# PROPERTIES OF NATURALLY-DEGRADING SORBENTS FOR POTENTIAL USE IN THE CLEAN-UP OF OIL-SPILLS IN SENSITIVE AND REMOTE COASTAL HABITATS

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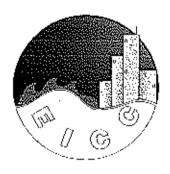
Marine Ecology Laboratories (A11)

University of Sydney

NSW 2006

June 2001

# **FINAL REPORT FOR AMSA**





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# EXECUTIVE SUMMARY:

The Australian Maritime Safety Authority (AMSA) is responsible for co-ordinating the clean-up of oil-spills in Australia's coastal waters. AMSA is currently evaluating the use of naturally-degrading sorbents as part of its clean-up strategy for oiled foreshores. The strategy envisaged is that sorbent will be deployed to capture and immobilise oil on the shore, following which, the oiled sorbent will either be left *in situ* to biodegrade, or recovered to be disposed of on land or to be processed to be used again.

To inform its selection of a potentially suitable sorbent (or sorbents), AMSA commissioned the Centre for Research on Ecological Impacts of Coastal Cities (EICC) at the University of Sydney to review available, relevant information. Recommendations follow searches of the scientific literature (using computer data-bases) and approaches to manufacturers of sorbents identified on the World Wide Web.

AMSA stipulated 8 key issues pertaining to sorbents that required investigation. Our major findings and recommendations for each of these issues are summarised below.

# 1. The range of naturally-occurring, biodegradable sorbents currently available (either as purpose-made products or waste-materials)

At most, there were 41 different kinds of natural oil-sorbents. Thirty three of the 41 types of sorbent were plant-based sorbents, the remainder were from animals. Most sorbents were made from readily available and relatively cheap materials and were in the form of loose granules or fibres. Few sorbents were woven or formed into sorbent devices. Many sorbents were treated in some way to increase their affinity for oil and their ability to repel water. For some materials, notably feathers, wool and cotton, the raw state was recommended, because excessive refinement might strip surface chemicals that were important for capturing oil. Only a few sorbents contained supplements to enhance the degradation of oil. Three sorbents were supplemented with oil-degrading *Pseudomonas* bacteria, one was supplemented with nutrients to stimulate naturally-occurring bacteria and one contained both nutrients and bacteria (of unknown species).

# 2. Physical and chemical actions of the sorbents on different kinds of oils

Sorbents can capture oil by three mechanisms: (1) adsorption to the surface of the sorbent; (2) absorption into spaces *among* aggregated granules or fibres of sorbent (primary absorption); (3) absorption into spaces *within* individual granules or fibres of sorbent (secondary absorption). All sorbents appeared to exploit at least two of these mechanisms. The most significant contrast in terms of mechanism was between fibrous and granular sorbents. Unlike granules, woven or tangled fibres provide stable spaces for primary absorption that make them particularly useful for immobilising and/or recovering spilt oil.

The best quantitative data for discriminating amongst sorbents in terms of their ability to capture oil were in reports by Environment Canada. These cover most of the different kinds of sorbents discovered. Capture of oil was quantified using initial oil pick-up (IOP; Table 8) and maximal oil pick-up on re-use (MOP; Table 9). There was no attempt to quantify the relative contributions of adsorption, primary absorption and secondary absorption. MOP is an important consideration where the aim is to recover and re-use the sorbent. Each sorbent examined by Environment Canada was tested with a range of oils of widely differing viscosities.



A wool-based sorbent, *Wool Kmop*, stood out as having the greatest IOP and MOP for the greatest range of oils. *Wool Kmop* performed well for oils as different in viscosity as cyclohexane and 7-day Crude (Tables 8 and 9). Other sorbents that performed well in terms of IOP and MOP were the *Conwed* sorbent blanket (refined cellulose) and *Verdyol* treated vegetable fibres.

In determining MOP, the researchers who evaluated sorbents for Environment Canada were also able to estimate the maximal number of effective re-uses for each sorbent. The sorbents that showed the greatest re-usability with the greatest range of oils were, in no particular order, the Seaclean (feather pillow), Verdyol, Wool Kmop and CAP Cork (cork granules; Table 10).

Other relevant actions evaluated in the Environment Canada reports were initial water pick-up (IWP) and maximal water pick-up on re-use (MWP). Great affinity for water is an undesirable feature for an oil-sorbent, because it directly interferes with the capture of oil and could eventually cause the sorbent to sink. Sorbents that exhibited little IWP generally also showed little MWP. The sorbents which showed the least IWP and MWP with the greatest range of oils were, in no particular order, *CCD Woodchips*, the *Seaclean* sorbent pillow and *Verdyol* (Tables 11 and 12).

The Environment Canada reports also provided a more qualitative evaluation of sorbents in terms of their behaviour following 48-hours exposure to oil on water. The main object of this test was whether sorbents would continue to float after prolonged exposure. Most of the sorbents previously recommended based on their affinity for oil and repellence to water performed well in these tests. Exceptions were the *Seaclean* sorbent pillow, which sank with most oils and *Verdyol*, which sank with the less viscous oils (Table 13).

# The rate of degradation of oils in the different sorbents and of the sorbents themselves

There is very little information to discriminate amongst sorbents based on their degradability or their effect on the degradability of oil. Degradability was not measured for any of the sorbents reviewed, but sorbents made from woody material, wool or feathers would probably take the longest to biodegrade. Sorbents made from non-woody plant material (e.g. peat, cotton, milkweed) or refined cellulose fibres would probably degrade more quickly. The beeswax-based sorbent *Petrol Rem* would be expected to degrade quickest of all because it dissolves in oil without leaving a solid residue. How quickly it would degrade in the absence of oil is unclear.

In terms of effects of sorbents on the degradability of oil, supplements of oil-degrading bacteria and/or nutrients to stimulate them appear to be effective in laboratory trials. Commercially available examples of supplemented sorbents include *Petrol Rem*, which contains nutrients and *Oclan-Sorb Plus*, which contains both nutrients and bacteria.

# The leachability of oil from different sorbents and information on potential environmental and biological impacts

Of those sorbents considered of some value on other grounds, Conwed, Seaclean, Verdyol, CCD Woodchips, CAP Cork and Wool Kmop, only Seaclean and Verdyol cause problems of leaching (seen as discolouration of the oil-water mixture; Table 13). No other information was available to discriminate among sorbents in terms of leaching. No information is available on potential ecological impacts.



# Methods for applying the different sorbents and an assessment of whether they could easily deployed on floating slicks or oiled foreshores

Virtually nothing is known about the relative ease of deployment of the different sorbents. All of the loose, particulate sorbents should be amenable to deployment by hand, via blower or air-drop. Structures formed from sorbents (mats, booms, pillows, *etc.*) generally need to be manually deployed in the places they are most needed (Table 14).

There have been no substantial evaluations of the performance of natural sorbents in real oil-spills and no field trials were available to provide recommendations.

# Reported advantages/disadvantages or limitations of available sorbents in oilspill events

None of the sorbents had any unique advantageous or disadvantageous properties that have not already been mentioned.

# Reported experiences of actual use of naturally-degrading and/or nutrient enriched sorbents in oil-spill events

The performance of natural sorbents has never been evaluated in actual oil-spills.

# 8. Current indicative costs, storage requirements and shelf-lives of different sorbents

The available information about storage and shelf-life identifies only that all the potentially useful sorbents have simple storage requirements and long shelf-lives. Dry conditions were stipulated for many sorbents, but this is probably a sensible precaution for all sorbents. All the sorbents considered are organic, so they will all be more or less prone to natural processes of decay due to fungi and bacteria, organisms which are most active when damp. Moreover, exposure of sorbents to moisture during storage would be likely to reduce their affinity for oil when deployed. Yet again, no information was provided that would allow us to recommend any particular sorbent.

There was no accurate, current information on costs to allow comparisons among sorbents.

#### Recommendations on sorbents

The best types of sorbents are those with great capacity for primary absorption of oil. These are primarily sorbents formed from long fibres, such as wool, cotton and so forth. One wool sorbent, Wool Kmop, has the greatest IOP (initial oil pick-up) and MOP (maximal oil pick-up) of any sorbent considered. It could also be re-used a substantial number of times (in terms of laboratory tests). Wool-based sorbents have further merits. They are natural, available on a sustainable basis and handling, storage and transport of wool are routine in many parts of Australia. Other possible sorbents with useful properties were also identified, using a diverse set of criteria.

## Uncertainties and limitations on recommendations

Apart form the lack of any information on several of the key issues, much of the best comparable data came from laboratory tests by Environment Canada. Comparability was reduced because techniques and methods changed from time to time.

The validity of results for real use, in the field, cannot be determined from such laboratory trials (however well they are done) and no field assessments could be found.



A decision to deploy or to deploy and retrieve sorbents must be precautionary in environmental terms, regardless of the actual materials chosen. Thus, deploying a sorbent is sensible (and essential) if the ecological consequences are less than leaving the oil alone (which is not always the case in coastal marine habitats) or retaining oil is some area is of paramount importance to protect other areas. In the latter case, any degradation due to sorbents is justifiable in terms of the potentially greater damage elsewhere.

Similarly, deciding to retrieve oil-soaked sorbents must be based on knowledge that retrieval will do less damage than leaving the material on-site. This is likely not to be realistic in some habitats.

Decision-making is hamstrung by a lack of field trials to determine the scale and nature of any environmental threats.

It is strongly recommended that the necessary field experiments are done with any sorbent chosen for use.



# INTRODUCTION

The Centre for Research on Ecological Impacts of Coastal Cities (EICC) is contracted to the Australian Maritime Safety Authority (AMSA) to provide a literature-based review of properties of different, naturally-occurring, biodegradable sorbent materials that could potentially be used in cleaning oiled foreshores. Such materials have been identified by AMSA as potentially useful in situations where the remoteness of the incident and/or environmental features make it impractical or ineffective to contain and recover the oil at sea, or when issues of environmental sensitivity make it inadvisable to use chemical dispersants.

Using sorbent materials to clean oil spilt in the marine environment relies on the fact that oil is captured and retained within the structure of the sorbent, reducing the oil's mobility and so minimising the area covered by a spill. Binding of oil to the sorbent also reduces the oil's initial volatility, thereby reducing contamination of water and sediments by the lighter, more toxic species of hydrocarbon present in oil (e.g. benzene, polyaromated hydrocarbons, etc.).

There is currently a large range of sorbents at various stages of technical and commercial development as tools for cleaning marine oil-spills. AMSA is principally interested in using naturally-occurring, biodegradable sorbents rather than synthetic, polymer-based or mineral sorbents. One reason for this is that the former materials would reduce the necessity of recovering and disposing of the oiled sorbent. At present, the only environmentally acceptable method of disposing of this material is in regulated landfill. In the future, the disposal of oiled sorbents in landfill will become increasingly problematic and expensive because of a lack of available sites and more stringent laws on the disposal of wastes. In situations where it is desirable and practical to remove oiled sorbent, naturally-occurring, biodegradable sorbents would also provide options for disposal other than landfill, e.g. composting and use as an agricultural fertiliser. Finally, because of the general advantages of biodegradability, AMSA is also interested in sorbents that are used in conjunction with nutrients and/or bacteria to accelerate the breakdown process.

AMSA have stipulated that the ideal sorbent for its purposes should have the following properties. It should:

- be cheap, readily available and amenable to long-term storage;
- be easily deployed on floating slicks or oiled foreshores;
- · be capable of a high degree of absorption and oil retention;
- not require recovery and disposal;
- not cause or exacerbate environmental impacts of oil on the foreshore and
- degrade rapidly along with adherent oil.

To aid AMSA in identifying a sorbent or sorbents that meet these requirements, this report provides a review of:

- the range of naturally-occurring, biodegradable sorbent materials currently available (either as purpose-made products or as waste-materials from other industries and activities);
- physical and chemical actions of the sorbents on different kinds of oils (e.g. crude, heavy, light, bunker, etc.);



- the rate of degradation of oils in the different sorbents and of the sorbents themselves;
- the amount of leachate from different complexes of oil and sorbent and information on potential environmental and biological impacts of the leachate;
- methods for applying the different sorbents and an assessment of whether they could easily
  deployed on floating slicks or oiled foreshores (e.g. via air-drop or spraying);
- reported advantages/disadvantages or limitations of available sorbents in relevant clean-up scenarios;
- reported experiences of actual use of naturally-occurring, biodegradable sorbents in oil-spill events and
- current indicative costs, storage requirements and shelf-life of the different sorbents.

#### MATERIALS AND METHODS

# Methods of searches for relevant information

Literature for the present review was obtained in two ways: (i) via searches of computerised databases of scientific publications (Table 1) and (ii) via searches on the world-wide web (WWW) for manufacturers of oil-sorbents.

**Table 1.** List of databases searched for published information on biodegradable oil-sorbents for the present review. All data-bases except the NERAC data-base are held by the University of Sydney.

| • | Aquatic Sciences & Fisheries Abstracts | * | Life Sciences Collection                 |
|---|--|---|--|
| • | Biological & Agricultural Index        | • | Environment Abstracts                    |
| • | Biological Abstracts (BIOSIS)          | • | EVA: Environmental Abstracts             |
| • | ELIXIR                                 | • | Geobase                                  |
| • | CAB Abstracts                          | • | SCANfile                                 |
| • | CARL Uncover                           | • | SciFinder Scholar                        |
| • | Current Contents                       | • | Zoological Record                        |
| • | Dissertation Abstracts                 | • | NERAC (Private database accessed via the |
|   |  |   | www)                                     |

Efficient searching for specific information held on computerised data-bases and the WWW requires the use of 'key-word' (or key-phrase) search-terms. We used the same search-terms to scrutinise computer data-bases of scientific publications and the WWW. These search-terms are listed in Table 2.



