Prolonged copper release rate study with three pleasure boat antifouling paints

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Preface

This is a report of a joint Nordic project aimed to evaluate whether a prolongation of a standard method for release tests of active substance, primarily copper, from antifouling products may give information which is of importance for the evaluation of the environmental effects of modern antifouling paints.

The project was carried out by a project group consisting of Kurt Haglund (project leader), Helena Casabona and Markus Johansson, Swedish Chemicals Agency, and supervised by the Nordic Biocides Group, which presently has the following members: Mary Iakovidou and Johan Helgesson, Swedish Chemicals Agency, Sanna Koivisto, Finnish Environment Institute, Anneli Kojo, Finnish National Product Control Agency for Welfare and Health, Jörgen Larsen and Annika Boye Petersen, Danish Environmental Protection Agency, Elin Gudmundsdottir, The Environment and Food Agency of Iceland, Astrid Gaustad, Susanne Hardt and Christian Dons, Norwegian Pollution control Authority.

The project was financially supported by the Nordic Chemicals Group under the Nordic Council of Ministers. The report was written by Åke Forsberg, AB Thalassa (test laboratory) and Kurt Haglund, Swedish Chemicals Agency.

Summary

The purpose of the study was to evaluate whether a prolongation of a standard method for release tests of active substance, primarily copper, from antifouling products is possible. The aim is to obtain more information about the release behaviour of the products, which may be of importance for the evaluation of the environmental effects of modern antifouling paints. Long-term copper release rate (122 days) has been measured from three different copper-containing pleasure boat anti-fouling paints available on the Swedish market. It is concluded that a prolonged test may give additional information as compared to a standard 45 days test, primarily regarding how the steady-state release of a paint is reached.

Introduction

The purpose of this project was to evaluate whether it is possible to extend a standard method for release (leaching) tests of active substance, primarily copper, from antifouling products in order to obtain information that improves the basis for evaluation of the environmental effects of modern antifouling paints. There is reason to assume that some new antifouling paints for pleasure boats have non-traditional release behaviour in that the copper release rate is low at start (e.g. the first 30 days) and then increases to a higher level. To date, the standard methods normally have a duration of 45 days and thus do not detect this kind of release pattern. Consequently, risks for the aquatic environment due to high release rates later in the service life of the paints will not be detected in the evaluation of antifouling products.

In the present project the default test duration of 45 days has been prolonged to 122 days. Two “modern” antifouling paints have been included in the project, as well as one “traditional” paint. During the planning of the project it was discussed whether additional parameters need to be checked to assure that the conditions of the test are maintained at an acceptable level throughout the test. However, after consultation with a person with good insight into standardisation of this type of test methods (Mr Alistair Finney, presently member of both the ISO and the ASTM standardisation groups) it was decided not to perform any additional measurements.

Depending on the outcome of the project, new suggestions may be made regarding what release test data should be required in the evaluation of antifouling products under the Biocidal Products Directive (98/8/EC).

1. Materials and methods

1.1 Method.

The method used in the study is published by the American Society for Testing and Materials, ASTM D 6442-05, "Standard Test Method for Determination of Copper Release Rate from Antifouling Coatings in Substitute Ocean Water" (ASTM 2005). Some minor modifications of the method versus the ASTM standard are listed in Table 1.

Table 1 Parameters and modifications used by Thalassa versus ASTM D 6442-05.

	ASTM D 6442-05	Thalassa
test material	Polycarbonate	Polycarbonate
temperature (°C)	25 ± 1	24.5 ± 1
rotation time (min)	60	60
painted area (cm ²)	200	180
cylinder diameter (cm)	6.4	6.2
rotation speed (min ⁻¹)	60	60
peripheral speed (m h ⁻¹)	720	720
beaker medium vol. (mL)	1500	1500
cylinder surface/medium volume	0.133	0.120

1.2 Summary of standard test procedure.

Painted and control cylinders are fixed in a holding tank filled with artificial seawater so that the painted surfaces are completely submerged. At the time of measurement, at intervals stated below, the cylinders are transferred from the holding tank to individual measuring beakers filled with new artificial seawater. Release rates are determined by rotating the cylinders in the beakers for 60 minutes. After the rotation is finished, the cylinders are transferred back to the holding tank and the copper concentrations in the beakers are measured. The copper concentrations are used to calculate the release rates of the paints.

1.3 Project-specific test modifications

In this study an additional release measurement was performed at start (day 0). The main modification was that the test duration was extended from the standard 45 days to 122 days.

1.4 Study duration.

The experimental part of the study was performed with start 1 August and end 1 December 2006.

1.5 Test parameters.

All test material during measurements and the holding tank were held in a thermostated room at the desired temperature, 24.5 ± 1 °C.

1.6 Studied paints.

The following three paints were chosen for the project.

- Paint 1: Fabi (International Paint), reg no: 3959.
- Paint 2: Mille Xtra (Hempel A/S), reg no: 4595.
- Paint 3: Hard Racing Xtra (Hempel A/S), reg no: 4596.

