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MONITORING OF ORGANOCHLORINE COMPOUNDS IN FINNISH INLAND WATERS POLLUTED BY PULP AND PAPER EFFLUENTS USING THE MUSSEL INCUBATION METHOD

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ABSTRACT

In the summer of 1988 a full-scale monitoring of chlorohydrocarbons, chlorophenols and aromatic chloroethers was carried out in the freshwater recipients of pulp and paper industry using the mussel incubation method, which has been developed and tested in Finland since 1984. The total number of incubation stations was 40. The results showed that the highest concentrations of chlorophenols originating from pulp bleaching processes were found in the vicinity of pulp mills with no biological waste-water treatment plant. Other chlorophenolic compounds — airborne or mainly originating from chloro-disinfection of water, combustion, wood preservation, sawmills etc. — were detected in small amounts at almost all the sites tested. The highest concentrations were found in the recipients of old sawmills. PCB was also detected in considerable concentrations in some recipients. In the summer of 1989 the monitoring was repeated at 20 incubation stations. The results of 1988 and 1989 are compared, with particular reference to those recipients where water protection measures and the construction of new activated sludge treatment plants were carried out during 1988.

KEYWORDS

Monitoring; mussel incubation; Anodonta piscinalis; pulp and paper industry; chlorohydrocarbons; chlorophenols; chloroanisoles; chloroveratroles.

INTRODUCTION

The pulp and paper industry is the major source of watercourse pollution and reduced utilizability in Finland. In addition to solid particles, dissolved organic compounds and nutrients, pulping effluents also contain high levels of different organic chlorine compounds, some with still unknown structures (Paasivirta 1988). Many of these compounds are toxic to aquatic life and directly deleterious to water quality. Methods available for the monitoring and evaluation of the classical components of watercourse loading - solids, dissolved organic material and nutrients - have already been developed to a rather dependable standard. However, monitoring and control of organic chlorine compounds directly from water samples is not yet feasible. The concentrations in watercourses are very low and vary widely in the original effluents. Sufficient sampling for the generation of statistically significant data is generally impossible to arrange for economic reasons. The effects of these compounds on watercourse biota are still incompletely known.

The common mussel (Anodonta piscinalis) living in Finnish inland waters filters water tens of litres daily in respiration and nutrient uptake. During these processes it accumulates e.g. metals and organic compounds, to the tissues. This property has been utilized in the development of a monitoring method for the small but rapidly changing concentrations of organic chlorine compounds occurring in watercourses affected by pulping effluents. The method has been under development since 1984. Most of the method testing has been carried out during the summer months, but it has also been shown that the mussel thrives well in very cold epilimnions (0.5 - 2.0 °C) during the winter. Accumulation of organic chlorine compounds in mussels during the winter, and the metabolism of the different compounds, is very different from that in summer, apparently partly due to reduced nutrient utilization and different solubility during winter. For these reasons the results of summer and winter incubations cannot be compared.

Similar methods have been applied in many countries, generally for monitoring of heavy metals in marine areas, e.g. the major Mussel Watch program in the USA (Anon, 1980). The mussel species generally used in the marine studies has been Mytilus edulis.

MUSSEL INCUBATION METHOD

In this work the freshwater lake mussel (Anodonta piscinalis) was used as test organism in monitoring of organochlorine compounds. This species is very common in the Finnish lake district, where it usually lives in shallow waters up to a depth of about five metres (Haukioja and Hakala 1974). It lives on the surface of the bottom mud and takes up nutrients by filtering water through its gills. In warm waters a single organism may filter up to about 50 litres of water through its gills in a single day (Purchon 1977).

The principle of the incubation method as developed in this work is simple: mussels of approximately uniform size are obtained from unpolluted watercourses, usually by diving, and maintained in the laboratory for two weeks in an aquarium in order to ensure that the tissues are free of chemical pollutants.

On the other hand this radical change of biotope causes the death of all the weak individuals from the mussel population. The mussels are then transferred to the monitoring sites, where they are maintained in open water out of range of shore effects. The test organisms are housed in plastic cages anchored usually at a depth of one metre. Exchange of water to the cage is unhampered and no chemical contamination originates from the cage material. After an incubation period of four weeks the mussels are taken from the cage and frozen (Herve et al. 1988b). In the laboratory the age of the organisms is estimated on the basis of shell markings. The mussels are weighed and the concentrations of the relevant organic compounds are determined from the soft tissues.