**Table 2.** Search-terms used to identify and locate published information on biodegradable oil-sorbents listed in computer data-bases of scientific publications and on the world-wide web.

| Oil + sorbent        | Oil + adsorption                                    |
|----------------------|---|
| Oil + bioremediation | Oil + cleanup                                       |
| Oil + biodegradation | Oil + spill   |
| Oil + absorption     | <ul> <li>Oil + nutrient enriched sorbent</li> </ul> |

It was not feasible for us to attempt to obtain every scientific publication found. Instead, we used the information provided in the data-base for each publication (title, abstract, etc.) to identify those publications that were ostensibly most relevant for our purpose (according to explicit criteria based on AMSA's requirements for knowledge). Occasionally, the summary information presented on data-bases to describe a publication is not a good indication of its actual contents. Consequently, some of the publications that appeared to be relevant were found not to be when we obtained them. There were undoubtedly some relevant publications we did not seek because their contents were not adequately conveyed by their title and/or summary. To reduce the likelihood of the latter occurring, we took a very liberal approach to selecting publications. Furthermore, our search for scientific publications relevant for this review did not end with the searches of data-bases. The publications we obtained as a result of these searches were also scrutinised for references to other relevant publications, which were subsequently sought. This iterative approach was continued as long as there was sufficient remaining time to obtain, read and summarise new publications.

We searched the WWW for manufacturers of oil-sorbents using the three most frequently-used search engines: (i) Excite, (ii) Alta Vista and (iii) Yahoo. Manufacturers identified by these searches were contacted to request relevant information for our review. This was done via email, where possible, or by printed letter. Each e-mail/letter requested each of the specific kinds of information required by AMSA (as listed in the introduction to this report) and explained our reason for seeking this information. Manufacturers who had not responded with six weeks of the initial contact were contacted a second time. Where no response was obtained from a manufacturer, their site on the WWW was our only source of information.

# Issues related to the different kinds of literature

Most of the 'scientific' publications obtained for this study came from outside the mainstream scientific literature; *i.e.* those publications commonly held in academic libraries. Here, this peripheral scientific literature (the so-called 'grey literature') was mostly reports of limited availability published by private research organisations and government agencies and some patents. The vast majority of scientific articles we obtained were in English, but we were also able to review a number of articles in French and Spanish. A problem with the grey-literature for a review such as this, is that it is often difficult (and sometimes impossible) to obtain quickly and/or cheaply. It usually requires a direct request to the author or publisher. Of more concern, however, is the fact that it is rarely subject to rigorous peer-review as occurs for most academic journals and texts. Consequently, much of the grey literature is potentially of questionable rigour and reliability. Given the large number of scientific articles included in our review, however, we were obliged to take major findings and conclusions at face-value. It was simply not feasible to critique the scientific methods and interpretations of all of the unrefereed scientific publications



we obtained. Indeed, in many cases, this would have been impossible because of inadequate presentation of the relevant information.

In the initial stages of reviewing the literature, scientific articles were treated separately from information about the products obtained from sorbent manufacturers. This was because of the great difference in purpose and objectivity between the two kinds of literature. Manufacturers' product-information is potentially less scientifically reliable and will tend to accentuate the positive and downplay the negative. We felt it necessary to make separate the two kinds of information at the initial stage so as not to blur this important distinction.

At this point, three of the scientific articles we obtained from our searches require special mention. These were three reports produced by the Canadian Federal Agency *Environment Canada*. These publications were produced as a series of 'updates' with the general title *Selection criteria and laboratory evaluation of oil-spill sorbents*. The particular reports we were able to obtain were *Updates II* (1983 <sup>31</sup>), *III* (1985 <sup>32</sup>) and *IV* (1991 <sup>33</sup>). [Environment Canada inform us that there will be future updates of this series. Contact details for Environment Canada are provided in Appendix 2].

The value of the Environment Canada reports for the present review is that each uses a clear, standardised method for evaluating individual sorbent materials and for comparing different materials. There are, however, some differences between successive updates reflecting progressive developments in methods of evaluation and presentation. As a set, these reports cover all of the major classes of sorbent material found in the other items of literature obtained from our search. In our initial treatment of the scientific literature, we decided to summarise the material in the Environment Canada reports separately from the rest of the scientific literature. This was done so that the valuable results of their standardised comparisons would not be obscured by being intermingled with information that was similar, but not strictly comparable having been obtained by different methods.

# Use of the literature

To summarise the literature, we sought the following information from each article:

- the objective of the study or report (for scientific publications only);
- whether the sorbent(s) discussed was natural and biodegradable;
- a physical and chemical descriptions the sorbent(s);
- the product name, source and current indicative cost of each commercially available sorbent cited;
- information on whether the sorbent(s) was evaluated in the field and/or in the laboratory;
- the method of applying the sorbent(s) to spilt oil;
- the mechanism(s) by which each sorbent interacts with oil;
- information on whether the sorbent(s) was enriched with microbes and/or nutrients to accelerate biodegradation;
- information on the effectiveness of the sorbent(s) with different kinds of oil;
- information on the leachability of different oils from the sorbent(s);



- information on the rate of biodegradation of the sorbent(s) with and without oil;
- information on the biological and ecological effects of the sorbent(s) (e.g. toxicity, etc.);
- the method of storing the sorbent(s) and shelf-life when properly stored;
- other reported advantages/disadvantages of the sorbent(s).

For the set of articles in each class of literature we obtained, the summary information extracted was compiled in tabular form. The tables of summarised information extracted from (i) miscellaneous scientific articles, (ii) the reports by Environment Canada and (iii) the product-information supplied by manufacturers identified via the WWW are each presented as Appendices to this report (in Microsoft Excel 97 files attached to the report).

### RESULTS

# Results from the scientific literature (excluding reports by Environment Canada)

The range of available biodegradable sorbents

Biodegradable sorbents reported fall in to two main classes: (1) plant-based sorbents composed mainly of cellulose and/or lignin fibres and (2) protein-based sorbent materials derived from animals. None of the sorbents found in this literature was nutrient-enriched. There was, however, a sorbent that was supplemented with oil-degrading bacteria.

Plant-based sorbent materials vary considerably in their physical structure and/or degree of refinement. In terms of physical structure, most of the plant-based sorbents were more or less fibrous (e.g. cotton <sup>5,7,8,10,13,14,17,22</sup>, coir <sup>11,15</sup>, sisal <sup>11</sup>, seagrass <sup>29</sup>, etc.), only a few were more granular in nature (e.g. sawdust <sup>25</sup>; pine needles <sup>29</sup>, etc.). The sawdust sorbent <sup>25</sup> was heat-treated to alter its chemical composition to make it more hydrophobic and, hence, more oleophilic. Peat is a mixture of partially decomposed and undecomposed plant material, mainly moss (e.g. Sphagnum spp.), but also vascular plants such as reeds and sedges <sup>18</sup>. In most instances where peat was trialled as a sorbent for oil, it was untreated. In one study <sup>1</sup>, the peat was washed (to remove soluble 'dirt'), dried at 60°C and then ground before being used. In another <sup>16</sup>, peat was washed and air-dried for 24 hours.

Different plant fibres that have been tried as sorbents for oil include wood fibres <sup>3, 15, 24</sup>, the aquatic plant Salvinia hertzogii <sup>1</sup>, milkweed (Asclepias sp.) <sup>4, 7, 14, 30</sup>, kapok (Ceiba petandra) <sup>4, 8, 9, 10, 11, 12</sup>, <sup>14</sup>, rosella (Hibiscus sabdariffa) <sup>8, 9, 10, 11, 12</sup>, sisal (Agave sisalana) <sup>11</sup>, coconut fibres (or coir; Cocos nucifera) <sup>11, 15</sup>, kenaf (Hibiscus cannabinus) <sup>7, 14</sup>, puffed millet <sup>15</sup> (species unknown; might be Setaria spp. or Echinochlea spp.), seagrass (or eeigrass; species unknown) <sup>29</sup>, pine needles <sup>29</sup> (species unknown) different grades of cotton fibres (Gossypium spp.) <sup>5, 7, 8, 10, 13, 14, 17, 22</sup> and miscellaneous waste fibres from tropical horticulture (e.g. banana stalks, palm fronds, pineapple crowns, etc.) <sup>23</sup>. Among these fibres, milkweed, cotton and kapok are unique in being seed-fibres, rather than structural fibres from the main body of the plant <sup>4, 30</sup>. In the majority of cases, fibres for trials were obtained with little or no processing of the original plant material. In one study, wood-fibres were heat-treated ('pyrolysis' at 200-500°C) to improve their hydrophobic and oleophilic properties <sup>3</sup>. The various plant wastes from tropical horticulture <sup>23</sup> were washed in 0.1 % aluminium sulphate, pressed to extract water, then dried and agitated to loosen bundles of fibres and hence to increase overall surface area and pore space. Where cotton has been used as a



sorbent for oil, it was generally unbleached, but there is at least one report where bleached cotton was used <sup>14</sup>.

In a number of cases, plant-based sorbents were blended with other synthetic components to improve overall sorbent capacity. Synthetic components contributed via their own sorbent characteristics, (e.g. <sup>9,22</sup>) and/or their structural properties (e.g. <sup>8,26</sup>). We only concerned ourselves with these reports of natural/synthetic blended sorbents where they provided information about the sorbent properties of the natural component.

Protein-based sorbents derived from animals appear much less frequently in the scientific literature (excluding reports by Environment Canada) than do plant-based sorbents <sup>2,4,5,14,17</sup>. These reports cover only five kinds of protein-based sorbent, two from crabshells (chitin and chitosan <sup>2</sup>), keratin from guil feathers <sup>2</sup>, untreated feathers <sup>15</sup> and wool fibres <sup>4,14,17,27</sup>. Chitin, chitosan, keratin and were all used in the form of coarse flakes.

### Mechanisms of sorbent action and the effectiveness of different sorbents

Among the sorbent materials for which information was reported in scientific articles (excluding reports by Environment Canada) there were three principal mechanisms for trapping oil: (i) adsorbtion to the surface of the sorbent material; (ii) absorption into air-spaces among aggregated granules or fibres of the sorbent material (which we term 'primary absorption') and (iii) absorption into pits, lacunae or lumina within individual granules or fibres of the sorbent material (termed 'secondary absorption').

Unfortunately, most studies either neglected to say which of these different oil-binding mechanisms occurred with particular sorbents or, where they did, failed to estimate or predict which of these three mechanism were the most important. Given, however, that most of the sorbent materials were relatively crude natural products, in the absence of reported information, we believe we can make fairly reliable predictions about which of the three process for binding oil should or should not apply to given sorbents. For instance, fibres of any material can be woven or will naturally tangle, so knowing that a material is fibrous implies that it will have good primary characteristics for absorption. Similarly, all plants have hollow internal conduits: xylem for transporting water and phloem for transporting dissolved nutrients. Any crude plant matter should therefore have some capacity for secondary absorption.

Note that in terms of recovering oiled sorbents, primary absorption is only useful if the spaces containing oil are physically stable. Thus, primary absorbency under recovery will be great for woven or matted sorbents, medium for loose, fibrous sorbents and small for more granular sorbents. Among loose fibrous sorbents, primary absorbency under recovery should increase with the length of fibres. Thus, loose fibres of wool (long fibres) should provide greater primary absorbency than loose fibres of peat (short fibres). When no recovery is attempted, both fibrous and granular sorbents could be relied upon to reduce the mobility of the spilt oil by increasing its overall viscosity. Again, however, the effect would be greatest for woven or tangled fibres because of the stability of spaces among individual fibres compared to that among granules.

Reported and predicted mechanisms of oil-sorption for the different plant and animal products found in our review of the scientific literature are summarised in Table 3. Entries in the table are supplemented with comments from the literature where they are available and pertinent. Where primary absorption is reported in Table 3 for a particular sorbent, we have provided an assessment of its relative importance for oil immobilisation/recovery based on its physical form (i.e. granules vs fibres, woven vs loose, etc.).



