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Development and properties of a new oil binding system for marine application

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ABSTRACT 299992:

Traditional marine oil response technology is based on ship borne techniques with oil/water separation by skimmer. These systems are very sensitive to weather conditions and have a long response time. Furthermore, conventional solid binder systems are unsuitable for marine application.

Within the research project BIOBIND, a new binder system for marine application was developed and evaluated. The oil binders are made of biogenic and biodegradable wood-fiber, which cause only a small environmental impact and are very cost-efficient. They show a high porosity of 85 %, a high oil absorption capacity of approx. 600 kg m^{-3} (especially for thin oil films down to 0.03 mm), and a high retention capacity for oil. On the water surface, these binders achieve an oil recovery rate of 80 % with a coverage dosage of 11 %. Having a square geometry of 50 x 50 mm and a thickness of 4 mm, the binder has superior properties for manufacturing, storage, oil adsorption and recovery. The binder system was produced in industrial scale and tested during a large scale field experiment at the Baltic Sea in the summer of 2013. Its binding capacity and flotation ability were evaluated in mesocosm tests. Because of its hydrophobic properties, the binder floated for more than 8 days. Experiments of airborne application, monitoring, and ship borne recovery confirmed the suitability of the binder system. Due to airborne distribution, the binder system is also suitable for application during bad weather conditions and on shallow water territories.

The paper describes the development of a solid oil binding system suitable for new marine application and presents the results of laboratory scale, mesocosm and field experiments.

INTRODUCTION:

The current state of marine technology for oil spill control is mostly based on mechanical or chemical treatment of oil spills. These methods use oil skimmers (Broje et al, 2005), oil booms and dispersants or controlled burning (Jensen et al, 2011). For bad weather conditions (wind force > 10 m s^{-1}) only the airborne application of dispersants are suitable. In some areas (e.g. Baltic Sea, North Sea) the use of dispersants is forbidden (HELCOM 1992).
The application of natural fiber based sorbents (e.g. kapok fiber or cotton grass) with and without microorganisms for oil cleanup of water surfaces was already studied in laboratory and mesocosm scale trials (Huang et al, 2005 and Suni et al, 2007). However the shapes as well as the floating and recovery behavior of these systems are not suitable for rough marine conditions. Because of this situation, the cooperation project “BIOBIND” has been started in 2011 (Siewert et al 2014). One objective of this project is focusing on the development of a biodegradable, wood-fiber based oil binding system. The binder system is focusing on oil spills up to 50 t in size. Due to its distribution by airplane and outstanding swimming ability, the binder is suitable for spills in shallow water territories or during bad weather conditions. Therefore the binders had to meet the following special application requirements:

- Suitability for storage to enable a fast application up to 2 hours after oil spill detection,
- Stability due to mechanical forces during storage, distribution and recovery,
- High and fast oil sorption rate,
- Suitable floating behavior, even under rough marine conditions,
- Nontoxic to the environment.

In addition the immobilization of oil degrading microorganisms on the binder surface and their use for oil degrading was also investigated in the BIOBIND cooperation project and will be described in Safonova et al 2014 and Hähnel et al 2014.

METHODS:

Binder development

Very important facts for marine oil spills are the rapid distribution of the oil spill to large areas after accidents or illegal oil discharges as well as the fast reduction of oil film thickness down to one-hundredth of one millimeter (see table 1 and 2).

Table 1: Crude oil film thickness vs. oil mass and lag- time (VPS 2013)

Lag-time in hours	**Oil film thickness [mm] at**				
	5 t	50 t	500 t	5000 t	50000 t
1	0.98	3.6	7.5	15.8	50.1
2	0.348	2.5	5.3	11.5	25.1
5	0.088	0.9	3.4	7	15.7
10	0.031	0.3	2.4	5.1	11.1
24		0.1	0.84	3.3	7.2
48			0.3	2.4	5.1
72			0.16	1.6	4.1
96			0.105	1.05	3.6
500			0.009	0.09	0.9

Table 2: Crude oil surface vs. oil mass and lag- time (VPS 2013)