Paints 2 and 3 were chosen to represent modern paints that do not have the same initial “surge” of copper release that often is found in older types of paints, but rather display a more flattened-out release rate curve over time. Release rate data on these paints submitted in 2003 (Hempel 2002a, b) to the Swedish Chemicals Agency (KemI) indicate that the release rate has not reached steady state after 45 days and may increase with time after 45 days. Paint 1 represents a traditional older type of paint with high initial release rate of copper. The paints were purchased from an ordinary shop for boat equipment in the town Västerås, Sweden. The reg. no refers to the Pesticides Register of the Swedish Chemicals Agency.

1.6.1 Application of paints.

A total of three paints were applied with brush on cylinders following instructions given by the respective manufacturer with the aim of producing a dry film thickness of minimum 100 µm. Triplicate cylinders were painted with each paint. The painted cylinders were left to dry for 7 days before start of the test. One cylinder was left unpainted to serve as blank control.

1.7 Seawater medium.

Synthetic seawater prepared according to ASTM D-1411-90 (ASTM 1998), excluding addition of trace metals (Solution 3), was used throughout the test. When following this recipe, the resulting salinity of the water was 35-36 ppt, which was further diluted to a salinity between 33 and 34 ppt. Before each release measurement, new seawater was prepared in two 25 L communicating plastic containers and recirculated over an ion exchange column (Amberlite IRC 718) to reduce cation (primarily Cu^{++}) content. This seawater was prepared just after finishing one measurement and then used at the following measurement. Salinity, pH and copper content were measured regularly.

1.8 Holding tank.

As holding tank served two 120 L PE (polyethylene) aquaria connected in series with 100 L of synthetic seawater in each tank. In Table 2 (Appendix A) they are referred to as Holding Tank I and Holding Tank II. The seawater was continuously recirculated using an aquarium pump (Eheim) at a rate of ca 350 L h^{-1} through nozzles that created a flow past the cylinders in the tank. Another similar pump recirculated the water, at a rate of ca 30 L h^{-1} , through an Amberlite IRC 718 ion exchange column which continuously removed Cu^{++} from the seawater.

The water in holding tank system was inspected regularly and monitored for pH, conductivity and temperature, see Table 3. The tanks were open so that the water surface was in contact with the air in the 4 m^2 testing room, which was temperature controlled. Over time some material from the test cylinders accumulated on the bottom of the tanks. Due to the circulation pattern in the tanks the debris is concentrated in spots on the bottom. With a special aspirator (a glass tube connected to a vacuum pump) the material was removed once per week from the system.

1.9 Release measurements.

Measurements of release rates were done at 0, 1, 3, 5, 8, 11, 14, 18, 22, 26, 30, 36, 40, 45, 52, 59, 66, 73, 80, 87, 94, 101, 108, 115 and 122 days after start of the test. The release measurement procedure followed ASTM D 6442-05 (paragraph 9.8) with the modifications indicated in Table 1. The pH of the seawater medium used for measurement was kept at 8.0 ± 0.1 . Care was taken to avoid drying of the painted surfaces whilst transferring them between the holding tank and the measuring beakers.

1.9.1 Sampling and analysis

Immediately after completion of the cylinder rotation and subsequent removal of the cylinders from the measuring beakers, samples of 20 mL, in duplicates, from each beaker were transferred to acid-washed and numbered PE scintillation vials using acid-washed pipette tips. The samples were stored in a freezer (-18 °C) until analysed. The samples were analyzed by a laboratory close to our facility (MeAna consult). Analyses of copper content in one of the samples from each beaker were done as single analysis using flame atomic absorption spectrophotometry (AAS) equipped with graphite furnace. The detection limit, defined as three times the variation between the blanks, has been slightly different at different analysis occasions, and varies between 2 and 5 µg L⁻¹.

1.10 Calculations.

The release rate (R) is expressed as µg Cu cm⁻² d⁻¹ and calculated as follows:

$$R = ((C_S - C_B) * V * D) / (T * A)$$

where:

C_S = copper concentration in sample (µg L⁻¹)

C_B = copper concentration in blank (µg L⁻¹)

D = hours/day

V = volume of seawater in measuring container (L, litres)

T = time of cylinder immersion in measuring container (h, hours)

A = surface area of paint film (cm²)

in this study:

D = 24 h

V = 1.5 L

T = 1 h

A = 180 cm²

which gives: $R = (C_S - C_B) * 0.20$

The cumulative release (R_C) over the test period is expressed as µg Cu cm⁻² and calculated as

$$R_{0,122} = \sum R_{i,j} (j-i) = \sum (R_i + R_j) / 2 * (j-i)$$

where:

$R_{0,122}$ = the cumulative release ($\mu\text{g Cu cm}^{-2}$) from the start of the trial through to Day 122,

$R_{i,j}$ = the mean release rate ($\mu\text{g Cu cm}^{-2} \text{ d}^{-1}$) between consecutive sampling days i and j for all data points between the start of the trial and Day 122,

i and j = time elapsed (d, days) since start of the trial for each pair of consecutive data points, specifically 0 and 1, 1 and 3, 3 and 7 days, etc., respectively, and

R_i and R_j = the mean release rates ($\mu\text{g Cu cm}^{-2} \text{ d}^{-1}$) for each set of triplicate test cylinders for each pair of consecutive days from the start of the trial through to Day 122, specifically Days 0 and 1, Days 1 and 3, Days 3 and 7, etc., respectively.

The blank (= control X) was with one exception below the detection limit, and therefore C_B has been set as zero in the equation.