Table 3. Reported or predicted mechanisms of oil-sorption by different natural materials based on information provided in the scientific literature (excluding reports by Environment Canada). Where comparative information was available, comments are provided on the relative performance of the different materials.

|   |   | Me  | chanisms of oil pick   | -up  |
|---|---|---|--|--|
| Sorbent   | Ref.                                      | Adsorption  | Primary<br>Absorption  | Secondary<br>absorption  |
| Plant products                                    | (Manager)                                 |   |  |  |
| Horticultural peat (mainly moss)                  | 1, 6, 15,<br>16, 18,<br>19, 20,<br>21, 29 | > than seagress and pine<br>needles <sup>20</sup> , but see Note 1.                           | ✓ Small > than seagrass and pine needles <sup>22</sup> , but see <b>Note</b> 1.  | > than seagrass and pine<br>needles <sup>29</sup> , but see Note 1.  |
| Heat-treated<br>sawdust                           | 25  | Pyrolysis produces eleophilic surface-compounds <sup>25</sup> .                               | ✓ Small  Not discussed, but likely to  Small relative to wood fibres.            | <b>*</b>   |
| Heat-treated wood<br>fibres                       | 3   | Pyrolysis produces eleophilic surface-compounds <sup>3</sup> .                                | ✓ Small  | ·  |
| Refined wood fibres<br>(cetlulose)                | t5  | *   | ✓ Small – Med.   | ~  |
| Water plant (Salvinia<br>hertzogli)               | 1   | > than peat 1   | ✓ Med. – Great   | ✓  |
| Milkweed ( <i>Asoleplas</i><br>sp.)               | 4, 7, 14,<br>24                           | > than cotton, similar to kapok<br>and wool <sup>4, 16</sup>                                  | ✓ Med. – Great   | Similar to kapok and > than cotton because of larger internal spaces 14  |
| Kapok (Ceiba<br>petandra)                         | 4, 8, 9,<br>10, 11,<br>12, 14             | > than cotton, similar to milkweed and wool * 11, > rosella, sisal & coir 15, but see Note 1. | ✓ Med. — Great<br>> rosella, sisal & coir <sup>13</sup> , but<br>see Note 1.     | Simitar to milkweed and > than cotton because of larger, more stable lumen <sup>11</sup> . > rosella, sisal & coir <sup>11</sup> , but see Note 1. |
| Rosella (Hibiscus<br>sabdariffa)                  | 8, 9, 10,<br>11, 12                       | < than kapok 11, but see Note 2.  | ✓ Med. – Great < than kapok <sup>11</sup> , but see Note 2.                      | < than kapok 11, but see<br>Note 2.  |
| Sisal (Agave<br>sisalana)                         | 11  | < Inan kapok <sup>11</sup> , but see<br>Note 2.   | ✓ Med. – Great<br>< than kapok <sup>11</sup> , but see<br>Note 2.                | < than kapok <sup>11</sup> , but see<br>Note 2.  |
| Coconut fibres / Coir<br>(Cocos nucifera)         | 11, 15                                    | < than kapok <sup>11</sup> , but see<br>Note 2.   | ✓ Med. – Great < than kapok <sup>11</sup> , but see Note 2.                      | < than kapok "but see<br>Note 2.   |
| Kenaf (Hibiscus<br>cannabinus)                    | 7, <b>1</b> 4                             | < than kapok <sup>11</sup> , but see<br>Note 2.   | ✓ Med. – Great < than kapok <sup>11</sup> , but see Note 2.                      | < than kapok " but see<br>Note 2.  |
| Puffed millet (Setaria italica & Echlnochloa sp.) | 15  | <b>*</b>  | ?  |  |
| Seagrass  | 29  | < than peat, > pine needles 20,<br>but see Note 1.  | ✓ Med. – Great<br>< than peat, > pine needles <sup>29</sup> ,<br>but see Note 1. | < than peat, > pine needles 20, but see Note 1.  |
| Pine-needles                                      | 29  | < than seagrass & pest <sup>39</sup> , but<br>see Note 1.                                     | ✓ Med,<br>< than seagrass & peat <sup>29</sup> , but<br>see Note 1.              | < than seegrass & peat <sup>20</sup> , but<br>see Note 1.  |



| Plant products                                | cent.                                |  |  |   |
|---|--------------------------------------|--|--|---|
| Unbleached cotton<br>(Gossy <i>pium</i> spp.) | 5, 7, 8,<br>10, 13,<br>14, 17,<br>22 | < than milkweed, kapok and<br>wool <sup>4</sup> and greater than<br>bleached cotton because of<br>claophilic surface-compounds | ✓ Med. – Great   | less than milkweed and kapok<br>because of smaller Internal<br>spaces <sup>14</sup> |
| Steached cotton                               | 14                                   | < than unbleached cotton<br>because of loss of oleophilic<br>surface-compounds <sup>14</sup>                                   | ✓ Med. – Great   | *   |
| Treated waste fibres<br>from tropical crops   | 23                                   | · · · · · · · · · · · · · · · · · · ·  | ✓ Med.   | ~   |
| Animal products                               |                                      |  |  |   |
| Chitin  | 2                                    | < than chitosan and keratin &<br>likely to be much less than<br>plant-sorbents because of<br>hydrophilic exterior <sup>2</sup> | ✓ Small  | 7   |
| Chitosan                                      | 2                                    | > than keratin & chitin and<br>likely to be much less than<br>plant-surbents because of<br>hydrophilic exterior <sup>2</sup>   | ✓ Small  | ?   |
| Keratin from gull<br>feathers                 | 2                                    | < than chitosan, > chitin & likely to be much less than plant-sorbents because of hydrophilio exterior 2                       | ✓ Small  | ?   |
| Untreated feathers                            | 15                                   | Facilitated by natural waxy cuticte of feathers and large surface area   | ✓ Med. – Great   | · ·   |
| Wool fibres                                   | 4, 14,<br>17, 27                     | Facilitated by oleophilic landin  17, 27 > than cotton, similar to milkweed, kapok 4   | ✓ Mad. – Great<br>< than milkweed and kapok <sup>4</sup> | ×   |

Note 1: It is reported 25 that peat has greater overall sorbent capacity than seagrass, which has greater capacity than pine needles, but reasons for these differences are not given. We expect that pine needles should be the poorest sorbent because their more granular nature provides little capacity for primary absorption.

Note 2: It is reported 11 that sisal, rossila and coir all have overall lesser sorbent capacities than kepok, but the reason for kapok's

superiority is not given.

From this comparison of the oil-sorption mechanisms and capacities of the different natural materials it is possible to identify several useful attributes of an oil-sorbent.

- It should have hydrophobic/oleophilic coating to promote floatation and oil-adsorption. Examples of such coatings include lanolin on wool <sup>4, 17, 27</sup>, resins produced on the surface of wood by pyrolysis <sup>25</sup> and the waxy coatings of plant fibres, such as kapok <sup>4</sup>, milkweed <sup>7, 30</sup> and, to a lesser extent, unbleached cotton 14, 28
- It should be fibrous, allowing the sorbent to aggregate, or be woven into a form that provides physically stable air-spaces for primary absorption and subsequent retention of spilt oil.
- Relative to its volume, the ideal sorbent should provide a large external surface to which oil can adsorb. This can be achieved by using a sorbent made of narrow fibres 27, or small granules. A textured surface (e.g. hairs, pits, scales, etc.) will also increase external surface area and adsorption capacity 5, 14, 17
- It should possess relatively large, non-collapsing internal spaces (lumina, lacunae, etc.) to give a large surface area for secondary absorption.



For all the reasons outlined above, it appears therefore that plant fibres make the best natural sorbents for oil. It is difficult, however, to be certain of this because of the lack of comparable data across the range of sorbent materials. The plant fibres for which there is the greatest amount of comparative information are milkweed, cotton, kapok and kenaf <sup>4, 7, 14</sup>. The pattern that consistently emerges from comparisons of these materials is that, for a broad range of oil-types (from fuel oil to crude), milkweed has the greatest sorption capacity and kenaf has the smallest (less by a factor of ~6 c.f. milkweed). The sorption capacities of kapok and cotton were similar and only slightly less than that of milkweed.

Although only a limited number of studies addressed the question <sup>8, 10, 11, 14</sup>, it seems that the form in which fibrous materials are exposed to oil is an important determinant of their overall sorption capacity. The three ways of deploying fibres as sorbents for spilt oil are: (i) as loose fibres; (ii) as formed bundles of unwoven fibres (form is maintained by loose stitching) and (iii) as woven materials. In one study, unwoven fibres were compared to woven fibres <sup>8</sup>; unwoven fibres were best for low viscosity fuel oils (23 cP at 25°C) and woven fibres best for medium to high viscosity fuel oils (86 – 1524 cP at 25°C). In another similar study <sup>10</sup>, unwoven fibres were better than woven materials for light, medium and high viscosity oils (viscosity range 12 – 330 cP at 24°C). The only study to compare the sorption capacities of loose, unwoven and woven fibres used only one, low viscosity oil (5.5. cP at 16°C) and found that loose fibres were better than unwoven fibres and both were better than woven fibres. The only other relevant study compared four natural fibres (kapok, sisal, rosella, coir) <sup>11</sup> and concluded that, for a range of viscosities (10 – 332 cP at 24°C), a smaller packing density produced a greater oil sorption capacity than a greater packing density.

One of the potential benefits of using sorbent materials to clean up spilt oil is that they can be physically retrieved so that the oil can be extracted (by mechanical squeezing) and the sorbent reused. It is, therefore, relevant to note that the sorbent capacities of many natural sorbents decline markedly with repeated use <sup>5, 7, 14</sup>. In one study <sup>5</sup>, it was reported that sorption capacity of cotton with light crude (0.0551 poise at 37.8°C) was reduced to ~60 % of its initial capacity after (unquantified) repeated use. A second study <sup>7</sup> of three plant fibres (milkweed, cotton and kenaf) exposed to three kinds of oil (No.2 Diesel fuel oil (s.g. at 15.6°C = 0.846), light crude (s.g. at 15.6°C = 0.854) and No.6 'Bunker C' fuel oil (s.g. at 15.6°C = 1.027)), reported that 90 % of oil could, on average, be extracted by simple mechanical action, but re-use reduced capacity to 74 – 85 % of initial capacity.

The scientific literature we reviewed here presented considerable additional data on the interaction of particular sorbents with particular oils. Note, however, that in the literature there is much variation in the kinds of oils used, the ways the oils are described, the methods of assay and the units in which results are presented. This makes it extremely difficult to make reliable comparisons of the different sorbents. Because of the complexity and heterogeneity of this additional information, we concluded that the only sensible way of reporting it is to provide a summary for each individual scientific article. These summaries are provided in Appendix 1.

Use of sorbents in the field: techniques of deployment and environmental interactions. The scientific literature reviewed here provided no evaluations of the relative performance of different natural sorbents for treating oil-spills in natural marine habitats.



One patent <sup>25</sup> for a sorbent comprising a natural (cellulosic) core encapsulated in synthetic exterior reported that, when deployed on the sea in the form of a boom, it performed as well as a similar product that was entirely synthetic. No corroborating data were provided.

Following laboratory trials that showed peat moss was an effective sorbent, one study reported a number of crude, non-comparative trials of peat moss on actual oil-spills. The first trial was on a small, floating patch of Bunker C oil. It was not said how the peat moss was deployed, but once spread on the oil, the slick could be easily controlled and moved with the aid of a metal screen of quarter-inch mesh. The second trial of peat moss was on spots of Bunker C oil (of a few cm diameter) deposited on a sandy beach. Peat moss was spread on the beach, mixed with the oil and picked up with rakes. It was reported that this resulted in the removal of at least 95 % of the oil. The third trial was an attempt at a full clean-up of a moderate-sized oil-slick (1,500 x 200 feet) that washed ashore on beaches and rocky shores in the St Lawrence River. Four cubic feet of peat moss was used for every 100 square feet of shore. It was not said how effective the method was for beach habitats, but, on rocky shores, 90 % of the spilt oil was recovered.

The literature provided almost no information on the actual or predicted biodegradability of the sorbent or the oil-sorbent complex in field situations. The only report that had any specific focus on biodegradation was a study of the effect of *Pseudomonas* sp. bacteria on the degradation of heavy oil in an aqueous system in the presence of the natural sorbents keratin, chitin and chitosan <sup>2</sup>. This study did not report any information about the effect of *Pseudomonas* sp. bacteria on the degradability of the sorbents. On average, the presence of *Pseudomonas* sp. bacteria caused a three-fold reduction in the time before degradation commenced and they significantly increased rate of biodegradation, particularly for lighter weight *n*-alkanes. The only comment on the sorbents in relation to degradation was that they facilitated degradation by providing a large, stable surface-area for bacterial colonisation and digestion of the oil.

Although no data or supporting information were provided, one report <sup>24</sup> on the use of natural-synthetic, blended sorbents based on wood-pulp fibre, offered the comment that, because wood pulp is highly lignified, it should have relatively low biodegradability compared to other, similar organic materials.

# Reported advantages and disadvantages of different sorbents

The advantages and disadvantages of different natural materials with regards to their mechanisms and capacity for oil sorbency have already been discussed, so we confine our report here to other, aspects of their performance.

Buoyancy and water-repellency are important attributes for an oil-sorbent. Buoyancy is primarily a function of density, but small particles that are denser than water can float by virtue of water-proof (hydrophobic) coatings that prevent them from breaking the water's surface tension. In terms of buoyancy and water-repellency, the proteinaceous sorbents, chitin, keratin and chitosan are the most inferior materials of those discussed here <sup>2</sup>. This is not because they are proteins *per se*, but because they are purified proteins. Feathers and wool are protein-based, but, in their raw state, have a natural waxy, water-proof coating. Without such coatings, many proteins are very hydrophilic and would quickly absorb water and sink when deployed in the sea.

A reduction in performance because of 'processing' can also occur with wood-based sorbents. Moderate heat-treatment of wood particles/fibres (200-350°C) improves their sorbency because it causes the production of oleophilic resins <sup>3</sup>. Beyond 350°C, however, chemical reactions no



longer favour the production of oleophilic resins and interstices between fibres collapse increasing the wood's density.

Mechanical reclamation of oil from oiled sorbents can also reduce the buoyancy and sorbency of sorbent materials. For cotton <sup>6</sup>, this occurs because oil-reclamation strips natural oleophilic chemicals from the sorbent and crushes interstices.

Fibres can be deployed in loose form or woven and formed into sorbent structures (booms, pillows, etc.). Granular sorbents only be spread over spilt oil in loose form. This may not be a problem, however, if the aim is to use the sorbent in situations (i.e. remote and/or sensitive coastal habitats) where the oiled sorbent is not retrieved, but left in situ to biodegrade. In such situations, it may not be practical to deploy people to place sorbent structures in strategic positions to contain the spilt oil. Second, if such structures were deployed, their greater physical integrity compared to loose sorbents may slow the degradation and physical break-up of the oiled sorbent as it ages. Sorbent structures deployed and left on spilt oil may also be more unsightly than loose sorbents.