Lag-time in hours	**Oil covered area [km²] at**				
	5 t	50 t	500 t	5000 t	50000 t
1	0.006	0.016	0.076	0.36	1.14
2	0.016	0.023	0.107	0.496	2.28
5	0.065	0.065	0.169	0.784	3.64
10	0.183	0.183	0.24	1.11	5.15
24		0.518	0.68	1.72	7.98
48			1.93	2.43	11.3
72			3.54	3.54	13.8
96			5.45	5.45	15.6
500			64.8	64.8	64.8

Table 1 and table 2 show that the oil film thickness of 5 and 50 tons discharges after 10 hours will be reduced to 0.03 and 0.3 mm. Therefore, the new oil binder system has to be as thin as possible and the application should be very fast by airplane.

The new BIOBIND binder system is a sorbent material, made of pine wood fiber combined with about 10 % of a hydrophobizing additive (Figure 1). During investigation, the binder geometry was set to a square geometry of 50 x 50 mm and a thickness of 4 mm. The density of the binder was 250 to 280 kg m^{-3}. This geometry fits the requirements of stability, storage, free flowing ability and oil adsorption of small oil films. The developed binders were used for laboratory-scale, mesocosm and field experiments.

Figure 1: wood-fiber binder 50 x 50 mm

Laboratory-scale Oil Adsorption and Floating Tests

For oil adsorption tests, 3 different kinds of oils were used:

- Light fuel oil (Heizöl EL)
- Crude oil (Rohöl REB 1 (Russian export blend 1))
- Heavy fuel oil (Heizöl schwer)

Oil Adsorption Capacity

At first the maximum adsorption capacity of pure oil was investigated. A sample of binder was put in the oil filled petri dish (10 mm oil film) and the maximum oil adsorption rate of the binder was tested. These results were used to adjust the necessary binder and oil volume for further lab experiments.

Water Absorption and Floating Tests

Water absorption and floating time were measured in closed Polypropylene-boxes with a shaking frequency of about 70 r/min. Tap water and seawater from Baltic Sea ("Mecklenburger Bight", Germany) were used. Dry and oil saturated binders were tested for their water absorption and longtime floating. At first the weight increase of binder was measured every 5 minutes, after 15 minutes it was measured every quarter hour, and after 2 hours it was measured every hour. In long-term trials the weight increase was measured once per day.

Oil-/Water Adsorption

Adsorption experiments were carried out with crude oil on the water surface. The adsorption rate was determined for different temperatures (0°C, 10°C, 25°C). A steal bin with minimum oil adsorption on its surface was used. Transpiration effects of water and oil were taken into account. According to Table 1 (scenario 5 to 50 Tons after 10 h) an oil film thickness of 0.03 to 0.3 mm was set. The binder dosage was adjusted to the oil volume in consideration of the maximum oil binding capacity. At first the weight increase of binder was measured every 5 min, after 15 min every quarter, and after 2 hours every hour. In long term trials the weight increase was measured once per day. The shaking frequency was about 50 Hz.

Determination of Cleaning Rate

After termination of the trial the amount of residual oil and water in the bin was measured according to standard LTwS-27, 1999. For that the residual oil in the water was isolated with a separation funnel, and a mass balance of oil and water, with consideration of transpiration effects and test rig losses, lead to information about sorption capacity of the binder and the cleaning rate of the experiment.

Oil Storage Capability

It is necessary that the binders do not lose any oil due to mechanical stress during the recovery of binders with a net-boom. For this reason the oil storage capability of the binder was tested. According to standard LTwS-27, 1999, an overload pressure of 0.1 bar was applied to the oil-water saturated binder (3 day floating). This was achieved by using a weight of approximately 2.5 kg (fig. 8).

Mesocosm Experiments

The oil adsorption and floating ability of the new oil binder were tested in several tanks in July 2013. In this paper only the results of water and oil-water adsorption in two tanks (V and VII) will be presented. Each tank was filled with 290 L Baltic Sea water (surface area 7238 cm^2) from the "Mecklenburger Bight", Germany. In Tank VII 184 g crude oil was poured in to simulate an oils spill. The oil film thickness was approx. 0.3 mm. The water was circulated with aquarium pumps. Both tanks were filled with 32 pieces of oil binders (800 cm^2). The coverage dosage was 11 %. The different variations are specified in Table 3.

