Defense Technical Information Center Compilation Part Notice

ADP010602

TITLE: Contamination from Marine Paints - A Norwegian Perspective

DISTRIBUTION: Approved for public release, distribution unlimited

This paper is part of the following report:

TITLE: Approaches to the Implementation of Environment Pollution Prevention Technologies at Military Bases [Approches de l'application des techniques de prevention de la pollution sur les bases militaires]

To order the complete compilation report, use: ADA388899

The component part is provided here to allow users access to individually authored sections of proceedings, annals, symposia, ect. However, the component should be considered within the context of the overall compilation report and not as a stand-alone technical report.

The following component part numbers comprise the compilation report:
ADP010583 thru ADP010608

UNCLASSIFIED

CONTAMINATION FROM MARINE PAINTS – A NORWEGIAN PERSPECTIVE

Arnt Johnsen and Thor Engøy
Forsvarets forskningsinstitutt
Norwegian Defence Research Establishment
Division for Environmental Toxicology
P.O Box 25, NO-2027 Kjeller, Norway

1. Introduction

Marine paints have been used for over 100 years to protect ships from weathering and biological and chemical degradation (1). In order to obtain the right marine paint quality various substances increasing the anticorrosive, antifouling, mechanical flexibility, weatherability, chemical and cold resistance properties were added. Many of the additives that have been used and are still being used today are toxic compounds for man and other species. Spills of paint residues and leakage from painted objects will eventually be deposited in the sea sediments and will therefore potentially pose a threat to the marine environment. Biocides and various other additives used in antifouling paints seem to give the most serious problems ranked according to impact on marine life.

Antifouling paints are designed to give a thin boundary layer in the water around the hull were the concentration of antifouling agent is high enough to kill algae and other organisms that would otherwise remain attached to the hull. With the water acting as a sink, there will therefore need to be a continuous release of toxic compounds from the hull. These compounds have high affinity to particles in the water column and will therefore quickly settle on the seabed. Contaminated sediment will subsequently be a source for resuspension or dissolution in the water column or a direct source for bottom feeders.

In Norway a majority of harbours and areas adjacent to main ship repair yards have highly contaminated sediments (2,3). This has resulted in elevated levels of toxic compounds in fish and shellfish living in these waters and guidance on their consumption has been issued by the Norwegian Food Control Authority (4). In many cases the prime concern is the elevated levels of PCBs (Poly Clorinated Biphenyls). At Haakonsvern Naval Base the Norwegian Defence Construction Service has commenced actions to remove contaminated sediment (5).

The sources of some of these contaminants, such as TBT (tributyl tin) have been firmly established to be antifoulants due to its unique application. However other contaminant sources remain elusive, such as PCBs, in part due to the mixing of multiple source signals over a period of several decades, in part due to the limited accessibility of the composition of historical and contemporary marine paints. An investigation into the link between contaminant concentration in sediments at Haakonsvern Naval Base and the use of marine paints is presented here. Estimation of the amount of paint residues washed into the harbour basin since the opening of the base in 1963 is lacking at present. However, there seems to be a correlation between especially copper and other heavy metals found in the sediments and compounds used in marine paints. It is shown that sufficient quantities of PCBs were present as part of chlorinated rubber additives in marine paints in the 60's and early 70's and can explain the current sediment concentration of PCB. Although the Norwegian use of PCB in marine paints was stopped in 1973, paint residues taken from a ship in 1996 showed significant levels of PCBs. This highlights the need to prepare adequate collection systems where marine paints are removed.

2. Biocides and anticorrosive additives in marine paint

The soluble matrix used in conventional antifouling paints released the biocide relatively quickly and the useful life time of the paint was approximately one year. In this type of paint the biocide was released as the binder dissolved. It was therefore necessary to repaint the hull each year, causing a high consumption of antifouling paints. Later insoluble-matrix-based antifouling paints were introduced and the life time was increased to two years, reducing the amount of copper and other toxic compounds released into the

Paper presented at the RTO SAS Symposium on "Approaches to the Implementation of Environment Pollution Prevention Technologies at Military Bases", held in Budapest, Hungary, 5-7 May 1999, and published in RTO MP-39.

environment. In order to further increase the life time, self-polishing copolymer paints were developed. With this matrix the life time increased to three years for organotin-free paints and five years for organotin containing paints which today have a market share of over 80 %. The increased life time for organotin paints is caused by the covalent bonding of the organotin compounds to the matrix giving a constant release rate of organotin. Table 1 gives an overview over the history of the development of antifoulants.