# Information not given in the scientific literature (excluding Environment Canada reports)

In the scientific literature reviewed here, some of the kinds of information sought by AMSA were entirely absent. The kinds of information not found included:

- the rate of degradation of oils in the different sorbents and of the sorbents themselves;
- the amount of leachate from different complexes of oil and sorbent;
- potential environmental and biological impacts of the leachate and
- the costs, storage requirements and shelf-lives of sorbents.

# Results from the reviews of sorbents by Environment Canada

# The range of available biodegradable sorbents

Updates II <sup>31</sup>, III <sup>32</sup>, and IV <sup>33</sup> of the ongoing review of oil-sorbents by Environment Canada provide evaluations of 13 different naturally-occurring, biodegradable sorbents/products. One, *Oclan-Sorb*, was evaluated (slightly differently) in two separate Updates (III and IV). Because of slight methodological differences of unknown consequence between subsequent updates, both sets of results for *Oclan-Sorb* are summarised and reported here.

The vast majority of organic oil-sorbents covered by the three Environment Canada reports (12 out of 14) were plant-based sorbent materials comprised of loose granules and/or fibres of varying lengths (Table 4). The only non-plant organic sorbents were *Wool Kmop* <sup>33</sup> and feathers (in the form of pillows; sold as *Seaclean* <sup>32</sup>). *Seaclean* <sup>32</sup> and *Conwed* <sup>31</sup> were the only non-granular sorbents covered in the reviews. *Seaclean*, as already mentioned, is a sorbent pillow, whilst *Conwed* is in the form of a loosely woven blanket. Of the plant-based sorbents, two were made wholly from peat moss. One of these was normal horticultural peat; the second (*Oclan-Sorb*) is peat that has been chemically dried to improve its sorbent characteristics. Note that this information for *Oclan-Sorb* was obtained independently from the manufacturer. Of the remaining plant sorbents, five were crude, wood or vegetable products ((i) sawdust <sup>33</sup>, (ii) woodchips (*CCD Woodchips* <sup>33</sup>), (iii) pine bark (*Zugol* <sup>32</sup>), (iv) ground cork (*CAP Cork* <sup>33</sup>) and (v) ground corn



cobs (Slikwik 31) and four were forms of processed/treated cellulosic fibres of wood or vegetable origin ((i) Bedex 31, (ii) Conwed 31, (iii) Verdyol 32 and (iv) Alfob W 33). None of the organic sorbents covered by the Environment Canada reports had been supplemented with oil-degrading bacteria or nutrients to stimulate their proliferation.

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Table 4. General properties of the different organic sorbents reviewed in Updates II, III and IV of the review of oil-spill sorbents by Environment Canada.

| a de la companya de |   | General proper  | ties of sorbents  | •  |
|---|---|---|---|--|
| Sorbent <sup>(et</sup>  | Composition   | Physical form<br>tested                                     | Bulk density<br>(kg m²)   | Forms<br>avallable                                   |
| Bedex <sup>31</sup>   | Wood-fibres (sold as animal bedding)                      | Loose fibres  | 27.2  | Loose  |
| Conwed <sup>31</sup>  | Surface-treated<br>cellulose (treatment<br>not specified) | Loosely woven pad   | 51.0  | Pads, booms,<br>blankets, strips                     |
| Peat moss 31  | Fibres of peat moss                                       | Loose fibres +<br>granules                                  | 82.0 to 171.0<br>depending on particle-<br>size and moisture<br>content | Loose  |
| Slikwik <sup>31</sup>   | Ground com cobs   | Loose granules  | 141.0   | Loose  |
| Oclan-Sorb 32   | Treated peat moss<br>(unspecified<br>treatment)           | Loose fibres +<br>granules                                  | 288.0   | Loose  |
| Seaclean 32   | Feathers  | Pillow (cover and<br>stitching of<br>unspecified materials) | 14.0  | Pillows  |
| Zugol <sup>32</sup>   | Modified pine bark<br>(unspecified<br>modification)       | Coarse, loose fibres +<br>granules                          | 250.0   | Loose  |
| Verdyol 32  | Treated vegetable fibres                                  | Loose fibres  | 300.0   | Loose  |
| Alfob W <sup>38</sup>   | Processed cellulose<br>fibre (unspecified<br>process)     | Laase fibres  | 127.0   | Loose  |
| CCD Woodchips 33  | Wood chips  | Coarse fibres +<br>granules                                 | 272.0   | Loose – 3 grades of<br>coarseness                    |
| CAP Cork 33   | Heat-treated cork   | Loose fibres +<br>granules                                  | 96.0  | Loose  |
| Oclan-Sorb 33   | Treated peat moss<br>(unspecified<br>treatment)           | Loose fibres +<br>granules                                  | 288.0   | Loose  |
| Sawdust 33  | Sawdust   | Loose fibres +<br>granules                                  | 400.0 – 480.0   | L∞se   |
| Wool Kmop <sup>33</sup>   | Treated wool<br>(unspecified<br>treatment)                | Loose 'spheres' of<br>fibres                                | 33.33   | Recommended use in<br>form of boorn, pillow,<br>efc. |

Densities (kg m<sup>-3</sup>) formed part of the general description of the different sorbents covered in the Environment Canada reports. It was not explained how this information should be used to assess the effectiveness or practicality of different sorbents. Presumably, a good sorbent would be one that combined small density with great sorbent capacity. Of the materials/products evaluated, the



least dense were *Seaclean* feather sorbent-pillows (14 kg.m<sup>-3</sup>), *Bedex* wood-fibres (27 kg.m<sup>-3</sup>) and *Wool Kmop* (33 kg.m<sup>-3</sup>). The most dense sorbent materials were sawdust (400-480 kg.m<sup>-3</sup>), *Verdyol* treated vegetable fibre (300 kg.m<sup>-3</sup>), *Oclan-Sorb* peat moss (288 kg.m<sup>-3</sup>), *CCD Woodchips* (272 kg.m<sup>-3</sup>) and *Zugol* modified pine bark (250 kg.m<sup>-3</sup>).

The addresses of the manufacturers of the different organic sorbents reviewed by Environment Canada in Updates II, III and IV are listed in Table 5.

Mechanisms of sorbent action and the effectiveness of different sorbents

Information on the oil-capturing mechanisms of the different materials was not provided by the Environment Canada reports. Nevertheless, from information in the scientific literature and what is generally known about the parts of plants and animals used to make the sorbents, we have made reliable, albeit general statements about their oil-capturing mechanisms (Table 6). As with the similar table for sorbents in the general scientific literature (Table 3), we have provided comments on each sorbent's capacity for primary absorption based on its physical form (i.e. granules vs. fibres, woven vs. loose, etc.).

With the exception of wool fibres, which do not have internal spaces (necessary for secondary absorption), all of the organic sorbents covered in the Environment Canada reports capture oil through a combination of adsorption to the external surface, primary absorption to spaces among granules /fibres and secondary absorption into spaces within granules /fibres. As discussed previously, effective primary absorption of oil into spaces among granules /fibres (necessary for the recovery of oil or its immobilisation if left *in situ*) should be greatest for woven fibres, intermediate for long, loose fibres and least for loose granules and short fibres. On this basis, the best sorbent material/products for immobilising or recovering spilt oil should be the *Conwed* sorbent blanket (cellulose fibres) and the *Seaclean* sorbent pillow (feathers). Of the loose sorbents, the best for immobilisation or recovery would be *Wool Kmop* (long, tangled fibres), followed by *Virdyol* and *Alfob W* (shorter, less tangled fibres).

Six aspects the different sorbents' overall effectiveness in capturing oil were compared among the three Environment Canada reports. Data were from a series of replicated trials in which sorbents were exposed to a set range of different oils, each in the form of a thin layer on water. The six variables compared were:

- initial oil pick-up (IOP) (g oil per g sorbent);
- maximal oil pick-up on re-use (MOP) (g oil per g sorbent);
- 3. number of effective re-uses;
- 4. initial water pick-up (IWP) (g water per g sorbent);
- maximal water pick-up on re-use (MWP) (g water per g sorbent);
- 6. response to 48-hour submersion in oil on water.



**Table 5.** Contact addresses for the manufacturers of the different organic sorbents investigated by Environment Canada in Updates II, III and IV of their review of oil-spill sorbents.

| Sorbent          | Address of manufacturer or distributor   |
|------------------|--|
| Update II, 1983  |  |
| Bedex            | (Distributor) Thermo-Cell Insulation Ltd.,<br>3268 Hawthorne Road, Ottawa, Ontario, Canada K1G 3W9           |
| Conwed           | (Distributor) CIL Inc.,<br>P.O. Box 836, Edmonton, Alberta, Canada T5J 2L4                                   |
| Peat moss        | No manufacturer or distributor given   |
| Slikwik          | (Distributor) Ashwell Feeds Ltd.,<br>139 Millwick Drive, Weston, Ontario, Canada M9L 1Y7                     |
| Update III, 1985 |  |
| Oclan-Sorb       | (Manufacturer) Hi-Point Industries Ltd,<br>P.O. Box 2535, Postal Station M, Calgary, Alberta, Canada T2P 2N6 |
| Seaclean         | (Distributor) Sea Clean Inc.<br>7000 SW 62 Avenue, Suite 555, Miami, Florida 33143, USA                      |
| Zugol            | (Manufacturer) Svensk Barkindustri AB,<br>Ostera 791 91, Falun, Sweden                                       |
| Verdyol          | (Distributor) Verdyol Plant Research Ltd<br>R.R. 1, Cookstown, Ontario, Canada L0L 1L0                       |
| Update IV, 1991  |  |
| Alfob W          | (Distributor) Absorbtion Corp.,<br>Suite 820, 1130 West Penter St., Vancouver, BC Canada V6E 4A4             |
| CCD Woodchips    | (Distributor) Carbontec Ind. Inc.<br>400 East Broadway, Bismark, North Dakota 58501, USA                     |
| CAP Cork         | (Distributor) Sevenson Environmental Products Inc.,<br>2749 Lockport Rd., Niagra Falls, New York 14302, USA  |
| Sawdust          | (Distributor) Lignum Sawdust Products<br>5204 Salaberry, Carignan, Quebec, Canada J3L 3P9                    |
| Wool Kmop        | (Distributor) Wool Research Organisation of New Zealand Inc., Private Bag, Christchurch, New Zealand         |



Table 6. Predicted mechanisms of sorbent-action for organic sorbents in the reports by Environment Canada. (i) Adsorbtion is adherence to the surface of the sorbent material; (ii) primary absorption is absorption into stable air-spaces <u>among</u> aggregated granules or fibres of the sorbent material (air-spaces must be stable if they are to aid recovery of oil) and (iii) secondary absorption is absorption into pits, lacunae or lumina <u>within</u> individual granules or fibres of the sorbent material.

|                                     | Me   | chanisms of oit pick<br>Primary | sup<br>Secondary |
|-------------------------------------|--|---------------------------------|------------------|
| Sorbent                             | Adsorption   | Absorption                      | absorption       |
| Plant-based                         |  |                                 |                  |
| Bedex 31 (Loose                     | ✓  | Small – Med.                    | ✓                |
| wood fibres)                        |  | Small - Med.                    |                  |
| Conwed 31 (Woven                    | ✓  | √<br>Great                      | ~                |
| loose cellulose                     |  | Great                           |                  |
| fibres)                             |  |                                 |                  |
| Peat moss 31                        | ✓  | S—-"                            | <b>✓</b>         |
| (Loose granules                     |  | Small                           |                  |
| and fibres)                         |  |                                 |                  |
| Slikwik 31 (Loose,                  |  | ~                               |                  |
| ground com cabs)                    | •  | Small                           | •                |
| ground corn cobs) Oclan-Sorb 32     |  |                                 |                  |
| (Loose fibres and                   | •  | Small                           | •                |
| granules of peat                    |  |                                 |                  |
|                                     |  |                                 |                  |
| moss)<br>Zugol <sup>32</sup> (Loose |  | ✓                               | ·                |
| fibres and granules                 | •  | Small                           | •                |
| of pine bark)                       |  |                                 |                  |
| Verdyol 32 (Loose                   |  | - A                             |                  |
| vegetable fibres)                   | *  | Small - Med.                    | •                |
| _                                   |  |                                 |                  |
| Alfob W 33 (Loose                   | <b>*</b>   | Small — Med.                    | ✓                |
| fibres)                             |  | Small – Med.                    |                  |
| CCD Woodchips 33                    | ✓  | ✓<br>Small                      | ✓                |
| (Loose fibres and                   |  | Smail                           |                  |
| granules)                           |  |                                 | ,                |
| CAP Cork 33                         | ··   |                                 |                  |
| (Loose fibres and                   | •  | Small                           | •                |
| granules)                           |  |                                 |                  |
| Sawdust 33 (Loose                   |  | <b>✓</b>                        | <b>✓</b>         |
| fibres and                          | •  | Small                           | •                |
| granules)                           |  |                                 |                  |
|                                     |  |                                 |                  |
| Animat-based                        | The state of the s |                                 |                  |
| Seaclean 32                         | 5-h  | S. A.                           | ✓                |
| (Feather pillow)                    | Enhanced by great surface-<br>area   | Great                           |                  |
| Wool Kmop <sup>32</sup>             |  |                                 | ×                |
| (Loose fibres)                      | ✓  | Med Great                       |                  |
| 120000 110100)                      |  |                                 |                  |



Unfortunately, comparing the different sorbents is complicated by the range of oils tested being similar, but not identical among the different reports. Only four oils were common to all three of the Environment Canada reports. These were: (i) 1-day old Diesel, (ii) 1-day old Crude, (iii) 7-day old Crude and (iv) 1-day old Bunker C. Three other kinds of oil/hydrocarbon were tested in at least two of the reports: these were (i) 7-day old Diesel 31, 32, (ii) cyclohexane 32, 33 and (iii) toluene 32, 33. 7-day old Bunker C was evaluated in only a single report 32. For the sake of simplicity, all of these test liquids are referred to as 'oils' in the following text, even though cyclohexane and toluene are not oils.