Table 3: Variations of mesocosm experiments

Tank No.	Water [L]	Oil [g]	Binder Pieces	coverage rate [%]
V	290		32	11
VII	290	184	32	11

At first the weight increase of binder was measured every 30 min and after 2 hours once per day.

Binder Dosage and Cleaning Rate for Open Sea Application

The results of laboratory scale and mesocosm experiments were used for simulation of real conditions on open sea application of the binder system. A worst-case scenario for a binder application on oil spills considering oil volume and lag-time was calculated.

Field Experiment

The binder system was produced in industrial scale and tested during a large scale field experiment at the Baltic Sea ("Mecklenburger Bight", Germany) in July 2013. Air borne and ship borne application, monitoring, and ship borne recovery with net booms were tested under marine conditions in two trials. The different variations are specified in Table 4. The water absorption of binders and their recovery rate with a net boom were determined.

RESULTS / DISCUSSION:

Laboratory-scale Adsorption and Floating

Maximum Oil Adsorption

For crude oil a maximum oil adsorption of 680 kg m^{-3} (oil/binder) was achieved. As shown in Figure 2 the results for all oil types vary only slightly between 600 and 680 kg m^{-3}. The Specific Gravity of the oil saturated binders is between 0.9 and 0.95 (in relation to water density for 20°C).

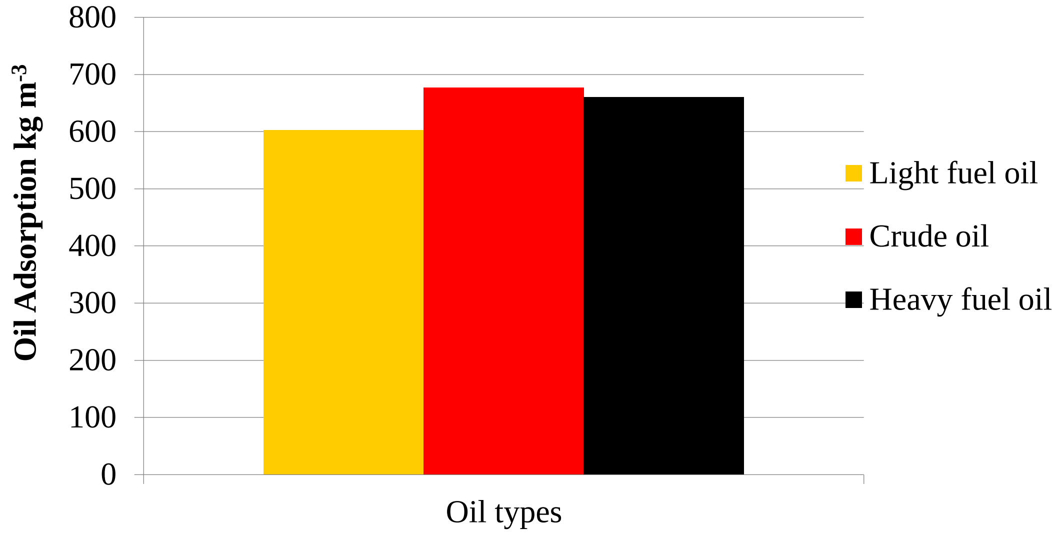

Figure 2: Maximum oil adsorption for different types of oil

Water Absorption and Floating Tests

Due to their hydrophobic properties, the water absorption of the binders is low. Therefore, the binder can float in water for at least 8 days (Fig. 3). This is enough for application in coastal areas. For high sea application an extension of the floating time is possible with adjusted material composition.