	Generic type	Binder	Biocides
Before 1950	Conventional	Rosin	Cu_2O
1950 - 1960	Long life	Rosin/vinyl	Cu_2O
Late 60's	Long life	Rosin/vinyl	Cu_2O/TBTO
Mid 70's	Self-polishing	TBT-copolymer Low-built	Cu_2O/TBTO
Early 80's	Self-polishing	TBT-copolymer High-built	Cu_2O/TBTO
Mid 80's	Self-polishing	TBT-copolymer Low tin	Cu_2O/TBTO
Late 80's	Ablative	Copolymer	Cu_2O/TBTO, other organic biocides
Early 90's	Self-polishing	Copolymer	Cu_2O/organic biocides

Table 1 Overview of the development of antifoulants

Various heavy metals have mainly been added to give the marine paint antifouling and anticorrosive properties. Marine paints have also been added pigments containing heavy metal. Copper has been the traditional compound used as a biocide in antifouling paints. The concentration of copper in antifouling paints is reported to be 10-30 %, but as much as 50 % has been used (1). Normally Cu_2O is used as the biocide, but also CuSCN and copper metal are in use.

Mercury was added to antifouling paints as a biocide in the past. Both inorganic mercury and organomercury were used (1). The concentration of mercury in paints is somewhat uncertain but about 5 % could have been added to the paint (6). Arsenic was also used in the past as a biocide in antifouling paints (1).

Lead has been added to antifouling paints as a stabilizer, a pigment and a biocide (1). Both inorganic and organolead compounds are used in marine paints. The concentration of lead in antifouling paints is typically 1-5 %. Lead was previously widely used in anticorrosive paints, but has now to a great extent been replaced by zinc and aluminium. Cadmium and chromium were also in the past added to give the paint anticorrosive properties and colour.

In the late 60's organotin compounds replaced the traditional copper-containing antifouling paints, because of its excellent antifouling properties. Tributyl tin (TBT) is the most used organotin compound but also triphenyl tin (TPT) is used. The amount of organotin compounds in paints is normally about 10-15 % (1). The use of organotin compounds was banned in most of the world in the 80's for vessels of length less than 25 meters and were replaced by other organic biocides. However, organotin compounds are still widely used on large ocean-going vessels.

Other organic biocides were used as a replacement for organotin. Several pesticides are used as a biocide in antifoulants. Examples of pesticides in use are Diuron and Zineb. DDT was also used as a biocide in antifoulants in the past (7) and it is possible that other persistent chlorinated pesticides have been used in antifoulants.

Prior to World War II and untill the early 90's chlorinated rubber was used as a binder in marine paint. To improve the quality of chlorinated rubber-based paints, PCBs were added as a plasticizer giving the paint good adhesive properties. PCBs also gave the paint excellent resistance against moisture, chemicals, corrosion, and flames. PCBs were added to chlorinated rubber in a concentration of about 10 % resulting in a total concentration of PCB in paints of about 2 %. PCB-containing paints were used as protective and decorative coatings for wood, metal, brick, stone, concrete and fabric surfaces (8). In 1973 OECD recommended restrictions on the use of PCBs (9), and PCBs in paints were gradually replaced by chlorinated paraffin. Norway banned all new use of PCB-containing products in 1980, but some products are still in use.

Table 2 shows the Norwegian paint producers use of PCBs (10). The amount of exported PCB-containing paints from these manufacturers is unknown. From Norwegian authorities it is estimated that about 44 tons of PCB-containing paints were used in Norway (11). Technical paint experts have estimated that about 10 - 15 % of this paint still can be found on ships today, meaning that about 7000 kg PCB are on ships today. If all of this is drained to the marine environment it would contaminate 47.000.000 m^3 of sediments with a PCB- level of 0.1 mg/kg.