Of potentially greater concern than differences among reports in the range of oils tested, are differences in the way evaluations were done to measure pick-up of oil and water and the re-usability of sorbents (Table 7). In general, evaluations involved soaking a known amount of sorbent in a layer of oil floating on water. The sorbent was then left to soak for a set time, drained and hydraulically pressed to extract oil and any water that had been captured. The differences among reports concerned the thickness of the layer of oil, the soak-time and, for the 48-hour test only, whether the system was agitated during the tests. In the 1983 report <sup>31</sup>, all oils were layered on water to a depth 1.0 mm. In the 1985 <sup>32</sup> and 1991 reports <sup>33</sup>, cyclohexane, toluene and diesel were deployed in a layer 2.5 mm deep and Crude and Bunker C oils in layers 5.0 mm deep. In Update II <sup>31</sup>, the soak time for all oils was 15 minutes; in Update III <sup>32</sup>, it was 1 hour and in Update IV <sup>33</sup>, it was 30 minutes. For the 48-hour submersion test, the sorbent-oilwater system was oscillated continuously in trials for the 1983 report, but left still in the 1985 and 1991 reports. Details of methodological differences between Environment Canada reports are summarised below in Table 7.

The significance of these methodological differences for the oil and water pick-up tests is hard to ascertain. The equivalence of findings among reports depends on the effects of thickness of oil and soak-time on the sorbents' performances. The most optimistic scenario would be if the shortest soak-times and thinnest layers of oil used were well in excess of those needed to achieve equilibrial conditions in the sorbent-oil-water system. The pessimistic scenario would be if the thicker layers of oil and longer soak times had increased oil and water pick-up, but lessened re-usability. For layer-thickness, we do not have any information to gauge which is the more likely scenario, but we do for soak-time.

The sorbent product *Oclan-Sorb* (treated peat moss) was tested in both the 1985 report <sup>32</sup> and the 1991 report <sup>33</sup> and reportedly attained generally greater IOP and MOP with a shorter soak-time (30 mins cf. 1 hour; see Tables 8 & 9) [Note: oil-layers were of equal thickness in the 1985 and 1991 reports]. IWP showed the same trend between 1985 and 1991 as did the oil pick-up variables (Table 11), but MWP (Table 12) was greater in 1985 with the longer soak-time. The reusability of *Oclan-Sorb* was also generally greater in the 1991 report with the shorter soak-time (Table 10). Differences in results for *Oclan-Sorb* between the 1985 and 1991 reports may have been caused by the difference in soak-time (unlikely given the counter-intuitive trend for IOP, MOP and IWP), or they may merely reflect different batches of the product. Overall, these results for *Oclan-Sorb* defy straightforward interpretation and add little to our knowledge of the general effect of soak-time. Clearly, though, there are grounds to doubt the comparability of results between different reports. Without further information, we can say little more.



**Table 7.** Methodological differences in oil and water pick-up tests among Updates II  $^{34}$ ,  $^{31}$  and IV  $^{33}$  of the on-going reviews by Environment Canada

|  | Methodologica   | l details specific to par     | ticular updates               |
|--|---|-------------------------------|-------------------------------|
| Paints of<br>difference<br>pervisor Updates  | Update II   | Update III                    | Update IV                     |
| Cyclo-hexane                                 | ×   | <u> </u>                      | ✓                             |
| Laver thickness                              |   | 2.5 mm                        | 2.5 mm                        |
| Toluene                                      | ×   | <u> </u>                      |                               |
| Layer thickness                              |   | 2.5 mm                        | 2.5 mm                        |
| 1-day Diesel                                 |   |                               |                               |
| Layer thickness                              | 1.0 mm  | 2.5 mm                        | 2.5 mm                        |
| 7-day Diesel                                 |   |                               | ×                             |
| Layer thickness                              | 1.0 mm  | 2.5 mm                        |                               |
| 1-day Crude                                  |   |                               | ····                          |
| l avec this leader                           | 1.0 mm  | 5.0 mm                        | 5.0 mm                        |
| Layer thickness 7-day Crude                  |   |                               | 5.011111                      |
| r-day ordae                                  | ✓   | ✓                             | ✓                             |
| Layer thickness                              | 1.0 mm  | 5.0 mm                        | 5.0 mm                        |
| 1-day Bunker C                               | <b>✓</b>  | ✓                             | ✓                             |
| Layer thickness                              | 1.0 mm  | 5.0 mm                        | 5.0 mm                        |
| 7-day Bunker C                               | ×   | ✓                             | ×                             |
| Layer thickness                              |   | 5.0 mm                        |                               |
| Soak-time for                                |   |                               |                               |
| measuring oil &                              | 15 minutes  | 60 minutes                    | 30 minutes                    |
| water pick-up                                | Only 1 variable given as                                  |                               |                               |
| Water pick-up<br>variables                   | Water pick-up'.  Wot specified whether initial or maximal | Initial and maximal on re-use | Initial and maximal on re-use |
| Conditions of 48-<br>hour submersion<br>test | Oll and water oscillated continuously                     | Oil and water kept still      | Oil and water kept still      |

The way we have presented results from the Environment Canada reports allows for uncertainty concerning the comparability of results from different reports. For each variable measured, results from the different Environment Canada reports are summarised in a single table, but they are grouped according to source. The written description of results for each variable proceeds as though results from the different reports were comparable. In the event, however, that a more precautionary view of the comparability of sorbents is deemed appropriate, the tables summarising results emphasise (in bold text) the best performing sorbent(s) for each evaluation in each of the three updates. For brevity and to avoid confusion with the alternate overview of results these separate evaluations for each report are not described in the text.

Further methodological details of specific tests and definitions of particular variables are provided below with a summary and interpretation of results.

### Initial oil pick-up (IOP)

The initial oil pick-up is the amount of oil captured on the sorbent's first exposure to oil. A useful sorbent for use on spilt oil would be one that exhibited great IOP. In all three of the Environment Canada reports, initial oil-pick-up (g oil per g sorbent) was calculated using the following equation:



Initial oil pick-up (a oil per a sorbent) =

Sorbents for oiled foreshores

Weight of oil, water & sorbent after initial exposure

Weight of water recovered

Initial weight of sorbent

Initial weight of sorbent

Results for the different sorbents with different oils are summarised in Table 8.

Table 8. Initial oil pick-up (g oil per g sorbent) for a range of organic sorbents in for the 1983 31, 1985 32 and 1991 33 reviews by Environment Canada. Note that the strict comparability of the results from different reports is suspect because of methodological differences of unknown consequence (see Table 7). Results emphasised in bold Indicate the best performing sorbent(s) in each category of evaluation for each of the three reviews. (nt - not tested).

|  |                 | In    | itial oil p        | ick-up (c | oil/g so | orbent) |                   |              |
|--|-----------------|-------|--------------------|-----------|----------|---------|-------------------|--------------|
|  |                 |       |                    |           |          |         |                   |              |
|  |                 |       | Type of            | oilthydro | oppon te | sted    |                   |              |
| 1-1-1  |                 |       |                    |           |          |         |                   |              |
|  | rcio To<br>xane |       |                    |           |          |         | day 7<br>mker C B | day          |
| CONTRACTOR BY CONTRACTOR BY CONTRACTOR CONTR | Yelste          | Ø.    | <b>0000 64</b>     | 939 V     | urus v   | ****    | 4111-4- V         | alter or the |
| Sorbent  |                 |       | <u>XXXXXXXXXXX</u> |           |          |         |                   |              |
| Update II, 1983  |                 |       |                    |           |          |         |                   |              |
| Bedex  | nt              | nt    | 7.07               | 9.77      | 7.24     | 11.90   | 8,83              | nt           |
| Conwed   | nt              | nt    | 13.61              | 13,01     | 2.59     | 4.53    | 2.80              | nt           |
| Peat moss  | nt              | nt    | 3.38               | 5.96      | 2.35     | 4.21    | 1.65              | rst          |
| Slikwik  | nt              | nt    | 3.48               | 3.74      | 3.52     | 2.78    | 5.56              | nt           |
| Update III, 1985   |                 |       |                    |           |          |         |                   |              |
| Oclan-Sorb   | 4.39            | 4.68  | 4.88               | 5,76      | 5.84     | 2.39    | 10.21             | 6.21         |
| Seaclean   | 3.76            | 6.07  | 5.63               | 5.91      | 2.95     | 2.96    | 1,66              | 2.24         |
| Zugol  | 98,0            | 1.73  | 1.06               | 2.36      | 3.07     | 2.80    | 4.99              | 4.71         |
| Verdyol  | 9.01            | 9.79  | 9.41               | 10.33     | 2.26     | 12.57   | 6.21              | 8.80         |
| Update IV, 1991  |                 |       |                    |           |          |         |                   |              |
| Alfob W  | 2,36            | 2.78  | 2.51               | nt        | 2.88     | 3.71    | 5.84              | nt           |
| CCP Woodchips  | 0.51            | 0.82  | 0.54               | ηţ        | 0.78     | 1.84    | 3.65              | nt           |
| CAP Cork   | 3.73            | 5.00  | 4.65               | nt        | 3.78     | 3.82    | 2.14              | nt           |
| Oclan-Sorb   | 8,38            | 9.36  | 9.07               | nt        | 6.16     | 6,76    | 5,51              | nt           |
| Sawdust  | 5.28            | 5.20  | 4.08               | nt        | 5.29     | 6,65    | 9,75              | nt           |
| Wool Kmop  | 9.51            | 11.62 | 9.54               | nt        | 14.07    | 19.80   | 11.70             | nt           |

If we ignore the methodological differences among reports and treat all results as directly comparable, then Wool Kmop 33, stands out as having the greatest initial oil pick-up (IOP) for the greatest range of oils. Wool Kmop was not tested with 7-day Diesel or 7-day Bunker C, but for the 6 other oils Wool Knop had the greatest IOP for all but one kind of oil. With 1-day Diesel, 1OP for Wool Kmop (9.5 g.g<sup>-1</sup>) was second to that for the Conwed sorbent blanket <sup>31</sup> (13.6 g.g<sup>-1</sup>). Wool Kmop was tested in the 1991 report 33 with the thicker layers of oil (2.5 mm or 5.0 mm) and the intermediate soak time (30 minutes), so we caution that its IOP may have been less were it tested as per the 1991 report, which used a thinner oil-layer and a shorter soak time (1.0 mm and 15 mins, respectively). Verdyol 32 also performed well across many types of oil, other materials were much more hit-or-miss (Table 8).



As mentioned before, *Oclan-Sorb* peat moss was tested independently in the 1985 <sup>32</sup> and the 1991 reports. Results for *Oclan-Sorb* were generally comparable between reports, except for the test with 1-day Bunker C. In 1985, with a soak-time of 60 minutes *Oclan-Sorb* exhibited an IOP with 1-day Bunker C of 10.2 g.g.<sup>-1</sup>, a result second only to *Wool Kmop*. In 1991, however, with a soak-time of 30 minutes, *Oclan-Sorb* exhibited an IOP of only 5.5 g.g.<sup>-1</sup> with Bunker C. This difference emphasises the possible problem of comparing sorbents among reports.

# Maximal oil pick-up on re-use (MOP)

Maximal oil-pick-up (MOP) on re-use (g oil per g sorbent) was determined by calculating oil pick-up for each of several re-uses and noting the maximal value attained. Sorbents were continually re-used up to 10 times, or until the sorbent completely disintegrated, or oil pick-up fell below 50 % of IOP. MOP may be a more important consideration than IOP when selecting a sorbent that can be used repeatedly to remove spilt oil from the environment. Results for MOP are in Table 9 and results on re-usability are in Table 10.