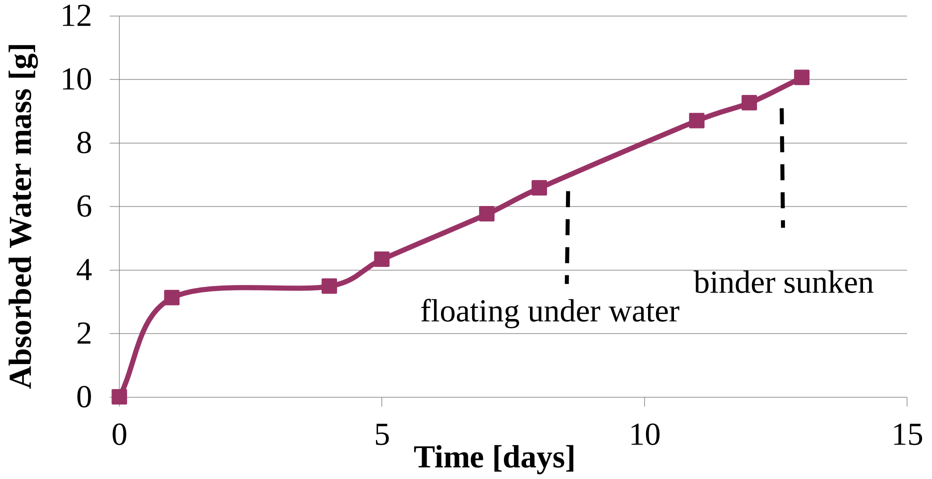

Figure 3: Water absorption and floating of binder (20 °C, frequency 70 rpm)

Oil-/Water Adsorption and Floating Test

As can be seen in the figures 4 to 6, the binder system shows a very fast oil adsorption in the first 20 minutes of the experiment. The results show furthermore, that the temperature between 0 and 25 °C has no noticeable effect on oil- and water adsorption (fig. 4). In the first 20 min at least 75 % of oil was recovered. At coverage dosage of 11 %, an oil- water adsorption of 650 kg/m³ was achieved (fig. 5). Analyses of the residual oil in the water with a separation funnel according to standard LTwS-27 showed that more than 80 % of the oil was adsorbed to the binder after 120 minutes (fig. 5).

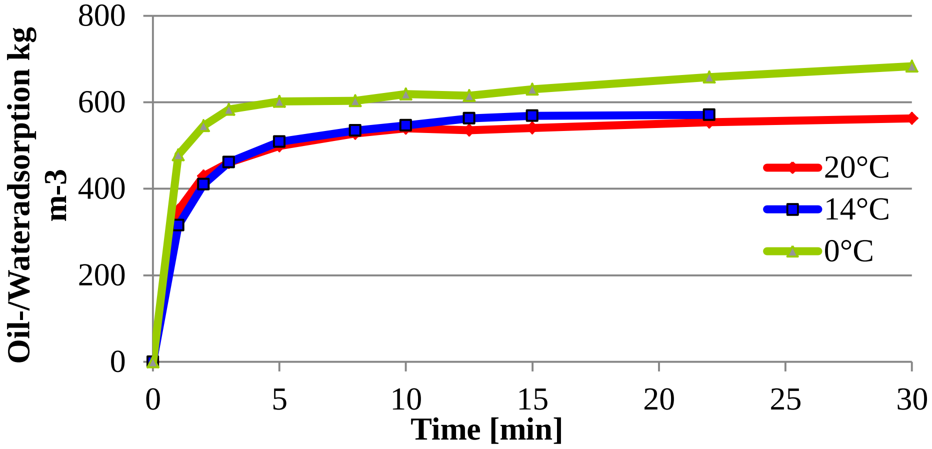

Figure 4: Oil-/Water adsorption of binder with different temperature (frequency 0.5 Hz, dosage 28 %)