2. Results and Discussion

2.1 Application of paints.

Some brush marks occurred in the resulting paint surface, as can be seen in the pictures of the painted cylinders before start and after test period, respectively, in Appendix C. When this type of paint is applied with brush it is not possible to get a completely even surface, and to some extent there will be marks from the brush depending on the properties of the paint, primarily its viscosity. However, previous experience from a ring test of the ISO copper release test method performed earlier (1997) shows that such unevenness of the surface does not significantly affect the test results.

2.2 Holding tank and test medium.

The pH of the seawater was kept at $\text{pH } 8.0 \pm 0.1$ during the test. The copper concentration in the holding tank was kept below $100 \mu\text{g L}^{-1}$ throughout the test; see Table 2 (Appendix A). The copper concentration in the test medium before release measurement was overall very low (below the detection limit of $2\text{-}5 \mu\text{g L}^{-1}$).

2.3 Copper release.

All raw data from copper analyses of water from release measurements of the different tested paints is included in Appendix B together with copies of the original test protocols from the analysis laboratory (MeAna consult). The analysis results are presented in Table 6 (Appendix B), with the uncertainty of the analysis indicated as coefficient of variation (CV, %), i.e. the relative standard deviation. Values below the detection limit are presented as half the detection limit value, a practice that may be used when a value must be used in calculations despite being below detection (Asante-Duah 1998).

The results are presented as release rates expressed as $\mu\text{g Cu cm}^{-2} \text{ day}^{-1}$, in Table 4 (Appendix A) and as graphs in Figure 1. The three different paints show very different release rate patterns. All three show low release rates day zero but whilst Fabi and Hard Racing Xtra increase rapidly Mille Xtra remains at very low release rates throughout the test. The copper concentrations obtained in the Mille Xtra measuring beakers were low throughout the test, and sometimes at or below the de-

tection limit. Therefore, the release values fluctuate more and are more uncertain for this paint. Hard Racing Xtra increases to the highest release rate during day 21 and after that slowly decreases during the rest of test period. Fabi increases very rapidly to the highest release rate during day 1, and decreases after that and from day 66 it is comparable to the low release rate from Mille Xtra.

The cumulative release of Cu cm^{-2} over the entire study period of 122 days is presented in Table 5 and as graphs in Figure 2.

The copper release from the “traditional” paint (Fabi) corresponds well with what could be expected from earlier data (International 1991), both regarding the level and the pattern of release. For the two “modern” paints Mille Xtra and Hard Racing Xtra, it is more difficult to relate to earlier data. New information was submitted in 2006 (Hempel 2006), i.e. after the planning of the present study, with release data that differed from that originally submitted in 2003 (Hempel 2002a, b). The increasing release rate with time which was obvious in the tests submitted in 2003 and also could be expected to continue after the actual test duration of 45 days was no longer present in the release studies submitted in 2006. The test duration of these more recent studies was 85 days, i.e. considerably longer than the normal 45 days, and furthermore this data corresponds quite well with the results obtained in the present study. It should also be mentioned that the actual average release rates were slightly different in the two submissions: for Mille Xtra $6 \mu\text{g/cm}^2/\text{d}$ (2006) as compared to $2 \mu\text{g/cm}^2/\text{d}$ (2003) and for Hard Racing Xtra $10 \mu\text{g/cm}^2/\text{d}$ (2006) as compared to $12 \mu\text{g/cm}^2/\text{d}$ (2003). The reasons for the observed differences are not clear, and one possibility is that the two paints have been modified since their introduction on the Swedish market in 2003. This part of the discussion which involves data previously submitted to KemI has been added to the report by KemI and the documents referred to (Hempel 2002a, b, 2006, International 1991) have not been disclosed to third party.

2.4 Conclusion.

It is concluded that the prolongation of a release test to 122 days may give additional information as compared to a standard 45 days test, primarily regarding how the steady-state release of a paint is reached. For the traditional type paint Fabi and the new type paint Hard Racing Xtra the release curves decrease and/or flatten out from 45 days and onwards, which could not easily be predicted from a 45 days test. For Mille Xtra a prolongation gives less additional information since the release rate is more or less constant over the entire 122 days period.

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Sammanfattning

Syftet med denna studie var att utvärdera om det är möjligt att förlänga en standardmetod för mätning av läckage av aktiv substans, i första hand koppar, från antifoulingprodukter. Målet var att erhålla mer information om produkternas läckageprofil, som kan vara av betydelse för utvärdering av deras effekter på den akvatiska miljön. Långtidsmätning (122 dagar) av kopparläckage har studerats för tre olika fritidsbåtfärger på den svenska marknaden. Slutsatsen av studien är att en förlängd test kan ge ytterligare information jämfört med en standardtest på 45 dagar, framför allt avseende hur läckaget hos en färg stabiliseras på en nivå som består under längre tid, s.k. steady-state.

Appendices

A. Figures.

Figure 1 Release rates of Cu from the three studied paints over the entire test period. Data points are means of three measurements. The release rates are also listed in Table 5. Note that there are different scales on the primary (left) and secondary (right) Y axes.

Figure 2 Cumulative release of Cu from the three studied paints over the entire test period. Data points are means of three measurements. The release rates are also listed in Table 6. Note that there are different scales on the primary (left) and secondary (right) Y axes.