**Table 9.** Maximal oil pick-up (g oil per g sorbent) for a range of organic sorbents examined in the 1983 <sup>31</sup>, 1985 <sup>32</sup> and 1991 <sup>33</sup> reviews by Environment Canada. Results are grouped according to source. Note that strict comparability of the results from different reports is suspect because of methodological differences of unknown consequence (see Table 7). (nt - not tested)

|                          |          | Ma      | ximal oi | l pick-up | (g oil/ g | sorbent) |           |              |
|--------------------------|----------|---------|----------|-----------|-----------|----------|-----------|--------------|
|                          |          |         | Type of  | oilhydro  | carbon te | sted     |           |              |
|                          | Cyclo- 7 | eluerre | i-day    | 7-day     |           |          | 1-day     | 7-dav        |
|                          | texane   |         | Diesei   | Diesel    | Grude     |          | Suriker C | ссасынымиска |
| Sorbent                  |          |         |          |           |           |          |           |              |
| De dete II 4002          |          |         |          |           |           |          |           |              |
| Update II, 1983<br>Bedex | nt       | nt      | 7.07     | 9.77      | 10,96     | 11.90    | 8.83      | nŧ           |
| Conwed                   | nt       | nt      | 13.61    | 13.01     | 12.60     | 15,00    | 4.21      | nt           |
| Peat moss                | nt       | nt      | 5.38     | 5.96      | 5.02      | 4.48     | 3.86      | nt           |
| Slikwik                  | nt       | nt      | 3.48     | 3.74      | 3.52      | 2.78     | 5.56      | nt           |
| Update III, 1985         |          |         |          |           |           |          |           |              |
| Ocian-Sorb               | 4.39     | 4.68    | 4.88     | 5.76      | 5.84      | 2,53     | 10.21     | 6.21         |
| Seaclean                 | 3.76     | 6.07    | 5,63     | 5.91      | 2.95      | 3.32     | 2.08      | 2.65         |
| Zugol                    | 0.88     | 1.73    | 1.06     | 2.36      | 3.07      | 2.80     | 4.99      | 4.71         |
| Verdyol                  | 9.01     | 9.79    | 9,41     | 10.33     | 4.14      | 12.57    | 10.09     | 10.43        |
| Update IV, 1991          |          |         |          |           |           |          |           |              |
| Alfob W                  | 2.36     | 2.78    | 2.51     | nt        | 2.88      | 3.71     | 5.84      | nt           |
| CCD Woodchips            | 0.51     | 0.85    | 0.54     | nt        | 0.78      | 1.84     | 3.65      | nt           |
| CAP Cork                 | 4,23     | 5.09    | 4.65     | nt        | 3.78      | 3.82     | 2.67      | nt           |
| Oclan-Sorb               | 8.38     | 9.36    | 9,07     | nt        | 6.16      | 7.15     | 5.51      | nt           |
| Sawdust                  | 5.28     | 5.20    | 4.08     | nt        | 5.29      | 6.65     | 9.75      | nt           |
| Wool Kmop                | 10.74    | 11.62   | 9.54     | nt        | 14.07     | 19.80    | 19.72     | nt           |

Comparisons between MOP and IOP for the same combination of oil and sorbent can be relied upon because the only methodological difference involved was re-use (i.e. these comparisons are not affected by the other methodological differences that confuse comparisons among sorbents in



different reports). For most combinations of oils and sorbents, the value of MOP was the same as IOP (Table 9 cf. Table 8). Out of 88 combinations of oils and sorbents in the three different reports, there were only 22 instances where MOP was greater than IOP. No sorbent had an MOP > IOP in all oils tested.

MOP as a percentage of IOP was greatest for *Conwed* <sup>31</sup> with 1-day Crude (486 %) and 7-day Crude (331 %), and untreated peat moss <sup>31</sup> with 1-day Bunker C (234 %) and 1-day Crude (214 %). Substantial increases in MOP relative to IOP also occurred for *Verdyol* <sup>32</sup> with 1-day Crude (183 %) and 1-day Bunker C (162 %), for *Wool Kmop* <sup>33</sup> with 1-day Bunker C (169 %) and untreated peat moss with 1-day Diesel (159 %). All other increases in MOP relative to IOP were in the range 101 % to 125 %.

Despite some large increases in MOP relative to IOP, the best performing sorbent for each oil based on MOP was exactly the same as that based on IOP; *i.e. Conved* <sup>31</sup> was best with 1-day Diesel and 7-day Diesel, *Wool Kmop* <sup>33</sup> was best with 1-day Crude, 7-day Crude, 1-day Bunker C, cyclohexane and toluene and *Verdyol* <sup>32</sup> was best with 7-day Bunker C. Note that most of the sorbents that attained the greatest MOP for each test-oil were also sorbents in the 1985 and 1991 reports, which used the thicker layers of oil (2.5 or 5.0 mm) and the longer soak-times (60 and 30 minutes, respectively). These conditions may have contributed to generally larger values of MOP than in the 1983 report.

A problem with MOP as a selection criterion is that we are not told when and how often MOP was attained for each combination of sorbent and oil. Given the criteria for stopping re-use (disintegration; oil pick-up < 50 % IOP, or a maximum of 10 re-uses), a sorbent may have attained its MOP on second re-use and then functioned at only 51% of IOP for a further 8 re-uses, or it could have continued functioning at MOP for all subsequent re-uses. The total oil pick-up over the sequence of re-uses would obviously be very different between these two scenarios. Where the goal is recovery of spilt oil, total oil pick-up with re-use, or even average pick-up, would be more useful selection criteria than MOP.

# Re-usability of sorbent materials/products

In each of the three Environment Canada reports, the number of effective re-uses for each sorbent in each oil was measured by re-using sorbents up to 10 times, or until the sorbent completely disintegrated, or oil pick-up fell below 50 % of IOP. Oil was replenished to the desired depth (differed among reports; see Table 7) after each re-use. Like MOP, re-usability is an important selection criterion when the intention is to use the sorbent repeatedly to remove spilt oil from the environment.

Among reports, the combinations of sorbents and oils that resulted in the greatest number of sorbent-re-uses were *Wool Kmop* <sup>33</sup> with cyclohexane and toluene (at least 10 uses in each case); *Seaclean* <sup>32</sup> and *Verdyol* <sup>32</sup> with 1-day Bunker C and 7-day Bunker C (at least 10 uses in each case); *Seaclean* with 7-day Crude (9 uses) and *Verdyol* with 1-day (9 uses). Note that no sorbent tested in the 1983 report gave the overall greatest number of re-uses with any oil, despite the fact that the 1983 tests used the thinnest oil-layers (1.0 mm) and the shortest soak time (15 minutes). It might have been expected that these conditions would have caused generally greater re-usability of sorbents compared to the conditions in tests in subsequent reports.



**Table 10.** Number of effective re-uses for a range of organic sorbents examined in the 1983 <sup>31</sup>, 1985 <sup>32</sup> and 1991 <sup>33</sup> reviews by Environment Canada. Results are grouped according to source. Note that the strict comparability of the results from different reports is suspect because of methodological differences of unknown consequence (see Table 7). (nt – not tested).

|                  |                  |         | Numt            | ser of effe     | ctive re        | -uses          |                   |                   |
|------------------|------------------|---------|-----------------|-----------------|-----------------|----------------|-------------------|-------------------|
|                  |                  |         | Турез           | of oil/hydro    | ocarbon         | tested         |                   |                   |
|                  | Cyclo-<br>hekanu | Tollane | 1-day<br>Diesei | 7-day<br>Diesel | 1-day<br>Crixic | 7-day<br>Crede | 1-day<br>Bunker C | r-day<br>Bonker C |
| Sorbent          |                  |         |                 |                 |                 |                |                   |                   |
| Update II, 1983  |                  |         |                 |                 |                 | _              | _                 |                   |
| Bedex            | nt               | ni      | 0               | 0               | 2               | 0              | 0                 | nt                |
| Conwed           | nt               | nt      | 2               | 2               | 2               | 2              | O                 | nt                |
| Peat moss        | nt               | nt      | 0               | 0               | 1               | 2              | 2                 | nt                |
| Slikwik          | nt               | nt      | 0               | 0               | 1               | 1              | 0                 | nt<br>            |
| Update III, 1985 |                  |         |                 |                 |                 |                |                   |                   |
| Ocian-Sorb       | 1                | 1       | 1               | 1               | 1               | 1              | 0                 | 0                 |
| Seaclean         | 3                | 3       | 7               | 7               | 1               | 9              | 10                | 10                |
| Zugol            | 1                | 1       | 1               | 1               | 1               | 1              | 2                 | 2                 |
| Verdyol          | 2                | 3       | 2               | 2               | 9               | 4              | 10                | 10                |
| Update IV, 1991  |                  |         |                 |                 |                 |                |                   |                   |
| Alfob W          | 1                | 1       | 1               | nt              | 2               | 1              | 2                 | nt                |
| CCD Woodchips    | 1                | O       | 0               | ŋŧ              | Ō               | 0              | Ð                 | nt                |
| CAP Cork         | 8                | 4       | 5               | nt              | 5               | 3              | 5                 | nt                |
| Oclan-Sorb       | 1                | 1       | 1               | nt              | 5               | 5              | 5                 | nt                |
| Sawdust          | Ď                | 0       | ٥               | nt              | 0               | 0              | D                 | лt                |
| Wool Kmop        | 10               | 10      | 5               | nt              | 5               | 5              | 5                 | лt                |

# Initial water pick-up (IWP)

Initial water pickup (IWP) (g water per g sorbent) is the amount of water captured when the sorbent is first exposed to oil on water. Because sorption-capacity taken up by water is not available to oil, a useful oil-sorbent for aqueous environments would be one with small IWP. IWP was calculated as follows:

| Initial water pick-up     | Weight of water recovered |  |  |  |
|---------------------------|---------------------------|--|--|--|
| (g water per g sorbent) = | Initial weight of sorbent |  |  |  |

No individual sorbent showed the absolute smallest IWP with all, or even a majority of oils (Table 11). The particular combinations of sorbents and oils that resulted in the absolute smallest IWP were *CCD Woodchips* <sup>33</sup> and *CAP Cork* <sup>33</sup> with cyclohexane, *CCD Woodchips* with toluene, Oclan-Sorb with 1-day Diesel, *Zugol* <sup>32</sup> with 7-day Diesel, *Seaclean* <sup>32</sup> with 1-day Crude, *CCD Woodchips* and *Oclan-Sorb* with 7-day Crude, *Alfob W* <sup>33</sup> with 1-day Bunker C and *Seaclean* with 7-day Bunker C.



**Table 11.** Initial water pick-up (g oil per g sorbent) for a range of organic sorbents in the 1983 <sup>31</sup>, 1985 <sup>32</sup> and 1991 <sup>33</sup> reviews by Environment Canada. Results are grouped according to source. Note that the strict comparability of the results from different reports is suspect because of methodological differences of unknown consequence (see Table 7). (nt – not tested).

|                  |                  | Initi  | al water       | pick-up                                 | (g oil per     | g sorbe        | int)*             |                    |
|------------------|------------------|--------|----------------|---|----------------|----------------|-------------------|--------------------|
|                  |                  |        | Туре           | of oil/hyd                              | rocarbon       | ested          |                   |                    |
| Sorbent          | Cyclo-<br>nexane | Тоюшче | 1-day<br>Diese | 7-dev<br>Diacal                         | 1-dev<br>Crude | 7-day<br>Crude | 1-day<br>Busker C | 7-day<br>Stinker C |
| Update II, 1983  |                  |        |                | *************************************** |                |                |                   |                    |
| Bedex            | nt               | nt     | 3.87           | 3.37                                    | 1.20           | 1.60           | 3.89              | nt                 |
| Conwed           | nt               | nt     | 0.25           | 0.25                                    | 0.80           | 0.66           | 1.12              | nt                 |
| Peat moss        | nt               | nt     | 3.71           | 3.53                                    | 1.39           | 0.41           | 0.64              | nŧ                 |
| Slikwik          | nt               | nt     | 0.22           | 0.57                                    | 0.37           | 1.17           | 2.43              | nt                 |
| Update Iff, 1985 |                  |        |                |   |                |                |                   |                    |
| Oclan-Sorb       | 0.07             | 0.30   | 0.00           | 0.07                                    | 0.15           | 0.02           | 0.06              | 0.11               |
| Seaclean         | 0.45             | 0.19   | 0.34           | 0.22                                    | 0.02           | 0.10           | 0.01              | 0,02               |
| Zugol            | 0.03             | 0.04   | 0.06           | 0.04                                    | 80.0           | 0.09           | 0.05              | 0.09               |
| Verdyol          | 0.11             | 0.08   | 0.13           | 0.21                                    | 0.07           | 0.19           | 0.12              | 0.06               |
| Update IV, 1991  |                  |        |                |   |                |                |                   |                    |
| Alfob W          | 0.03             | 0.04   | 0.06           | nt                                      | 80.0           | 0.11           | 0.00              | nt                 |
| CCD Woodchips    | 0.00             | 0.00   | 0.01           | nt                                      | 0.06           | 0.02           | 0.02              | nt                 |
| CAP Cork         | 0.00             | 0.05   | 0.03           | лt                                      | 0.12           | 0.04           | 0.06              | nt                 |
| Oclan-Sorb       | 0.07             | 1.09   | 0.10           | at                                      | 0.58           | 0.12           | 0.01              | лt                 |
| Sawdust          | 0.49             | 0.58   | 0.87           | at                                      | 0.33           | 0.03           | 0.38              | яt                 |
| Wool Kmop        | 0.31             | 0.83   | 0.80           | - nt                                    | 0.07           | 0.13           | 0.03              | nt                 |

# Maximal water pick-up (MWP)

Maximal water pick-up (MWP) with re-use (g water per g sorbent) was determined by calculating water pick-up for each of several re-uses and noting the maximal value attained. MWP may be a more important consideration than IWP when selecting a sorbent that can be used repeatedly to remove spilt oil from the environment. Assessments of MWP were only made in the 1985 and 1991 reports by Environment Canada reports. Results are summarised below in Table 12.

As with comparisons between MOP and IOP for each oil-sorbent system, comparisons of MWP and IWP are reliable because the only methodological difference involved was the re-use of sorbents (i.e. these comparisons are not affected by the other methodological differences that confuse comparisons among sorbents in different reports). Out of 68 combinations of oils and sorbents in the two different reports that measured MWP, there were 34 instances where MWP was greater than IWP, 31 instances where there was no change and 3 instances where MWP was less than IWP. A reduction in water pick-up with re-use is a desirable property in an oil-sorbent. All instances of this phenomenon occurred with Zugol <sup>32</sup>. MWP as a percentage of IWP was 33 % for Zugol with cyclohexane and 1-day Diesel and 75 % for Zugol with toluene. With all other oils with which Zugol was tested, it showed either no change or an increase in MWP relative to IWP.