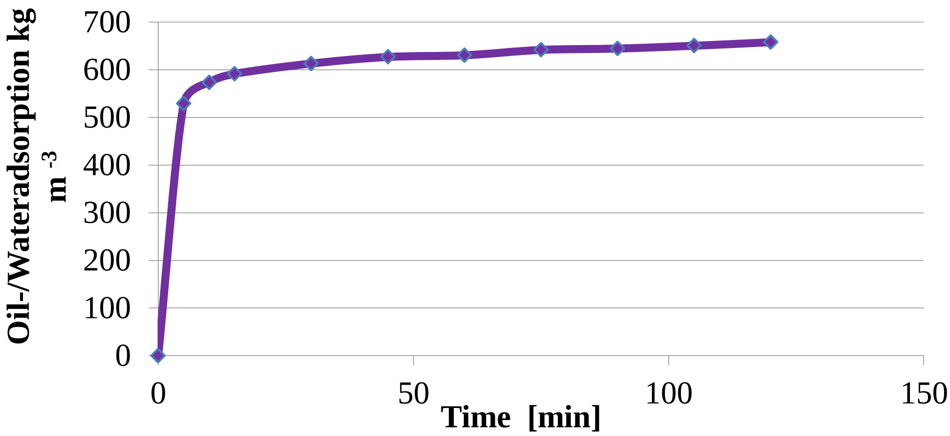

Figure 5: Oil-Water adsorption of binder with coverage dosage of 11 % (frequency 0.5 Hz, 20 °C)

Figure 6: Cleaning process with binder after 5, 10, 15 and 90 min (crude oil)

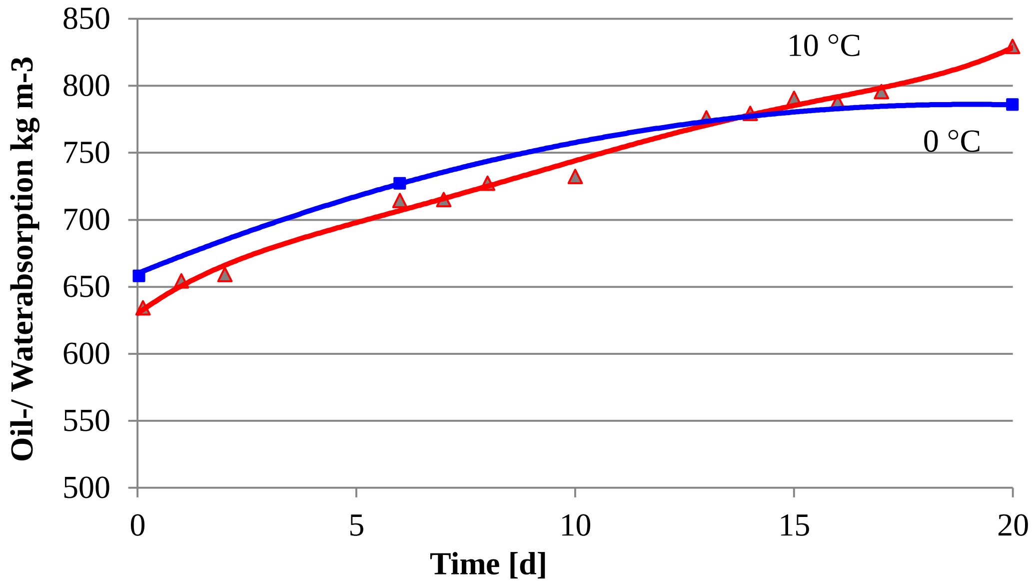

Figure 7: Water absorption and flotation of oil saturated binder (frequency 0.5 Hz, 20 d)
It was observed that the oil saturated binders had a specific gravity of 0.9 and were able to float for more than 20 days, advantageous for long response times during bad weather conditions (fig. 7).

Oil Storage Capability

For simulation of stresses during recovery of oil saturated binder, the oil storage capability was tested according to standard LTwS-27. An oil binder was saturated with oil- and water for three days, then placed between two metal plates and pressed with 27 N for 5 min. The binder did not lose any oil or water after being pressured, guaranteeing an environmentally friendly recovery.

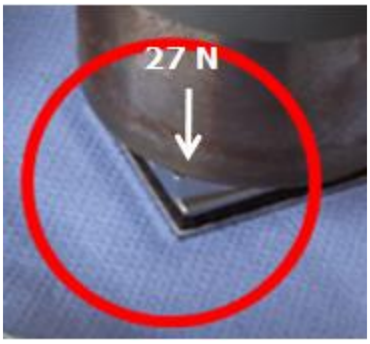

Figure 8: oil storage test

Determination of Cleaning Rate

According to table 1 and 2, the binder system has to be suitable for very thin oil film thickness. For that the required coverage dosage for every oil film thickness was investigated.