B. Tables.

Table 2 Concentrations of Cu ($\mu\text{g L}^{-1}$) in the test medium before release measurement (Test Water), in water from the control cylinder after release measurement (Control X) and in the holding tank water (Holding Tank I and II); n.a. = not analysed

	Day	Test Water	Control X	Holding Tank I	Holding Tank II
06 08 01	0	<5	<5	<5	<5
06 08 02	1	<5	<5	n.a.	n.a.
06 08 04	3	<5	<5	n.a.	n.a.
06 08 08	7	<5	<5	22	5
06 08 11	10	<5	<5	n.a.	n.a.
06 08 15	14	<5	<5	n.a.	n.a.
06 08 22	21	<5	<5	n.a.	n.a.
06 08 25	24	<5	<5	n.a.	n.a.
06 08 29	28	<5	<5	n.a.	n.a.
06 09 01	31	<5	<5	n.a.	n.a.
06 09 05	35	<5	<5	n.a.	n.a.
06 09 08	38	<5	<5	n.a.	n.a.
06 09 12	42	<5	<5	n.a.	n.a.
06 09 15	45	<5	<5	19	<5
06 09 22	52	<2	<2	n.a.	n.a.
06 09 29	59	<2	<2	n.a.	n.a.
06 10 06	66	<2	7.0	n.a.	n.a.
06 10 13	73	<2	<2	n.a.	n.a.
06 10 20	80	8	<2	n.a.	n.a.
06 10 27	87	<2	<2	10	3
06 11 03	94	<2	<2	n.a.	n.a.
06 11 10	101	<2	<2	n.a.	n.a.
06 11 17	108	<2	<2	n.a.	n.a.
06 11 24	115	<2	<2	n.a.	n.a.
06 12 01	122	<2	<2	<2	<2

Table 3 Results from measurements of pH, salinity and temperature in the holding tank water (Holding Tank) and test medium before release measurement (Test Water) during the study. Days of release measurement are marked with yellow background colour. nm = not easured

Date	Day	Holding Tank			Test Water		
		pH	Salinity	Temp	pH	Salinity	Temp
06 08 01	0	7.99	33.80	24.10	8.04	33.40	25.20
06 08 02	1	8.04	34.00	24.30	8.02	33.50	25.10
06 08 04	3	8.05	33.60	24.40	8.04	33.90	25.60
06 08 06	5	8.07	33.90	24.10	8.13	34.60	25.30
06 08 08	7	8.08	33.60	24.10	8.11	33.30	25.10
06 08 11	10	8.05	33.30	24.20	8.13	33.90	25.30
06 08 15	14	8.07	33.60	23.60	8.14	33.40	24.50
06 08 16	15	8.05	33.20	24.80	8.10	33.70	25.60
06 08 18	17	8.06	33.40	24.70	8.09	33.20	25.40
06 08 20	19	8.07	33.70	24.70	8.09	33.30	25.50
05 08 26	20	8.09	34.00	24.10	8.11	33.30	24.80
06 08 22	21	8.06	33.60	24.20	8.08	33.40	24.80
06 08 25	24	8.05	33.40	24.10	8.08	33.20	24.80
06 08 27	26	8.07	33.70	24.30	8.09	33.30	24.90
06 08 29	28	8.06	33.60	24.10	8.08	33.60	24.80
06 09 01	31	8.09	34.10	24.00	8.09	33.90	24.80
06 09 02	32	8.02	33.20	24.10	8.02	34.10	24.90
06 09 05	35	7.98	34.00	26.10	7.95	33.0	28.10
06 09 08	38	8.04	33.90	23.90	7.98	33.70	25.60
06 09 10	40	8.05	33.30	26.00	7.95	34.00	28.20
06 09 12	42	8.08	34.10	24.90	8.00	33.60	26.50
06 09 13	43	8.00	33.20	26.60	8.02	33.60	28.70
06 09 15	45	8.05	33.70	24.40	8.08	33.80	25.60
06 09 17	47	8.03	33.70	24.10	8.08	33.90	25.10
06 09 19	49	8.04	33.50	24.30	8.04	33.30	25.20
06 09 22	52	8.06	33.30	24.10	8.05	33.50	24.90
06 09 27	57	8.05	34.10	23.70	8.07	33.80	24.40
06 09 29	59	8.00	33.70	24.10	8.01	33.20	24.90
06 09 30	60	8.02	33.60	24.00	8.05	33.40	25.00
06 10 01	61	8.03	33.80	24.10	8.05	33.40	24.90
06 10 03	63	8.05	33.20	24.00	8.06	33.70	24.80
06 10 06	66	8.05	33.40	24.00	8.07	33.10	24.80
06 10 07	67	8.04	33.70	24.10	8.08	33.30	24.90
06 10 09	69	8.05	34.10	23.80	8.02	33.60	24.80
06 10 11	71	8.01	33.50	23.90	8.03	33.40	24.80
06 10 13	73	8.02	33.90	23.80	8.04	33.50	24.80
06 10 14	74	8.03	33.20	23.80	8.06	33.80	24.80
06 10 17	77	8.02	34.00	23.40	8.01	33.70	24.50
06 10 20	80	7.99	33.60	23.80	8.00	33.70	24.80
06 10 22	82	8.00	34.10	24.00	8.04	33.90	25.00
06 10 26	86	8.03	33.90	23.80	8.04	33.60	24.90
06 10 27	87	8.03	33.20	23.80	8.04	33.20	24.90
06 10 29	89	8.03	33.60	23.40	8.08	33.60	24.80
06 11 01	92	8.04	34.00	23.00	8.07	33.60	24.50
06 11 03	94	8.02	33.30	23.60	8.04	33.50	24.90
06 11 05	96	8.03	34.00	23.70	8.07	33.70	25.00
06 11 08	99	8.03	33.60	23.70	8.02	33.70	24.90
06 11 10	101	8.04	34.10	23.70	8.02	33.60	25.10
06 11 12	103	8.04	33.60	23.70	8.09	33.90	24.90
06 11 14	105	8.06	33.20	23.70	8.05	33.70	24.90
06 11 17	108	8.01	33.70	24.00	8.02	33.60	25.10
06 11 19	110	8.02	39.60	24.00	8.03	39.30	25.20
06 11 21	112	8.01	37.80	24.00	8.01	37.40	25.20
06 11 23	114	8.03	36.20	23.40	8.03	35.50	25.20
06 11 24	115	nm	nm	nm	nm	nm	nm
06 11 25	116	8.03	34.60	23.90	8.03	33.90	24.90
06 11 29	120	8.02	35.00	24.00	8.02	35.60	25.10
06 12 01	122	8.04	33.50	23.90	8.02	33.30	24.90