Table 12. Maximal water pick-up (g oil per g sorbent) for a range of organic sorbents in the 1985 <sup>32</sup> and 1991 <sup>33</sup> reviews by Environment Canada. Results are grouped according to source. Note that the strict comparability of the results from different reports is suspect because of methodological differences of unknown consequence (see Table 7). (nt – not tested).

|                  |                  | Maxi    | mal wate        | r capaci         | ty (g oll p    | er g sar       | bent)             |                   |
|------------------|------------------|---------|-----------------|------------------|----------------|----------------|-------------------|-------------------|
| ٠                |                  |         | Туре            | of oil/hyd       | ocarbon        | tested         |                   |                   |
| Sorbent          | Cyclos<br>hexane | Toluene | 1-day<br>Cresel | 7-day<br>Classet | 1⊷3ау<br>Слије | 7-day<br>Cruse | 1-day<br>Burker C | 7-day<br>Besker C |
| Update III, 1985 |                  |         | <b>-</b>        |                  |                |                |                   |                   |
| Ocian-Sorb       | 0.10             | 0.65    | 0.29            | 0.17             | 0.18           | 0.02           | 0.06              | 0,11              |
| Seaclean         | 1.26             | 0.38    | 0.44            | 0.33             | 0.04           | 0.33           | 0.05              | 0.04              |
| Zugot            | 0.01             | 0.03    | 0.02            | 0.05             | 0.08           | 0.11           | 0.06              | 0.10              |
| Verdyol          | 0.14             | 0.34    | 0.14            | 0.22             | 0.37           | 0.19           | 0.19              | 0.10              |
| Update IV, 1991  |                  |         |                 |                  |                |                |                   |                   |
| Alfob W          | 0.03             | 0,04    | 0.06            | nt               | 80.0           | 0.11           | 0.05              | nt                |
| CCD Woodchips    | 0.00             | 0.00    | 0.01            | nt               | 0.06           | 0.02           | 0.02              | лt                |
| CAP Cork         | 0.07             | 0.80    | 0.03            | nt               | 0.12           | 0.08           | 0.28              | វា                |
| Oclan-Sorb       | 0.07             | 1.09    | 0,10            | nt               | 0.58           | 0.65           | 0.29              | ni                |
| Sawdust          | 0.49             | 0.58    | 0.87            | nt               | 0.33           | 0.03           | 0.38              | nt                |
| Wool Kmop        | 0.31             | 0.83    | 0.80            | nt               | 0.86           | 0.31           | 0.34              | nt                |

Whilst a reduction in water pick-up with re-use is the most desirable attribute for an oil-sorbent, no increase is the next most desirable. From the results in Table 12, three sorbents stand out as showing no change in water pick-up with re-use across a broad range of oils. These were *CCD Woodchips* <sup>33</sup>, sawdust <sup>33</sup> and *Alfob W* <sup>33</sup>.

With very few exceptions, the combinations of oils and sorbents that gave the absolute smallest values of IWP also gave the absolute smallest values of MWP. The exceptions occurred with 1-day Diesel and 1-day Bunker C. For 1-day Diesel, the smallest IWP was obtained with Oclan-Sorb in the 1985 report, but the lowest MWP was obtained with CCD Woodchips. For 1-day Bunker C, the smallest IWP was obtained with Alfob W, but the lowest MWP was obtained with CCD Woodchips.

# Observations following 48-hour submersion in oil on water

As far as can be ascertained from the limited information available, each report used the same thickness of oil on water for the 48-hour tests of submersion as were used in tests to measure oil and water pick-up. So, the thicknesses of oil-layers differed among reports for the same kind of oil (details of differences were reported above). The methods used also differed among reports in terms of whether there was physical agitation of the sorbent-oil-water system. For the 1983 report, the sorbent-oil-water system was oscillated continuously, but for the 1985 and 1991 reports it was kept still. We do not know precisely how this difference would have affected the behaviour of the sorbent. Potentially, agitation could have increased a sorbent's exposure to the water beneath the oil and so possibly increased its tendency to absorb water and sink. So, as per



**Table 13.** Observations following 48-hour tests of submersion in oil on water for a range of organic sorbents in for the 1983  $^{31}$ , 1985  $^{32}$  and 1991  $^{33}$  reviews by Environment Canada. Results are grouped according to source. Note that the strict comparability of the results from different reports is suspect because of methodological differences of unknown consequence (see Table 7). (nt – not tested).

|                     | Ob   | servation  | is follow  | ing 48-ho   | our subm  | ersion in   | oil on w                                     | ater                               |
|---------------------|--|--|--|---|---|---|--|------------------------------------|
|                     |  |  | Туре   | of oil/hyd  | rocarbon  | tested  |  |                                    |
| Sorbent             | Decane<br>Decane   | Tolliens   | 1 dev<br>Draser                                    | 7-day<br>Diesel                                     | 1-day<br>Grude                                    | oay<br>Crude                                      | 1-day<br>Burker C                            | 7-day<br>Eunker C                  |
| Update II,<br>1983  | "  |  |  |   |   |   |  |                                    |
| Bedex               | nt   | nt   | 100 % affort                                       | 100 % affoat  | 100 % affoat                                      | 100 % affoat                                      | 11 % affoat                                  | 61 % สปิดส                         |
| Conwed              | nt   | nt   | 100 % affoat -<br>36 %<br>weakened                 | 100 % afloat -<br>38 %<br>weakened                  | 100 % affoat -<br>5 % stronger                    | 100 % afteat ~<br>12 %<br>weekened                | 100 % afloat -<br>53 %<br>weakened           | 100 % effect -<br>38 %<br>weakened |
| Peat moss           | nt   | nt   | 100 % affoat                                       | 100 % aftoat  | 100 % affoat                                      | 100 % affoat                                      | 100 % affoat                                 | 100 % affoat                       |
| Slikwik             | nt   | nt   | 100 % effoet                                       | 43 % afloat   | 100 % alloat                                      | 100 % affoat                                      | 100 % affoat                                 | 100 % afloat                       |
| Update III,<br>1985 |  |  |  |   |   |   |  |                                    |
| Oclan-Sorb          | Afloat -<br>swollen  | Partially sunk -<br>swollen                                | Afloat -<br>swollen                                | Afloat —<br>symllen —<br>discolouration<br>of water | Affoat -<br>metted                                | Affoat -<br>matted                                | Aftoat -<br>matted                           | Afloat –<br>matted                 |
| Seaclean            | Partially sunk   | Partially sunk -<br>matted -<br>discolouration<br>of weter | Afloat   | Afloat  | Partially sunk                                    | Partially sunk                                    | Pedially sunk                                | Partielly sunk                     |
| Zugol               | Afloat   | Afloat -<br>matted -<br>discolouration<br>of water         | Aftoat   | Afloat  | Aftoat  | Afloat -<br>matted                                | Afloat -<br>matted                           | Afloat –<br>matted                 |
| Verdyol             | Partialty sunk -<br>matted -<br>discolouration<br>of water | Portlally sunk -<br>matted -<br>discolouration<br>of water | discolouration                                     | Partially sunk -<br>discolouration<br>of water      |   | Afloat -<br>matted                                | Afloat -<br>matted                           | Afloat –<br>metted                 |
| Update IV,<br>1991  |  |  |  |   |   |   |  |                                    |
| Alfob W             | Affort -<br>saturated<br>with test<br>liquid               | Afloat -<br>saturated<br>with test<br>liquid               | Afjoat -<br>saturated<br>with test<br>liquid       | nt  | Afloat -<br>saturated<br>with test<br>liquid      | Affoat -<br>seturated<br>with test<br>figuid      | Affoat -<br>saturated<br>with test<br>liquid | nŧ                                 |
| CCD                 | Afloat   | Afloat   | Afloat   | nt  | Afloat  | Afloat  | Afloat                                       | រាវ                                |
| Woodchips           |  |  |  |   |   |   |  |                                    |
| CAP Cark            | Affost -<br>completely<br>dispersed -<br>saturated         | Aflost -<br>partially<br>dispersed -<br>saturated          | Affoat -<br>completely<br>dispersed -<br>saturated | nt  | Affoat -<br>partially<br>dispersed -<br>saturated | Affoat -<br>partially<br>dispersed -<br>saturated | Afficially dispersed - partially saturated   | nt                                 |
| Oclan-Sorb          | Afloat -<br>completely<br>dispersed                        | Affoat -<br>completely<br>dispersed                        | Afloat -<br>completely<br>dispersed                | nt  | Aftigat -<br>completely<br>dispersed              | Afloat  | Afloat                                       | пt                                 |
| Sawdust             | Afloat -<br>partially<br>dispersed                         | Afloat -<br>partially<br>dispersed                         | Afloat -<br>partially<br>dispersed                 | nt  | Afloat -<br>partially<br>dispersed                | Afloat -<br>partially<br>dispersed                | Sunk   | nt                                 |
| Wool Kmop           | Affoat   | Affoat   | Afloat   | nt  | Affoat  | Afloat  | <b>Af</b> loat                               | nt                                 |



previous evaluations, methodological differences prevent strict comparability of results among different reports. Observations from the 48-hour submersion tests done in each of the three Environment Canada reports are summarised in Table 13.

It was easier to identify the poorly-performing sorbents than to identify those that performed particularly well. Degrees of good performance were not noted. The most poorly-performing sorbents were those that either sank (environmentally undesirable and unhelpful for recovery), physically weakened (noted only for sorbent structures rather than loose materials) or caused discolouration of the water (indicative of leaching). Sorbents that performed well with particular oils (emphasised in bold in Table 13) can only be deduced by elimination of those that performed poorly. Seaclean <sup>32</sup> performed badly because it sank with all oils tested except 1-day and 7-day Diesel. With toluene, Seaclean also caused discoloration of the water. Verdyol <sup>32</sup> also sank and caused discolouration, but only with cyclohexane, toluene, 1-day Diesel and 7-day Diesel. The Conwed sorbent blanket <sup>31</sup> floated on all combinations of oil and water, but its physical structure substantially weakened with use with all oils. Bedex <sup>31</sup> partially sank with 7-day Bunker C and almost entirely sank with 1-day Bunker C (it floated with all other oils). Slikwik ground corncobs <sup>31</sup> partially sank with 7-day Diesel, but floated with all other oils. All other combinations of oil and sorbent resulted in more or less satisfactory performances.

Use of sorbents in the field: techniques of deployment and environmental interactions

The only information presented in the three Environment Canada reports (1983<sup>31</sup>, 1985<sup>32</sup> and 1991<sup>33</sup>) on the use of sorbents in actual oil-spill situations was obtained from the sorbent manufacturers rather than independent evaluations by Environment Canada. Most of the information provided is so superficial and generic that it provides little opportunity for discriminating amongst sorbents (Table 14).

The only striking difference about deployment of sorbents is that those comprising loose granules or fibres can be spread manually, or blown or dropped on to spilt oil, whilst structures formed from sorbent, the *Conwed* sorbent blanket <sup>31</sup> and the *Seaclean* feather pillow <sup>32</sup>, need to be manually placed where they are needed. Among the loose sorbents, there are some differences in the methods of deployment described, but we suspect that these differences reflect varying degrees of detail in the information provided by manufacturers. Loose granules or fibres should all be more or less deployable by the same methods, regardless of their differences in composition. In strong winds, the least dense, loose sorbents (e.g. Bedex wood-fibres (27 kg.m<sup>-3</sup>) and *Wool Kmop* (33 kg.m<sup>-3</sup>)) should be hardest to deploy, particularly if they are blown or dropped on to the oil-spill from any great distance. All sorbents are reported to begin capturing oil more or less immediately on deployment.

A similar distinction between loose sorbents and structures made from sorbents is evident for the stated methods of recovery. The structures must be individually retrieved, whilst loose sorbents (where specified) appear generally amenable to manual recovery (shoveling, raking, skimming, etc.), or mechanical retrieval (mechanised skimmers, suction devices, etc.).