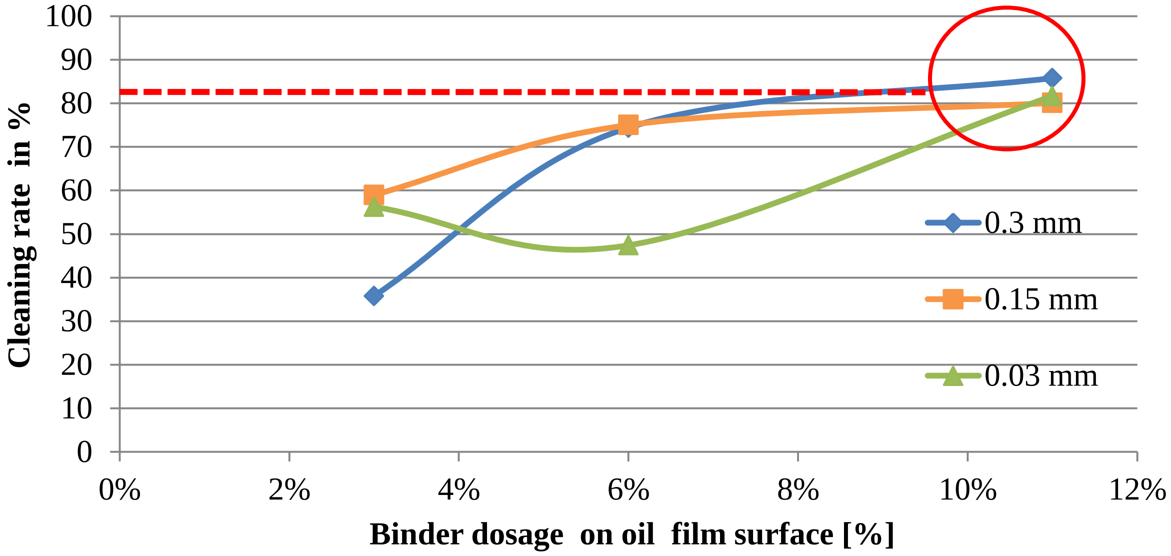

Figure 9: Oil cleaning rate vs. coverage dosage and oil film thickness, (crude oil 0.03 – 0.3 mm)

As shown in the figure 9, the cleaning rate is depending on oil film thickness and binder dosage and rises with increasing binder dosage. With a coverage dosage of at least 11 % (0.11 $m^2\ m^{-2}$) a cleaning rate of at least 80 % was achieved for all selected oil film thicknesses.

Mesocosm Experiments

Oil cleaning rate and floating time were evaluated in mesocosm experiments. The results show that the Oil-Water adsorption in Tank VII is higher than the water sorption within Tank V (fig. 10).