Table 4 Raw data from analyses of samples from each cylinder in release measurements presented as the concentration of copper, together with the mean value for each paint and sampling occasion ($\mu\text{g Cu l}^{-1}$). Values below the detection limit are presented as half the detection limit value. CV = Coefficient of variation. , # = MeAna sample no.

Day	#	Fabi	#	Mille Xtra	#	Hard Racing Xtra
2006 08 01 0	5	33	8	8	11	13
	6	39	9	12	12	21
	7	28	10	11	13	15
	Mean	33.3	Mean	10.3	Mean	16.3
2006 08 02 1	CV	16.6	CV	20.2	CV	25.5
	16	159	19	8	22	17
	17	157	20	2.5	23	17
	18	179	21	2.5	24	16
2006 08 04 3	Mean	165.0	Mean	4.3	Mean	16.7
	CV	7.4	CV	74.0	CV	3.5
	27	135	30	10	33	66
	28	105	31	6	34	64
2006 08 08 7	29	106	32	5	35	65
	Mean	115.3	Mean	7.0	Mean	65.0
	CV	14.8	CV	37.9	CV	1.5
	40	67	43	6	46	100
2006 08 11 10	41	70	44	2.5	47	147
	42	73	45	2.5	48	124
	Mean	70.0	Mean	3.7	Mean	123.7
	CV	4.3	CV	54.6	CV	19.0
2006 08 15 14	51	95	54	8	57	150
	52	95	55	6	58	152
	53	92	56	8	59	170
	Mean	94.0	Mean	7.3	Mean	157.3
2006 08 22 21	CV	1.8	CV	15.6	CV	7.0
	62	66	65	7	68	174
	63	66	66	11	69	196
	64	68	67	2.5	70	185
2006 08 25 24	Mean	66.7	Mean	6.8	Mean	185.0
	CV	1.7	CV	62.5	CV	6.0
	73	57	76	2.5	79	186
	74	56	77	7	80	184
2006 08 29 28	75	54	78	2.5	81	190
	Mean	55.7	Mean	4.0	Mean	186.7
	CV	2.8	CV	65.0	CV	1.6
	84	50	87	2.5	90	148
2006 09 01 31	85	51	88	2.5	91	175
	86	49	89	2.5	92	168
	Mean	50.0	Mean	2.5	Mean	163.7
	CV	2.0	CV	0	CV	8.6
2006 09 05 35	95	43	98	2.5	101	166
	96	43	99	2.5	102	162
	97	46	100	2.5	103	158
	Mean	44.0	Mean	2.5	Mean	162.0
2006 09 08 38	CV	3.9	CV	0	CV	2.5
	106	40	109	2.5	112	145
	107	38	110	2.5	113	177
	108	38	111	2.5	114	177
2006 09 09 38	Mean	38.7	Mean	2.5	Mean	166.3
	CV	3.0	CV	0	CV	11.1
	117	42	120	2.5	123	170
	118	41	121	2.5	124	170
2006 09 10 38	119	44	122	2.5	125	162
	Mean	42.3	Mean	2.5	Mean	167.3
	CV	3.6	CV	0	CV	2.8
	128	21	131	6	134	162
2006 09 11 38	129	23	132	2.5	135	154
	130	25	133	2.5	136	131
	Mean	23.0	Mean	3.7	Mean	149.0
	CV	8.7	CV	54.6	CV	10.8

Table 4 continued.