Mussels aged 6 - 8 years are used in monitoring, with a mean length of 7 - 8 cm and total weight of almost 20 g. The weight of the soft tissues is about 10 - 12 g and the dry weight percentage is 8.5 - 10 %. Fat content is approximately 6 % of the dry weight. Sixteen mussels in two cages are usually incubated at one monitoring site. The lake mussel is a very resilient test organism, usually surviving even under heavily polluted conditions. Even in the most polluted sites investigated, a maximum of only 1 - 2 mussels have usually succumbed during the four week incubation period.

For the laboratory handling of mussels incubated at one sampling site, three composite samples of five mussels are prepared for analyses. This economical method of composited samples (Paasivirta and Paukku, 1989) has been used in mussel incubation studies in Finland since 1986. The final monitoring result is taken as the mean value of these three composited samples.

Before extraction, measured amounts of internal standards were added: 2,4,6-trichlorobiphenyl for chlorohydrocarbons, 2,3,6-trichlorophenol for chlorophenols, 2,3,6-trichloroanisole for chloroanisoles/veratroles and ^{13}C-labelled 2,3,7,8-dibenzo-p-dioxin for PCDD/PCDFs. The sample was then

extracted in a
ether (40 - 60
evaporated first
the residue was

COMPO

The following c
of mussels (abbr

Chlorohydrocarbo
2,3,6-Trichloro
2,3,6-Trichloro
Hexachlorobenze
Lindane or gamm
Oxychlordane
Gamma-chlordane
Alpha-chlordane
Trans-nonachlor
p,p'-Dichloro-D
p,p'-Dichloro-D
p,p'-Dichloro-D
Polychlorinated

Chlorophenols
2,4-Dichlorophe
2,6-Dichlorophe
2,4,6-Trichloro
2,4,5-Trichloro
2,3,4,6-Tetrachl
Pentachlorophen
4,5-Dichloroguai
3,4,5-Trichloro
4,5,6-Trichloro
Tetrachloroguaia
2,6-Dimethoxy-tr

Chlorinated anisc
2,4,6-Trichloroa
2,3,4,6-Tetrachl
3,4,5-Trichlorov
Pentachloroanisc
Tetrachloroverat

Polychlorinated d
1,2,3,6,7,8-Hexa
1,2,3,4,6,7,8-He
2,3,7,8-Tetrachl
1,2,3,4,6,7,8-He
Octachlorodibenz

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groups according

S1PCP = 246TCP +
combustion, chlo

S2PCP = 24DCP + 2
from pulp bleach

RESULT

The mussel incuba
the occurrence of
all the pulp and

extracted in a Soxhlet apparatus with hexane-acetone-diethyl ether-petroleum ether (40 - 60°), 2.2:5.5:1:9 (v/v/v/v) for six hours. The solvent was evaporated first in a Rotavapor and finally in a stream of nitrogen gas and the residue was weighed to determine the fat content.

COMPOUNDS ANALYSED

The following compounds have been analysed and detected in the soft tissues of mussels (abbreviations in brackets):

Chlorohydrocarbons

2,3,6-Trichlorocymene	(CYMS)
2,3,6-Trichlorocymenene	(CYMD)
Hexachlorobenzene	(HCB)
Lindane or gamma-hexachlorocyclohexane	(LIND)
Oxychlordane	(OXY)
Gamma-chlordane	(GAMMA)
Alpha-chlordane	(ALPHA)
Trans-nonachlor	(TRANS)
p,p'-Dichloro-Diphenyl-Dichloroethylene	(DDE)
p,p'-Dichloro-Diphenyl-Dichloroethane	(DDD)
p,p'-Dichloro-Diphenyl-Trichloroethane	(DDT)
Polychlorinated biphenyls	(PCB)