Year	Tons
< 1969	35 - 40
1969	10
1970	12
1971	11
1972	2 - 3
1973	0

Table 2 Use of PCB by Norwegian paint manufacturers

3. Paint removal and waste handling

There are two ways of removing old paint and fouling from the hull, sand blasting or the use of high pressure water washing. Waste from sand blasting is generally collected and handled in proper ways today, but in the past the greater part of this waste was drained to the harbour basin. Waste from high pressure water cleaning of the hull is more difficult to collect than waste from sand blasting and even today this waste is mainly drained to the harbour basin. Ship repair yards in Norway have few or no collection systems for waste from high pressure water cleaning of the hull, implying that contamination of harbour basins with paint residues, including antifoulants, continues.

During the spray painting of a vessel a significant fraction (up to 30 %) is released to the environment (12) and the greater part of it is drained to the harbour basin. The application of marine paints is therefore a considerable source of sediment and seawater contamination in harbour basins.

4. Contamination of sediments and sea water with toxic compounds in marine paints

Several investigations of the contamination in marine sediments along the Norwegian coastline shows high concentration of some heavy metals, organotin compounds, PCB and PAH in harbour basins, outside ship repair yards and marine paint factories. This is mainly explained by leakage of biocides from antifouling paints during port call, drainage of marine paints from ship repair yards and paint disposal from paint factories. There is also leakage of oil products from vessels visiting harbours which will give high levels of hydrocarbons in harbour sediments.

The Norwegian State Pollution Control Authority has given priority to cleaning up the sediments in about 20 harbours. These harbours have heavy ship traffic, and often one or several ship repair yards are present or have been present in the past. The ranking of the harbours is based on analyses of a few sediment samples and it is therefore likely that there will be more than these 20 harbours where clean-up efforts will be deemed necessary as further investigations are carried out.

At Haakonsvern, the main naval base in Norway, clean-up activities have been initiated (5). This pilot project demonstrates that it is very costly to clean-up marine sediments and that there are several technical difficulties in attaining the stated objectives. Both the depth and bottom contours make it difficult to meet the requirements from the authorities regarding rest concentrations of toxic compounds in sediments.

The importance of marine paints as a source of PCB contamination of sediments in Norway has recently been addressed by various institutions (13,14,15). Samples of antifouling paints taken in 1996 from a wooden Navy vessel were analysed for content of PCBs at Forsvarets forskningsinstitutt (Norwegian Defence Research Establishment). The maximum concentration of PCB in the paint samples was a surprisingly high 270 mg/kg dry sample and the PCB mixture was preliminarily determined to be Aroclor 1248/1254. It was reported that the vessel was sand blasted in 1985 and repainted several times between 1985 and 1996 (16). Due to findings in 1996 all marine paints used in the Norwegian Navy were analysed for content of PCBs. The results from this investigation showed no signs of PCBs in paints used today.

There is a good correlation between contamination in sediments and ship activities at Haakonsvern. High levels of PCB, TBT and inorganic contaminants are found outside of ship repair yards and around quay structures. Table 3 shows the mean concentration of pollutants in sediments and in seawater (17,18). Based on the fact that these contaminants were widely used in antifouling paints, it is obvious that drainage of antifoulants from ship repair yards and direct release from the hull during port calls are responsible for a considerable part of the contamination found in the sediments. Results from a risk assessment (6) shows that it is necessary to reduce the level of PCB in sediments to about 0.1 mg/kg if consumption restrictions on fish and shellfish is to be repealed.

	Sediments, mg/kg	*Seawater, µg/l*
Hg	*3.8*	*na*[1]
Cu	*510*	*0,8*
Pb	*270*	*0,06*
Zn	*290*	*3,6*
PAH	*5.3*	*na*[1]
Σ 7-PCB	*0.55*	*0,0002*[2]

Table 3 Average sample concentrations of contaminants in sediments and seawater at the Haakonsvern naval base.