Date	Day	#	Fabi	#	Mille Xtra	#	Hard Racing Xtra
2006 09 12	42	139	15	142	2.5	145	118
		140	17	143	2.5	146	115
		141	14	144	2.5	147	110
		Mean	15.3	Mean	2.5	Mean	114.3
2006 09 15	45	CV	10.0	CV	0	CV	3.5
		152	22	155	2.5	158	126
		153	19	156	2.5	159	126
		154	20	157	2.5	160	116
2006 09 22	52	Mean	20.3	Mean	2.5	Mean	122.7
		CV	7.5	CV	0	CV	4.7
		163	11	166	5.5	169	110
		164	13	167	6.7	170	109
2006 09 29	59	165	14	168	5	171	100
		Mean	12.7	Mean	5.7	Mean	106.3
		CV	12.1	CV	15.3	CV	5.2
		174	14	177	6.4	180	121
2006 10 06	66	175	14	178	5.5	181	110
		176	15	179	6	182	105
		Mean	14.3	Mean	6.0	Mean	112.0
		CV	4.1	CV	7.5	CV	7.3
2006 10 13	73	185	6.2	188	11	191	99
		186	6.7	189	6	192	102
		187	12	190	4.6	193	102
		Mean	8.3	Mean	7.2	Mean	101.0
2006 10 20	80	CV	38.7	CV	46.7	CV	1.7
		196	5	199	7	202	113
		197	6	200	7	203	120
		198	6	201	5	204	113
2006 10 27	87	Mean	5.7	Mean	6.3	Mean	115.3
		CV	10.2	CV	18.3	CV	3.5
		207	13	210	8	213	97
		208	7	211	10	214	100
2006 11 03	94	209	5	212	11	215	94
		Mean	8.3	Mean	9.7	Mean	97.0
		CV	50.0	CV	16.0	CV	3.0
		220	1	223	3	226	83
2006 11 10	101	221	1	224	5	227	78
		222	1	225	3	228	82
		Mean	1.0	Mean	3.7	Mean	81.0
		CV	0	CV	31.0	CV	3.0
2006 11 17	108	231	2	234	4.7	237	112
		232	1	235	3.9	238	88
		233	2.8	236	4.3	239	87
		Mean	1.9	Mean	4.3	Mean	95.7
2006 11 24	115	CV	47.0	CV	9.0	CV	15.0
		242	2	245	4.9	248	75
		243	1	246	5.8	249	77
		244	3.2	247	5.7	250	76
2006 12 01	122	Mean	2.1	Mean	5.5	Mean	76.0
		CV	52.4	CV	8.9	CV	1.3
		253	4.1	256	6.9	259	88
		254	3.9	257	5.9	260	77
2006 12 01	122	255	4.4	258	5.5	261	76
		Mean	4.1	Mean	6.1	Mean	80.3
		CV	6.1	CV	10.8	CV	8.3
		264	1	267	5.5	270	69
2006 12 01	122	265	1	268	4.2	271	62
		266	1	269	4.1	272	54
		Mean	1	Mean	4.6	Mean	61.7
		CV	0	CV	17.0	CV	12.2
2006 12 01	122	277	1	280	3.7	283	49
		278	3	281	3.8	284	75
		279	1	282	3.8	285	51
		Mean	1.7	Mean	3.8	Mean	58.3
2006 12 01	122	CV	67.7	CV	1.6	CV	24.8

Table 5 Copper release rates for the three tested paints at the respective release measurement occasions (means of three measurements, $\mu\text{g Cu cm}^{-2} \text{ day}^{-1}$).

Day	Fabi	Mille Xtra	Hard Racing Xtra
0	6.7	2.1	3.3
1	33	0.9	3.3
3	23.1	1.4	13
7	14	0.74	24.7
10	18.8	1.5	31.5
14	13.3	1.4	37.0
21	11.1	0.8	37.3
24	10	0.5	32.7
28	8.8	0.5	32.4
31	7.7	0.5	33.3
35	8.8	0.5	33.5
38	4.6	0.74	29.8
42	3.1	0.5	22.9
45	4.1	0.5	24.5
52	2.5	1.1	21.3
59	2.9	1.2	22.4
66	1.7	1.4	20.2
73	1.1	1.3	23.1
80	1.7	1.9	19.4
87	0.2	0.74	16.2
94	0.38	0.86	19.1
101	0.42	1.1	15.2
108	0.8	1.2	16.1
115	0.2	0.92	12.3
122	0.34	0.76	11.7

Table 6. Cumulative copper release for the three tested paints (means of three measurements, $\mu\text{g Cu cm}^{-2}$).

Day	Fabi	Mille Xtra	Hard Racing Xtra
1	19.9	1.5	3.3
3	76	3.8	19.6
7	150	8.0	95
10	199	11.4	179
14	264	17,2	316
21	349	24,9	576
24	381	26,8	681
28	418	28,8	812
31	443	30,3	910
35	476	32,3	1044
38	496	34,2	1139
42	511	36,7	1244
45	522	38,2	1315
52	545	43,8	1475
59	564	51.8	1628
66	580	60.9	1778
73	590	70.4	1929
80	600	81.6	2078
87	607	90,8	2202
94	609	96.4	2376
101	611	103	2446
108	616	111	2556
115	619	119	2655
122	621	125	2739

C. Analysis protocols (6 pages).

Sid 1(1)

RAPPORT
utfärdad av ackrediterat laboratorium
REPORT issued by an Accredited Laboratory