Chlorophenols

2,4-Dichlorophenol	(24DCP)
2,6-Dichlorophenol	(26DCP)
2,4,6-Trichlorophenol	(246TCP)
2,4,5-Trichlorophenol	(245TCP)
2,3,4,6-Tetrachlorophenol	(TeCP)
Pentachlorophenol	(PeCP)
4,5-Dichloroguaiacol	(45DCG)
3,4,5-Trichloroguaiacol	(345TCG)
4,5,6-Trichloroguaiacol	(456TCG)
Tetrachloroguaiacol	(TeCG)
2,6-Dimethoxy-trichlorophenol	(DMP)

Chlorinated anisoles and veratroles

2,4,6-Trichloroanisole	(246TCA)
2,3,4,6-Tetrachloroanisole	(2346TeCA)
3,4,5-Trichloroveratrole	(345TCV)
Pentachloroanisole	(PeCA)
Tetrachloroveratrole	(TeCV)

Polychlorinated dibenzodioxins and - furans

1,2,3,6,7,8-Hexachlorodibenzodioxine	(123678HxCDD)
1,2,3,4,6,7,8-Heptachlorodibenzodioxine	(1234678HpCDD)
2,3,7,8-Tetrachlorodibenzofurane	(2378TCDF)
1,2,3,4,6,7,8-Heptachlorodibenzofurane	(1234678HpCDF)
Octachlorodibenzofurane	(OCDF)

In the handling of results the studied chlorophenols were divided into two groups according to their origin (Herve et al., 1988):

S1PCP = 246TCP + TeCP + PeCP; common pollutants from wood preservation, combustion, chlorination and pesticide use

S2PCP = 24DCP + 26DCP + 245TCP + 45DCG + 345TCG + 456TCG + TeCG + DMP; mainly from pulp bleaching.

RESULTS AND DISCUSSION

The mussel incubation method was used in the summer of 1988 to investigate the occurrence of organic chlorine compounds in August in the recipients of all the pulp and paper mills in the vicinity of inland watercourses in

Finland. A total of 40 observation stations were chosen for inclusion in the investigation. The incubation was repeated in the summer of 1989 at 20 of these stations, chosen on the basis of the results from the previous year. Water temperatures during the incubations varied mainly between 15 and 20 °C.

Of the chlorinated hydrocarbons only PCB concentrations increased markedly in the vicinity of some pulp and paper mills. Exceptionally high concentrations - up to 39 µg/g in fat - were recorded in lake Kernaalanjärvi, the recipient of effluents from the oldest paper mill in Finland. The effluents from this mill were earlier led to the watercourse without any purification. This pollution was shown as a result of the investigation to continue tens of kilometres downstream from the discharge site. A PCB leakage reaching lake Päijänne via a watercourse from the north, which started in 1984 or even earlier (Herve et al. 1988a), was apparently still as strong as before. In this case the PCB was not discharged with effluents from the new kraft pulping mill. The source of pollution may be contaminated filling earth used in filling of the shoreline.

Chlorophenols (S2PCP) are produced mainly in chlorine bleaching of cellulose. These compounds were most abundant in the vicinity of pulping mills which do not yet employ biological water purification but rely only on mechanical purification. The concentrations of S2PCP-compounds in the fat of mussels incubated near such mills were about 4 - 6 µg/g. The corresponding concentrations in the fat of mussels incubated in the recipients of pulping mills employing biological purification were only about 1 - 3 µg/g.

The significance of biological waste water treatment in the removal of organic chlorine compounds from effluents can clearly be seen from the analysed results from the observation station at Kuusaankoski in the recipient of the Äänekoski pulp and paper mill during the period 1984 - 1989:

Year	S2PCP (µg/g in fat) in 4-week incubated mussels
1984	10.677
1985	3.618
1986	3.119
1987	1.774
1988	1.836
1989	3.596

Biological effluent purification was introduced at the factory in the spring of 1985. At the same time considerable process alterations were made at this kraft mill.

A similar reduction in S2PCP-concentrations was recorded in the river Kymijoki between 1988 and 1989. In 1988, when the waste waters of this large pulp and paper mill were still purified only by mechanical means, the S2PCP-concentration of incubated mussels was about 5 µg/g in fat. The new activated sludge water treatment plant started up in spring 1989 and by August of the same year the corresponding concentration in mussel fat had decreased to only about 0.7 µg/g.