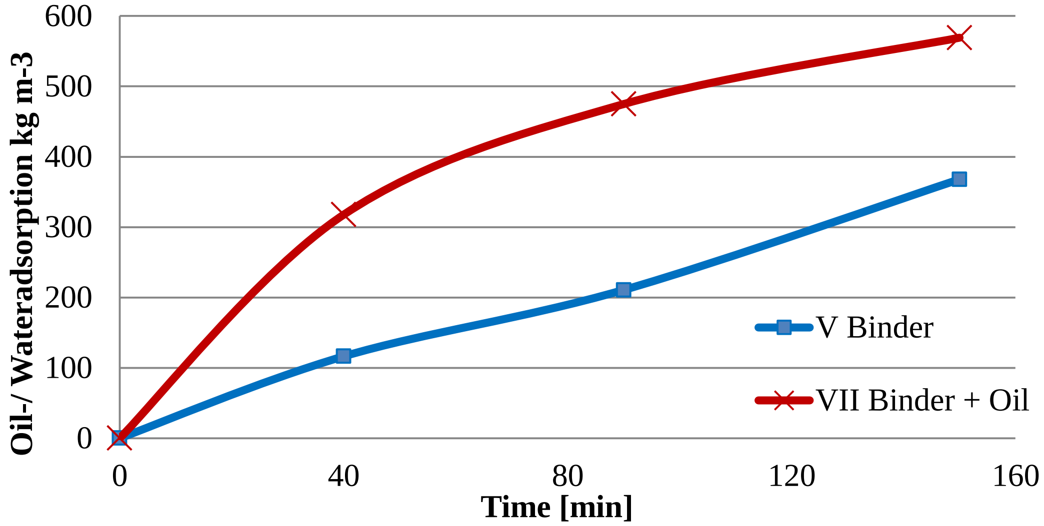

Figure 10: Oil- Water adsorption of binder vs. floating time

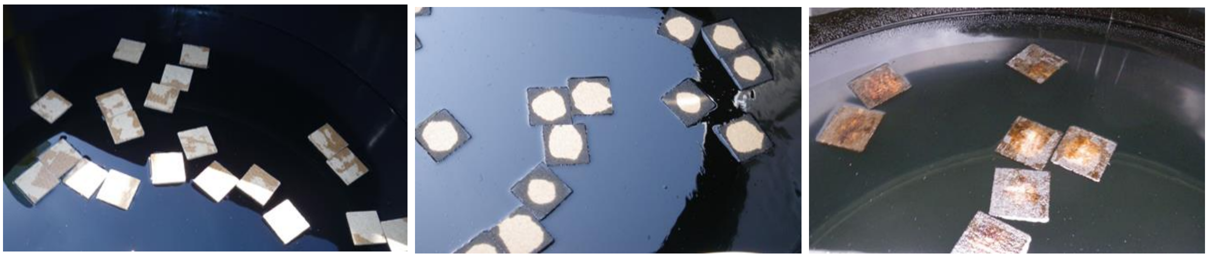

Figure 11 a-c: Cleaning process from beginning (a) and after 30 min (b) an 12 h (c) (Tank VII)
After 12 hours the water surface was nearly clean (fig. 11 c). A detailed description of the mesocosm experiments can be found in Hähnel et al 2014 and Safanova et al 2014.

Binder Dosage and Cleaning Rate for Open Sea Application

The demand of binder was calculated based on the results of laboratory and mesocosm trials and informations about the time dependent dissemination of the oil spill. Figure 12 shows the binder demand depending on the oil volume and lag time. It can be used as a tool for the director of operation to clan marine oil spills with the binder system.

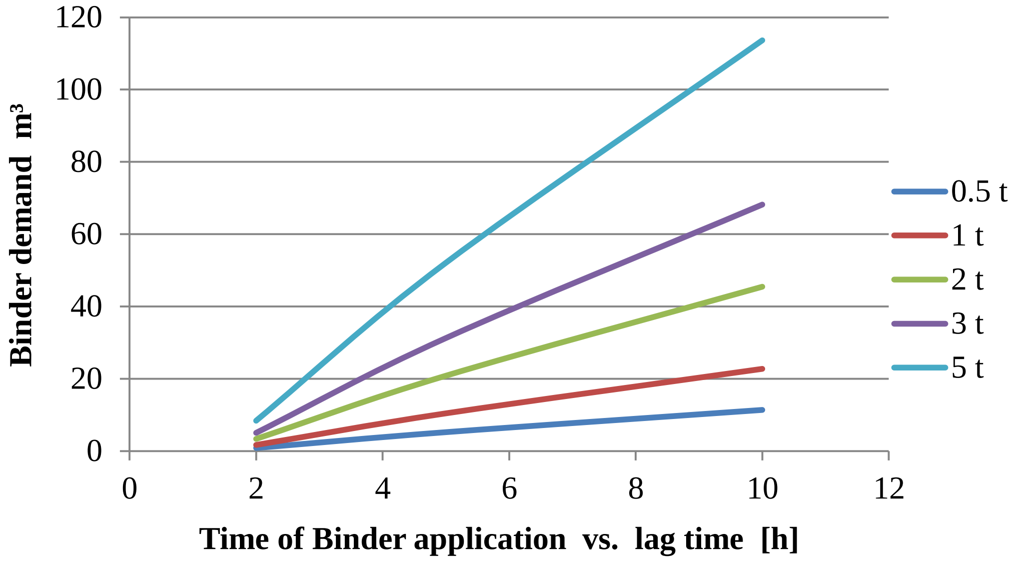

Figure 12: Binder demand depending on oil weight and lag time (dosage 0.11 m²/m², cleaning rate > 80 %)

Field Experiment

In Table 4 the variations and results of the two days field experiment are specified. Due to the favorable weather condition the recovery rate of binder with the net boom was very high. Figure 13 shows the distribution of the binders by plane, the flotation of the binders on the water and their recovery by a net boom. A detailed description of the field experiment can be found in Siewert 2014.