Uppdragsgivare:	THALASSA AB	Rapportmottagare:	Åke Forsberg		
Utskriftsdatum:	060810	Analysdatum:	060809-10		
		Ankomstdatum:	060808		
<p>Provets art: Vatten (syntetiskt havsvatten)</p> <p>Provet taget f.o.m: Ingen uppgift t.o.m: Av: Ingen uppgift</p> <p>Provtagningsplats: Thalassa Uppsala</p> <p>Analysmetod: GFAAS instrument Perkin-Elmer 4100 ZL</p>					
Prov Nr	Cu µg/l	Prov Nr	Cu µg/l	Prov Nr	Cu µg/l
1	<5	25	<5		
2	<5	26	<5		
3	<5	27	135		
4	<5	28	105		
5	33	29	106		
6	39	30	10		
7	28	31	6		
8	8	32	5		
9	12	33	66		
10	11	34	64		
11	13	35	65		
12	21	36	<5		
13	15	37	22+-2		
14	<5	38	5		
15	<5	39	<5		
16	159	40	67+-1		
17	157	41	70+-1		
18	179	42	73+-1		
19	8	43	6		
20	<5	44	<5		
21	<5	45	<5		
22	17	46	100+-1		
23	17	47	147+-10		
24	16	48	124+-2		
<p>Kommentarer/Upplysningar: Certifierat ref. material SPS-SW1 cert. halt=20+-1 ppb uppmätt 19,0+-0,6 ppb n=6 Angiven osäkerhet baseras på två olika spädningar. Resultaten ej korrekt avrundade m.a.p. mätosäkerheten.</p>					
<p>Mätosäkerhet: Se bilaga 2:1 2005-06-15. De uppmätta värdena baseras på sötvatten.</p> <p><i>Roland Uhrberg</i> Roland Uhrberg, Analysansvarig</p>					

Denna rapport får endast återges i sin helhet, om inte utfärdande laboratorium i förväg skriftligen godkänt annat."

Sid 1(2)

RAPPORTutförd av ackrediterat laboratorium
REPORT issued by an Accredited Laboratory

Uppdragsgivare:	THALASSA AB	Rapportmottagare:	Åke Forsberg		
Utskriftsdatum:	060927	Analysdatum:	060925-27		
		Ankomstdatum:	060915		
Provets art: Vatten (syntetiskt havsvatten) Prov taget f.o.m: Ingen uppgift t.o.m: Av: Ingen uppgift Provtagningsplats: Thalassa Uppsala Analysmetod: GFAAS instrument Perkin-Elmer 4100 ZL					
Prov Nr	Cu µg/l	Prov Nr	Cu µg/l	Prov Nr	Cu µg/l
49	<5	73	57	97	46
50	<5	74	56	98	<5
51	95	75	54	99	<5
52	95	76	<5	100	<5
53	92	77	7	101	166
54	8	78	<5	102	162
55	6	79	186	103	158
56	8	80	184	104	<5
57	150	81	190	105	<5
58	152	82	<5	106	40
59	170	83	<5	107	38
60	<5	84	50	108	38
61	<5	85	51	109	<5
62	66	86	49	110	<5
63	66	87	<5	111	<5
64	68	88	<5	112	145
65	7	89	<5	113	177
66	11	90	148	114	177
67	<5	91	175	115	<5
68	174	92	168	116	<5
69	196	93	<5	117	42
70	185	94	<5	118	41
71	<5	95	43	119	44
72	<5	96	43		
Kommentarer/Upplysningar: Certifierat ref. material SPS-SW1 cert. halt=20±1 ppb uppmätt 19,7±0,3 ppb n=17 Resultaten ej korrekt avrundade m.a.p. mätosäkerheten.					
Mätosäkerhet: Se bilaga 2:1 2005-06-15. De uppmätta värdena baseras på sötvatten.					
 Roland Uhrberg, Analysansvarig					

Denna rapport får endast återges i sin helhet, om inte utfärdande laboratorium i förväg skriftligen godkänt annat."

Sid 2(2)

RAPPORTutfärdad av ackrediterat laboratorium
REPORT issued by an Accredited Laboratory

Uppdragsgivare:	THALASSA AB	Rapportmottagare:	Åke Forsberg		
Utskriftdatum:	060927	Analysdatum:	060925-27		
		Ankomstdatum:	060915		
Provets art: Vatten (syntetiskt havsvatten) Provet taget f.o.m: Ingen uppgift t.o.m: Av: Ingen uppgift Provtagningsplats: Thalassa Uppsala Analysmetod: GFAAS instrument Perkin-Elmer 4100 ZL					
Prov Nr	Cu µg/l	Prov Nr	Cu µg/l	Prov Nr	Cu µg/l
120	<5	144	<5		
121	<5	145	118		
122	<5	146	115		
123	170	147	110		
124	170	148	<5		
125	162	149	19		
126	<5	150	<5		
127	<5	151	<5		
128	21	152	22		
129	23	153	19		
130	25	154	20		
131	6	155	<5		
132	<5	156	<5		
133	<5	157	<5		
134	162	158	126		
135	154	159	126		
136	131	160	116		
137	<5				
138	<5				
139	15				
140	17				
141	14				
142	<5				
143	<5				
Kommentarer/Upplysningar: Certifierat ref. material SPS-SW1 cert. halt=20±1 ppb uppmått 19,7±0,3 ppb n=17 Resultaten ej korrekt avrundade m.a.p. mätosäkerheten.					
Mätosäkerhet: Se bilaga 2:1 2005-06-15. De uppmätta värdena baseras på sötvatten.					
 Roland Uhrberg, Analysansvarig					

Denna rapport får endast återges i sin helhet, om inte utfärdande laboratorium i förväg skriftligen godkänt annat."