Chlorophenols originating from bleaching degrade in the recipient, although rather slowly. Discharge of the recipient, mixing conditions of the effluent at the point of release to the watercourse, and the molecular size of the organic chlorine compounds released, all have a significant effect on the nature and amounts of the compounds recovered from the recipient watercourse. Using the monitoring network it was possible to show that a 2 to 3-day residence time in well mixed and diluted river water (mean discharge almost 300 m^3/s) was insufficient to bring about any decrease in S2PCP-concentrations in incubated mussels. At another observation station, at which the effluent is discharged to a river-like lake with a residence time of several

weeks, the corresponding decrease in S2PCP-concentrations was of the order of 50 - 70 %. With increased residence time, and therefore dilution, the degradation of chlorophenols also increases. When the residence time exceeds one year it becomes practically impossible to detect chlorophenols originating from bleaching. This result indicates that the majority of pulp and paper mills situated along side Finnish inland watercourses have no significance as sources of organic chlorine compounds in the Baltic Sea.

A particularly sensitive indicator of bleaching effluents in recipients was the sum of 3,4,5-trichloroguaiacol and tetrachloroguaiacol. The maximum combined sum of these compounds in incubated mussels exceeded 5 µg/g in fat. Of the two compounds, it appears that 3,4,5-trichloroguaiacol extends further into the recipient.

Chlorophenols of the so-called S1PCP group may reach watercourses from other sources than pulp bleaching, e.g. wood preservation, chlorodisinfection of water, sawmills and combustion processes. These compounds are distributed over long distances, partly via airborne routes, and therefore may be detected in small quantities almost everywhere. In the monitoring carried out in the summer of 1988 unusually high S1PCP-concentrations were observed in the vicinity of three towns. In all three cases the high concentrations resulted mainly from the major components of a wood preservative (Ky-5), namely tri-, tetra- and pentachlorophenol. Further, more detailed investigation revealed that the responsible polluting agents were old sawmills and wood preservation installations. In the case of one of the sawmills the concentrations were so high that soil removed from the area had to be treated as hazardous waste.

The occurrence of polychlorinated dibenzodioxins (PCDD) and dibenzofurans (PCDF), considered as extremely potent environmental toxins, was also clarified in this investigation. All the concentrations analyzed in incubated mussels were very low, generally below 50 pg/g (in fat) as total chlorinated TCDD-equivalents (Nord 1988). The highest concentrations, 200 - 500 pg/g (in fat) were recorded in 1988 in mussels incubated in the river Kymijoki. Biological waste water treatment apparently efficiently reduces dioxin concentrations in pulp and paper effluents.

Many chlorophenols cause major flavour defects in fish and thus reduce the utilizability of the watercourse for fishing (Paasivirta et al. 1987). The most deleterious compounds are certain degradation products of chlorophenols, chloroanisoles and chloroveratroles. These compounds have not been detected in pulping effluents but they are found in all mussel samples incubated in pulp mill recipients (Herve 1989). They must therefore be products of mussel metabolism.

2,3,6-Trichlorocymene and -cymenene were found to bioaccumulate significantly to mussels in the recipients of pulp and paper mills. These compounds are therefore clear indicators of pollution by chlorobleaching effluents.

CONCLUSION

Trials with the mussel incubation test were started in 1984 at observation stations downstream from a few pulping mills in Central Finland. By the summer of 1988 the method was already in use in full scale monitoring applications. The results obtained using the method have been encouraging. Chlorophenol discharges from the pulping industry have easily been detected even in watercourses in which no evidence of water quality changes could be detected using classical methods of analysis. Mussel incubation tests now constitute an important part of monitoring for environmental toxins in Finnish inland watercourses. The method is used in particular for monitoring recipients of the pulp and paper industry, but it is also suitable for the detection and monitoring of toxic pollutants from waste pits, sawmills, mining and metalworking industries and power stations, as well as for investigation and monitoring of the watercourse effects of agricultural pesticides.

Use of the mussel incubation method for the monitoring of organic chlorine compounds in Finnish inland waters will continue at about 20 observation stations in recipients of the pulp and paper industry at yearly intervals. Furthermore in the summer of 1990 a new project will be initiated with the aim of determining which species could be used in order to develop similar monitoring capabilities in the brackish waters of Finnish coastal marine areas.

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