[1] *Not analysed*
[2] *Uncertain measurements*

With the assumption that the concentration of PCB in marine paints were about 2 % it is easy to understand that even spills from a minor fraction of the marine paints used will cause a substantial contamination of the sediments. If 1000 litres of PCB-containing marine paints are drained to the harbour basin about 200.000 m^3 of sediments will be contaminated to a level of 0.1 mg PCB/kg. Assuming that the PCB contamination is distributed to a depth of 15 cm, this would lead to a contaminated area of 1.300.000 m^2. The mean concentration of PCB in sediment samples at Haakonsvern is about 0.5 mg/kg[1]. The contaminated area at Haakonsvern is estimated to be about 660.000 m^2. If the mean contaminated depth is set to 15 cm, only about 2500 litres of marine paints would be required to give this contamination level. On average about 2000 litres of PCB-containing paints were used on a new ship (11). If we bear in mind that a lot of the paint can be lost during painting and that some is lost during cleaning of the hull, it is likely that marine paints are responsible for most of the PCB contamination at Haakonsvern Naval Base. The total amount of marine paints used each year and the ship traffic is high at Haakonsvern. In addition there is evidence that the PCB mixture found in the sediments are the same as used in marine paints.

Improved estimates will be attempted when a record of the paint used and their various compositions can be obtained. It is hoped that such estimates can aid in evaluating the amount of PCB removed from the sediments in the area either by uptake in biota or by dissolution and particle transport in the water phase.

As mentioned above, the concentration of PCB in paint residue from the hull can still be high today. It is therefore still a risk that PCB is being supplied to the marine environment and this should be considered when clean-up operations are planned. If paint on vessels today can contain up to 270 mg PCB/kg paint, it

[1] More recent estimates which are based on a total of 312 samples give the concentration of *Σ 7-PCB* at 0.22 mg/kg.

is possible that substantial sediment areas can be contaminated with PCB after the area is cleaned-up. It is therefore necessary to collect as much as possible of the paint residue coming from sand blasting or other cleaning methods. This waste has to be specially treated according to regulations from the authorities. In Norway there are plans to introduce new legislation requiring analysis of all paint waste for content of PCBs. Paint waste with a PCB concentration greater than 50 mg/kg has to be treated as toxic waste (19).

The concentration of PCBs and heavy metals in seawater around Haakonsvern Naval Base is low although the concentration of these compounds is high in the sediments. As seen in table 3, the concentration factor between sediments and seawater for PCBs and copper is about 10^6, but for lead and zink it is an order of magnitude higher and lower respectively. This indicates that both PCB and heavy metals are relatively immobile and only a slow rate of resuspension or dissolution into the water column or biological uptake in the marine food web takes place.

5. Effect on marine life and consumption restrictions

At Haakonsvern Naval Base fish and shellfish have elevated levels of PCB and mercury. PCBs are very stable in the environment and organisms have a low ability to degrade them, the net effect being bio-accumulation. High levels of mercury are found in fish and shellfish because inorganic mercury is converted to organomercury compounds in the environment and organomercury compounds tend to bio-accumulate. It is also reported (1) that organomercury compounds have been used as a biocide in antifouling paints. Analysis done by Forsvarets forskningsinstitutt shows that about 70 % of the total amount of mercury in mussels is organomercury compounds at Haakonsvern Naval Base.

Other heavy metals, except tin, commonly found in harbour sediments have not been seen to give serious impacts on marine organisms. This may be caused by a regulated uptake and secretion of these metals preventing bio-accumulation.

Release of organotin compounds to the environment has caused imposex in some species of mussels and snails. Imposex in snails has been observed along most of the Norwegian coastline and in some places these snails have disappeared altogether.

6. Conclusion

It is clear that toxic compounds used previously and today in marine paints are responsible for some of the present marine pollution problems in coastal waters. Antifouling paints are the source of most of the contamination of organotin compounds in harbour basins. Large amounts of copper and to some extent lead and mercury found in the sediments originate from these paints as well. There is also evidence that a part of the PCB contamination in harbour sediments has come from marine paints and will continue to do so due to the small, but not insignificant, amounts of PCB that are still incorporated in the coating of older ships. Paint samples removed from a Norwegian naval vessel in 1996 contained up to 270 mg PCB/kg paint residue on a dry weight basis.

In order to establish the importance of marine paints as a contaminant source relative to other sources, more detailed information is required on composition and amounts of applied paints as well as the procedures for paint removal. At Haakonsvern Naval Base, being a major Navy service base and having ship traffic predominantly of naval vessels, it is hoped that sufficient information can be pieced together on past and present practices to give a complete source term for sediment contamination.