Sid 1(2)

RAPPORTutförd av ackrediterat laboratorium
REPORT issued by an Accredited Laboratory

Uppdragsgivare:	THALASSA AB	Rapportmottagare:	Åke Forsberg
Utskriftdatum:	061121	Analysdatum:	061116-21
		Ankomstdatum:	061101
Provets art: Vatten (syntetiskt havsvatten)			
Provet taget f.o.m.: Ingen uppgift		t.o.m.:	
Provtagningsplats: Thalassa Uppsala		Av: Ingen uppgift	
Analysmetod: GFAAS instrument Perkin-Elmer 4100 ZL.			
Låga halter spädda 1-3 kalibr. St.add. Övriga spädda 1-5 vanlig kalibrering.			
Prov Nr	Cu µg/l	Prov Nr	Cu µg/l
161	<2	185	6,2+-8,6%
162	<2	186	6,7+-13,8%
163	11+-2,1%	187	12+-13,8%
164	13+-3,8%	188	11+-2,9%
165	14	189	6
166	5,5+-2,5%	190	4,6+-4%
167	6,7+-12,8%	191	99
168	5	192	102
169	110	193	102
170	109	194	<2
171	100	195	<2
172	<2	196	5
173	<2	197	6
174	14+-10,7%	198	6
175	14+-0,7%	199	7
176	15+-3,3%	200	7
177	6,4+-5,7%	201	5
178	5,5+-17%	202	113
179	6	203	120
180	121	204	113
181	110	205	8
182	105	206	<2
183	<2	207	13
184	7,0+-10%	208	7
Kommentarer/Uppllysningar: Certifierat ref. material SPS-SW1 cert. halt=20+-1 ppb uppmätt 18,0+-0,4 ppb n=4 Angiven osäkerhet baseras två två olika spädningar. Resultaten ej korrekt avrundade m.a.p. mätosäkerheten.			
Mätosäkerhet: Se bilaga 2:1 2005-06-15. De uppmätta värdena baseras på sölvatten.			
 Roland Uhrberg, Analysansvarig			

Denna rapport får endast ålæges i sin helhet, om inte utförande laboratorium i förväg skriftligen godkänt annat."

MeAna - Konsult
MILJÖANALYSER

utfärdad av ackrediterat laboratorium
REPORT issued by an Accredited Laboratory

[illegible]

EKEBYVÄGEN 10 A7 752 75 UPPSALA - SWEDEN TEL 018-50 60 60 FAX 018-50 60 65 e-mail Uhrberg@telia.com www.meana.se

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REPORT issued by an Accredited Laboratory

Uppdragsgivare:	THALASSA AB	Rapportmottagare:	Åke Forsberg
Utskriftdatum:	061215	Analysdatum:	061205-11
		Ankomstdatum:	061203

Provets art: Vatten (syntetiskt havsvatten)

Provet taget f.o.m: Ingen uppgift t.o.m: Av: Ingen uppgift

Provtagningsplats: Thalassa Uppsala

Analysmetod: GFAAS instrument Perkin-Elmer 4100 ZL.

Låga halter spädda 1-3 kalibr. St.add. Övriga spädda 1-5 vanlig kalibrering.

Prov Nr	Cu µg/l	Prov Nr	Cu µg/l	Prov Nr	Cu µg/l
229	<2	251	<2	273	<2
230	<2	252	<2	274	<2
231	2+-12,9%	253	4,1+-16%	275	<2
232	<2	254	3,9+-0,6%	276	<2
233	2,8+-77%	255	4,4+-5,4%	277	<2
234	4,7+-2%	256	6,9+-13,2%	278	3+-8%
235	3,9+-1,2%	257	5,9+-3,1%	279	<2
236	4,3+-7%	258	5,5+-2,3%	280	3,7+-7,3%
237	112+-1,8%	259	88+-2,9%	281	3,8+-11,9%
238	88+-1,8%	260	77+-3,4%	282	3,8+-6,1%
239	87+-0,5%	261	76+-1,6%	283	49+-4%
240	<2	262	<2	284	75+-1,3%
241	<2	263	<2	285	51+-2%
242	2+-25%	264	<2		
243	<2	265	<2		
244	3,2+-3,0%	266	<2		
245	4,9+-4,7%	267	5,5+-2,2%		
246	5,8+-8,8%	268	4,2+-2,3%		
247	5,7+-4,9%	269	4,1+-9,8%		
248	75	270	69+-1,1%		
249	77	271	62+-1,6%		
250	76	272	54+-3,5%		

Kommentarer/Upplysningar: Certifierat ref. material SPS-SW1 cert. halt=20+-1 ppb
uppmätt 19,1+-0,9 ppb n=5
Angiven osäkerhet baseras två två olika spädningar.
Resultaten ej korrekt avrundade m.a.p. mätosäkerheten.

Mätosäkerhet: Se bilaga 2:1 2005-06-15. De uppmätta värdena baseras på sötvatten.

Roland Uhrberg
Roland Uhrberg, Analysansvarig

Denna rapport får endast återges i sin helhet, om inte utförande laboratorium i förväg skriftligen godkänt annat."

D. Photographs of test cylinders (before and after testing).