Table 4: Variations of the field experiment

Date	Distribution by	Binder Pieces	floating time hours	Recoverd in Netboom Pieces	Recovary Rate %	Water Absorption kg m^{-3}
03.07.2013	Airplane	26600				
	Boat	3000				
	Ship	500				
	Σ	**27100**	**2.5**	**26087**	**96**	**330**
04.07.2013	Airplane	76000				
	Boat	630				
	Σ	**76630**	**5**	**56136**	**74**	**410**

Figure 13 a-c: distribution (a), floating (b) and recovery (c) of binders (source: Univ. Rostock)

CONCLUSION:

A new wood fiber based oil binder system was developed and evaluated in laboratory scale as well as mesocosm and field experiments. The binder system is suitable for spills of light fuel oil, crude oil and heavy fuel oil. It shows a high oil binding capacity up to 600 kg m^{-3} especially for thin oil films on the water surface. It is suitable for air borne and ship borne marine application and net-boom based recovery. The binder system achieved an oil recovery rate of more than 80 % with a coverage dosage of 11 %. Oil binding capacity and flotation time were evaluated in mesocosm trials. The binder system was produced in industrial scale and tested during a large scale field experiment at the Baltic Sea in summer 2013. The results of airborne application, flotation, monitoring and ship borne recovery confirm the suitability of the binder system for marine application.

In comparison to conventional binder systems or traditional oil response technologies, the new developed binder system offers the following advantages:

- short response time,
- application during bad weather conditions or on shallow water territories,
- high oil cleaning rate,
- no environmental impact.

REFERENCES:

V. A. Broje, A. A. Keller. 2005: A method to characterize materials to be used on oleophilic skimmers. In: International Oil Spill Conference Proceeding: 2005, 837 – 840

J. Hähnel, J. Jeschek, R. Zimmermann, D. Schulz-Bull. 2014: Qualitative and quantitative determination of microbial oil degradation effects in Baltic Sea water samples by various analytical methods. In: International Oil Spill Conference Proceeding: 2014

HELCOM: Convention on the Protection of the Marine Environment of the Baltic Sea Area, 1992, http://helcom.fi

X. Huang, T.T. Lim. 2005: Experimental evaluation of a natural hollow hydrophobic-oleophilic fiber for its potential application in Napl. spill cleanup. In: International Oil Spill Conference Proceedings: 2005, 815 – 818

H. V. Jensen, J.H.S. Andersen, S. L. Gyltnes. 2011: Oil spill response technology development through industry commitments - The Norwegian Way. In: 2011 International Oil Spill Conference Proceedings: 2011, 2011-344

LTwS-27. 1999: Storage and transport of substances hazardous to waters (Lagerung und Transport wassergefährdender Stoffe (LTwS)). Nr. 27. Umweltbundesamt UBA (Germany's main environmental protection agency)

E. Safonova, S. König. 2014: Novel oil-degrading algal-bacterial associations for the treatment of oil pollution in the Baltic Sea. In: International Oil Spill Conference Proceeding: 2014

M. Siewert, M. Powilleit, F. Saathoff. 2014: BioBind - Airborne clean-up of oil pollution at sea with biogenic oil binders. In: International Oil Spill Conference Proceeding: 2014

S. Suni, K. Koskinen, S. Kauppi, E. Hannula, T. Ryynänen, A. Aalto, J. Jäänheimo, J. Ikävalko and M. Romantschuk. 2007: Removal by Sorption and In Situ Biodegradation of Oil Spills Limits Damage to Marine Biota: A Laboratory Simulation,

DOI: http://dx.doi.org/10.1579/0044-7447(2007)36[173:RBSAIS]2.0.CO;2

VPS_2013: Contingency planning for marine pollution control in German coastal zones: http://www.vpsserver1.de/vpsweb/%28S%28zrzzq355pxmstfzwanruu245%29%29/vps_info/vps_info_en/vps_system/ziele_en.aspx

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