency (Umweltbundesamt) sponsored the development and optimization of an analytical method for the quantitative determination of organotin compounds in several biological matrices. Especially triorganotin compounds which are mainly used as biocides are very toxic. Additionally, it is known that some of these compounds act as endocrine disruptors at least in sensitive marine snails.

From the marine ecological systems of North Sea and Baltic Sea brown algae, mussels, eel-pout muscles, and sea gull eggs of several years between 1985 and 1996 were analysed. The marine samples had been prepared following the German Federal Environmental Specimen Bank-guidelines and were stored at -150°C. Aim of these investigations was the retrospective monitoring of organotin compounds in order to identify if recent use restrictions had resulted in lower levels in biological samples. For the interpretation of the results, data on production, use pattern, environmental fate, bioaccumulation, and ecotoxicological effects were compiled.

Monobutyl tin (MBT), dibutyl tin (DBT), tributyl tin (TBT), diphenyl tin (DPhT) and triphenyl tin (TPhT) were analyzed following a protocol documented as a standard operation procedure. For the analysis of tin-organic compounds the biological materials were dissolved in tetramethyl ammonium hydroxide-solution at 60°C. After acidification the solution was extracted using a hexane/tropolone-mixture. Then, a derivatization with n-pentylmagnesium bromide was performed (Grignard method). Afterwards, the extracts were cleaned up using sodium sulfate/silica gel/Florisil columns, and concentrated. The quantification was performed by capillary gaschromatography and atomic emission detection using three internal standards. The limits of detection were between 1 and 5 µg/kg (depending on compound and matrix; referring to fresh weight). The method was validated by analyses of a certified reference material (CRM 477 from BCR, mussel tissue) and by performance of recovery experiments for all matrices and compounds.

The major contaminants in all matrices were TBT and TPhT. Representative concentrations in North Sea organisms sampled in 1996 were: algae: 6 µg/kg TBT, < 5 µg/kg TPhT; mussels 20 µg/kg TBT, 10 µg/kg TPhT; eel-pout muscle 21 µg/kg TBT, 27µg/kg TPhT; seagull egg 3 µg/kg TBT, < 5 µg/kg TPhT (referring to fresh weight). While the concentration of TPhT was decreasing in recent years, the concentration level of TBT remained relatively constant during the whole period analyzed. For example, in 1985 the concentration levels were 5 µg/kg TBT and 14 µg/kg TPhT in algae and 21 µg/kg TBT and 98 µg/kg TPhT in mussels. The corresponding di- or monoorganotin-compounds were detected only at lower concentration levels (partly below the limit of detection). It was concluded that preferentially the non-polar triorganotin-compounds were taken up by the marine organisms.

These findings were discussed in relation to the use pattern of organotin compounds. The relatively constant TBT-concentrations reflect that although the use of TBT-containing antifouling paints was banned for small ships in Germany in 1990, they are still used for large vessels (> 25 m). TPhT was used till 1985 in antifouling paints and then phased out.

An important aspect for the assessment of toxic compounds is the evaluation if there is a biomagnification in the food web. However, for the organotin compounds there were no clear hints for such an effect. For example, concentrations in fish were not generally higher than in mussels, and concentrations in seagull eggs were lower than in fish.

It is suggested to include analyses of organotin compounds into the routine spectrum of the Federal Environmental Specimen Bank-Program. For this purpose the monitoring of fishes seems to be most appropriate. Further, it should be considered to sample water and sediment together with the routinely sampled organisms from representative sites, so that the pattern of organotin compounds in the biological samples can be assessed in relation to the concentrations in the aqueous phase and sediment.

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