Prevention of further contamination of the marine environment in harbours requires collection of as much as possible of the paint residues from sand blasting, high pressure water cleaning and paint scraping during ship repairs. Removal of contaminated sediment is probably more costly and not near as effective as preventive measures at the source. Even if all the waste is collected at ship repair yards, toxic compounds in antifouling paints will be released continuously from the hull and contaminate harbour sediments. It is therefore necessary to develop antifouling paints containing toxic compounds, which have specific effects on target organisms and are easily degraded in the environment.

References

1. Arne Willy Henriksen (1999), Jotun Paints A/S, Sandefjord, Norway. Personal communication
2. State Pollution Control Authority (1998) *Forurensede marine sedimenter. Oversikt over tilstand og prioriteringer (Contaminated marine sediments. Status overview and priorities).* SFT-rapport 98:11. In Norwegian
3. NOTEBY Norsk teknisk byggkontroll AS (1997) *Kartlegging av miljøgifter i marine sedimenter i Møre og Romsdal (Assessment of the contamination in sediments in Møre og Romsdal county).* Fylkesmannen i Møre og Romsdal, Molde, Norway. In Norwegian
4. http://www.grida.no. United Nations Environment Programme, GRID-Arendal
5. Laugesen J., Mørch T. (1999) *Haakonsvern Naval Base, Bergen-Norway Pollution Prevention of PCB-Contamination in Sea Sediments.* Joint symposium of RTA Studies, Analyses and Simulation (SAS) Panel, and Committee on the Challenges of Modern Society (`CCMS), on Approaches to the Implementation of Environmental Pollution Prevention Technologies at Military Bases, Budapest, Hungary
6. Det Norske Veritas AS (1995) *Sediment- og marinbiologisk tiltaksundersøkelse – Haakonsvern orlogsstasjon, Bergen kommune 1995 (Sediment and marine biological investigation – Haakonsvern Naval Base, Bergen municipality 1995).* Norwegian Defence Construction Service, Oslo, Norway. In Norwegian
7. Schulze, P. E. (1997) *PCB på skipsverftene (PCB at ship repair yards).* Naturvernforbundet, rapport nr 2/97. In Norwegian
8. Kummeneje Sivilingeniør Ottar Kummeneje a/s (1997) *Miljøtekniske grunnundersøkelser. Hovedrapport – Tekstdel (Assessment of ground pollution. Main report – textual part).* Norwegian Defence Construction Service, Oslo, Norway. In Norwegian
9. Arne Fagerhaug (1999), NOTEBY Norsk teknisk byggkontroll AS, Ålesund, Norway. Personal communication
10. Una C Haug (1999), Jotun Paints A/S, Sandefjord, Norway. Personal communication
11. Monsanto Chemical Company (1948) *AROCLORS as used in chlorinated rubber*, Technical Bulletin No. P-124, St Louis 4, Missouri, USA
12. OECD Environment Directorate (1973) *Polychlorinated Biphenyls. Their use and control.* OECD Environment Directorate, Paris, France
13. Liseth, P., (1973) *Polyklorerte bifenyler (PCB). Utredningsoppdrag for Miljøverndepartementet (Poly Chlorinated Biphenyls (PCB). Report tasked by the Ministry of Environment).* I/S Miljøplan, Høvik, Norway. In Norwegian
14. State Pollution Control Authority (1998) *PCB I BYGNINGMATERIALER. Fugemasse, betongtilsats, gulvbelegg og maling/skipsmaling (PCB IN BUILDING MATERIALS. Grouting, concrete additives and paint).* SFT-rapport 98:09. In Norwegian
15. State Pollution Control Authority (1992) *Kartlegging av helse- og miljøskadelige stoffer i maling, lakk, lim, m.m. Vurdering av alternativer (Assessement of toxic compounds in paint, varnish, adhesive, etc. Evaluation of alternatives).* SFT-rapport 92:09. In Norwegian
16. Roald Hennø, Haakonsvern Naval Base, Bergen, Norway. Personal communication
17. ENCO Environmental Consultants (1998) *Sluttrapport for mudring av delområde 1 på Haakonsvern orlogstasjon i Bergen kommune (Clean-up of subarea 1 at Haakonsvern Naval Base in Bergen. Final report).* Forsvarets bygningstjeneste, Oslo, Norway. In Norwegian
18. Bente Sleire (1999), State Pollution Control Authority, Oslo, Norway. Personal communication