**Table 14.** Information about use of different sorbents reviewed in the Environment Canada reports in actual oil-spills. Data came from sorbent manufacturers, rather than from evaluations by Environment Canada.

| Canaca.                        | Pra  | ctical aspe  | cts of the u   | se of sorbo   | ents on spi   | lt oil         |
|--------------------------------|--|--|--|---|---|----------------|
|                                | Method of<br>deployment                          | Spill-type<br>and best<br>surbent oil<br>Ratio   | Reaction<br>time   | Method of retrieval   | Method of<br>disposal                                   | Toxicity       |
| Sorbent                        |  |  |  |   |   |                |
| Upđate II, 1983                |  |  |  |   |   |                |
| Bedex                          | Manual, blown,<br>dropped                        | Oil on water or<br>land (cover with 5<br>cm Bedex)   | Immediate  | On water: scrop,<br>suction hose.<br>On land: scrape,<br>shovel | Landfill  | Non-toxic      |
| Conwed                         | Manual<br>placement                              | Fresh crude,<br>bunker fuels,<br>distillate fuels<br>(1:16 – 1:20 by<br>weight)                | 8 – 30 seconds   | Manuaj  | Landfill,<br>incineration                               | Non-toxic      |
| Peat moss                      | Manual, blown                                    | 1:8 – 1:12 by<br>weight  | Not known  | Manual, skimmer   | Landfill,<br>incineration                               | Non-toxic      |
| Slikwik                        | Manual, blown                                    | 1:5 by weight  | Immediate  | Manual, skimmer   | Landfill,<br>incineration                               | Noл-toxic      |
| Update III, 1985<br>Oclan-Sorb | Manual, blown                                    | Fresh crude and<br>distillate fuels on<br>shore & water<br>(1;3 - 1:5, tass<br>for heavy oils) | Immediate  | Manual, suction<br>hose, skimmer                                | Landfill,<br>indineration                               | Non-toxic      |
| Seaclean                       | Manual<br>placement                              | light oils,<br>solvents and<br>heavy oils (1:28)   | Fully saturated in<br>15 mins                                | Manual with boat hook, fork, etc.                               | Landfill,<br>incineration                               | Non-toxic      |
| Zugol                          | Manual   | Light and heavy<br>oils (1:3)  | Immediate  | Manual  | Landfill,<br>incineration                               | No information |
| /erdyol                        | Manual, blown                                    | On water, oils<br>ranging from<br>No.2 Fuel oil to<br>Bunker C (1:13 –<br>1:19)                | Varied with<br>viscosity of oil                              | Manual, skimmer   |   | No information |
| Jpdate IV, 1991                |  |  |  |   | •   |                |
| Alfob W                        | Manual, blown                                    | All oils, fuels,<br>emulsions on<br>shore and water<br>(1:3 by weight)                         | Immediate  | Manual, suction<br>hose   | Landfill,<br>incineration                               | Nan-toxic      |
| CCD Woodchips                  | Manual, blown,<br>dropped                        | Grades 1& 2 (1:1<br>- 1:4); Grade 3<br>(1:3 - 1:10)  | Immediate  | Manual, burnt in<br>situ  | Landfill,<br>incineration                               | Non-texic      |
| CAP Cork                       | Manual, blown                                    | All oifs, non-polar<br>solvents (1:1 by<br>volume)   | Immediate to<br>several minutes<br>depending on<br>viscosity | Manual, skimmer   | In situ<br>biodegradation,<br>landfill,<br>incineration | Non-texic      |
| Öclan-Sorb                     | Manual, blown,<br>O <i>clan-Sorb</i><br>spreader | All oils and fuels<br>(1:12 by weight)   | Immediate  | Manual,<br>skimmer, suction<br>hose                             | Landfill,<br>incineration,<br>composting                | Non-toxic      |
| Sawdust                        | Manual,<br>mechanical                            | All oifs and feels<br>(1:20 by weight)   | Immediate to fast  |   | Not specified   | Non-texic      |
| Wool Kmop                      | Manual   | Viscous oils<br>(1:35 by weight)   | Immediate if agitated  | Not specified   | Not specified   | Non-toxic      |



The particular kinds of oils for which the different sorbents can be used and the recommended ratios of sorbent to oil cannot be summarised here any more effectively than in Table 14. Almost all manufacturers recommend their sorbents for use on both light and heavy oils. For *Wool Kmop* <sup>33</sup>, the only recommendation is for viscous oil, but we suspect this was not meant to imply that it could not also be used on lighter oils.

Because the different sorbents in the Environment Canada reports are organic, methods for disposing of them when oiled should be similar. The different methods of disposal recommended by the sorbent manufacturers were landfill, incineration and composting. There is insufficient information to determine whether any method might be better for a particular sorbent. Where information was available, all the sorbents were reportedly non-toxic, but no information about toxicity tests was provided.

# Storage of sorbents

Data on the shelf-lives and storage requirements of sorbents (Table 15) provides little or no opportunity for discriminating amongst them. All the sorbents have long storage lives (20 years to indefinite), and most either have no special storage requirements or only need dry conditions. The only sorbents for which special conditions are stipulated are *Conwed*<sup>31</sup>, and *Wool Kmop*<sup>33</sup>. *Conwed*, must be kept away from ultraviolet light and should not be allowed to reach temperatures > 107° C (unlikely in normal storage). *Wool Kmop* should be kept in an insect- and rodent-free environment, but this is probably true for most organic sorbents.

**Table 15.** Shelf-lives and recommended storage-conditions for sorbents in the reports by Environment Canada.

| Ondov                          | Indefinite    | Dry warehouse   |
|--------------------------------|---------------|---|
| Bedex                          | Indefinite    | Below 107°C; away from ultraviolet light              |
| Conwed                         |               |   |
| Peat moss                      | Not specified | Dry conditions  |
| Slikwik                        | Indefinite    | No other special considerations if in plastic<br>bags |
| Update III, 1985<br>Ocian-Sorb | Indelînite    | Dry conditions  |
| Seaclean                       | Indefinite    | Dry conditions  |
| Zugol                          | Indefinite    | Dry conditions  |
| Verdyol                        | Indefinite    | Dry conditions  |
| Update IV, 1991                |               |   |
| Alfob W                        | Indefinite    | None specified  |
| CCD Woodchips                  | Indefinite    | Dry conditions  |
| CAP Cork                       | Indefinite    | No special conditions                                 |
| Sawdust                        | Indefinite    | Dry conditions  |
| Wool Kmop                      | 20 years +    | Dry, rodent- and insect-free                          |

# Information not given in the Environment Canada reports

In the reports by Environment Canada some of the kinds of information sought by AMSA were entirely absent, including:



- the rate of degradation of oils in the different sorbents and of the sorbents themselves;
- the amount of leachate from different complexes of oil and sorbent;
- potential environmental and biological impacts of the leachate;
- unique advantages and disadvantages of particular sorbents and
- the costs of sorbents.

### Results from manufacturers on the World-wide Web

# Overview

Our search for manufacturers of sorbents on the World-wide web (WWW) uncovered 68 companies which, on initial inspection, appeared relevant to this review (Appendix 5). All companies were contacted at least twice to request information. Only six actually produced the kinds of sorbents that are the subject of this report *and* responded to requests for information, or provided relevant information on their web-site (Table 16). On the whole, we were surprised by the reluctance of most manufacturers to respond to our requests and the paucity of information provided by those that did. We suspect manufacturers would have been more forthcoming with

**Table 16.** Commercially available organic sorbents and their manufacturers identified on the WWW. These were the only manufacturers that responded to requests for information.

| Ref<br>no. | Product name (and kind of sorbent)   | Menulacturer and WWW<br>address                                 | E-mail address for contact                     |
|------------|--|---|--|
| 34         | Sea-Sweep<br>(Heat-treated wood-pulp)  | Sea-Sweep Inc., USA<br>www.Seasweep.com                         | seasweep@seasweep.com<br>Safewaste@ddaa.com.au |
| 35         | AbsorbentW<br>(Based on wood-pulp)   | The Westford Chemical<br>Corporation, USA<br>www.wsbiosolve.com | Pbiosolve@aol.com                              |
| 36         | Spill-Sorb<br>(Based on dried sphagnum<br>moss)  | Spill-Sorb Canada Inc.,<br>Canada<br>www.spillsorb.com          | Info@spillsorb.com                             |
| 37         | Sphag-Sorb<br>(Dried sphagnum moss)  | Pacific Soil Co., USA<br>www.sphagsorb.com                      | Sphag@linknet.net                              |
| 38         | Oclan-Sorb (Dried peat moss) Oclan-SorbPlus (Dried peat moss, enriched ith nutrients and microbes) | Hi-Point Industries, Canada www.oclansorb.com                   | Oclansorb@nf.sympatico.com                     |
| 39         | Petrol Rem<br>nutrients micro-encapsulated<br>in beeswax)  | Petrol Rem Inc., USA<br>www.petrolrem.com                       | Info@petrolrem.com                             |

information if we had been potential customers of their products rather than reviewers. The product-names and WWW and e-mail address for the manufacturers that responded to our approaches are in Table 16. It is difficult to make unambiguous comparisons of the different sorbents from information provided by their manufacturers because they have not used common



methods of description and evaluation.

# The range of available biodegradable sorbents

Six sorbents of the seven are fibrous, plant-based products and one comprises bacteria and nutrients micro-encapsulated in beeswax (Table 16). Of the six fibrous plant-products, two, Sea-Sweep <sup>34</sup> and Absorbent W <sup>35</sup>, were based on wood-pulp and four were based on peat-moss; (i) Spill-Sorb <sup>36</sup>, (ii) Sphag-Sorb <sup>37</sup>, (iii) Oclan-Sorb <sup>38</sup> and (iv) Oclan-Sorb Plus <sup>38</sup>. Detailed descriptions of these products follow below.

# Sea-Sweep

Sea-Sweep <sup>34</sup> is manufactured from wood fibres (of no specified kind) through a patented thermolytic process, not involving any additional chemicals. The process is designed to breakdown hemicelluose in the wood, whilst leaving cellulose intact. This increases the porosity of the wood fibres and thus their capacity for absorbing oil. Sea-Sweep is available as loose fibres or in the form of booms, socks and pillows. The manufacturer does not describe the additional materials used in the construction of these devices.

# Absorbent W

The only information available about *Absorbent W*<sup>35</sup> is that it is manufactured from wood-pulp wastes from the paper-making industry. It is available in loose form or in booms, socks and pillows. The additional materials used to construct these sorbent devices are not described by the manufacturer.

# Spill-Sorb

This product is based on specially cultivated sphagnum peat-moss. Preparation of the product from the raw material involves aeration and heat-treatment to reduce the water-content from 90 % to approximately 10 %. Heat-treatment dispels water from pore spaces in the raw material, increasing its capacity to absorb oil and causing chemical changes making the material more oleophilic (and hydrophobic).

### Sphag-Sorb

Like Spill-Sorb <sup>36</sup>, Sphag-Sorb <sup>37</sup> is made from sphagnum moss and has a final moisture content of approximately 10 %. Information on how it is manufactured from the raw material was not provided.

### Oclan-Sorb

Oclan-Sorb <sup>38</sup> is made from chemically dried peat fibres. The kind of peat and the details of the chemical drying process are not specified in information obtained via the WWW, nor in the 1991 Environment Canada report. It is, therefore, not known whether the processing leaves any potentially toxic chemical residues in the material.

# Oclan-Sorb Plus

Oclan-Sorb Plus 38 is a peat-based product, presumably made from the same kind of material used to make the basic Oclan-Sorb 38 product described above. Oclan-Sorb Plus differs from Oclan-Sorb and the other peat-based sorbents in that it is supplemented with (unspecified) non-pathogenic, oil-degrading microbes and nutrients (nitrogen, phosphorous and other 'trace nutrients') to stimulate the proliferation of these microbes. Oclan-Sorb Plus is not available as



formed sorbent devices, only in loose form because it is designed to be left where deployed rather than to be recovered and disposed of elsewhere.

#### Petrol Rem

Petrol Rem <sup>39</sup> comprises microscopic vesicles of beeswax containing unspecified oil-degrading microbes and nutrients to stimulate their proliferation. The kinds of microbes and nutrients incorporated in Petrol Rem were not specified. It is only available in loose form because, like Oclan-Sorb Plus <sup>38</sup>, it is designed to be left where it is deployed. Strictly speaking, Petrol Rem is less a sorbent than a delivery vehicle for oil-degrading bacteria and nutrients. Beeswax does adsorb to oil, but with Petrol Rem, this property is exploited to bring the bacteria and nutrients in close proximity to the oil rather than to sorb and retain the oil.

# Mechanisms of sorbent action and the effectiveness of different sorbents

For sorbent products identified in manufacturers' web-sites there is little information on precise mechanisms of sorbent action. In most cases, however, we can reliably predict the general mechanism based on information for similar sorbent materials described in the scientific literature. For ease of comparison among the different products, this information is summarised in tabular form (Table 17).

It is difficult to compare the effectiveness of the different sorbents described here, because the relevant data supplied by manufacturers (on their web-sites and/or in response to our request) were generally vague or incomplete for our purposes (i.e. effectiveness assessed for oils of unspecified characteristics), were assayed using different methods and summarised in different units.

# Sea-Sweep

1 kg of Sea-Sweep <sup>34</sup> sorbs 4.2 l of the '17° API' crude, 6.3 l of the '37° API' crude (oils with no explained properties), 8.17 l of Bunker C and 3.01 l of Jet fuel.

### Absorbent W

The only available information for Absorbent W <sup>35</sup> is that, per unit quantity, it sorbs 2-3 times more volume of oil than polypropylene sorbents and up to 14 times more volume than clay.

# Spill-Sorb

One kg of *Spill-Sorb* <sup>36</sup> is reported to sorb approximately 16 l or 13.9 kg of Bow River Alberta crude oil at temperatures from 14 to 17°C. Bow River Alberta crude has a specific gravity of 0.904 and a density of 0.873 kg.l<sup>-1</sup>.

### Sphag-Sorb

1 kg Sphag-Sorb <sup>37</sup> absorbs approximately 8.91 of unspecified oil.

### Oclan-Sorb

Oclan-Sorb 38 absorbs twelve times its own weight in medium oil.

### Oclan-Sorb Plus

Information on the sorbency to oil of *Oclan-Sorb Plus* <sup>38</sup> was not available, but, because it differs from the basic *Oclan-Sorb* <sup>38</sup> only in the addition of oil-degrading bacteria and nutrients, its sorbency is presumably similar; *i.e.* 1:12 weight of sorbent to weight of medium oil.



## Petrol Rem

An application ratio of 1:2 by weight of Petrol Rem <sup>39</sup> to oil is recommended for control and containment of spilt oil.

**Table 17.** A summary of reported or predicted mechanisms of oil-sorption and degradation for different products investigated via their manufacturers' web-sites. Mechanisms of sorbent action are based on information for similar materials described in the scientific literature. References to articles that were the basis for predictions are provided in the table.

| Sorbent   | Adsorption   | Primary  | Secondary   | Enhanced   |
|---|--|--|---|--|
| Product   |  | absorption   | absorption  | biodegradation   |
| Wood-based<br>products<br>Sea-Sweep <sup>34</sup> | √3. 15   | √ <sup>3, 15</sup>   | 3, 16-ي   | ×  |
|   |  | See Nate 1.  |   |  |
| Absorbent W 35                                    | √3. 15   | ✓ <sup>3, 15</sup><br>See Note 1.  | ✓ 3, £3   | ×  |
| Peat-based<br>products                            |  |  |   |  |
| Spill-Sorb 36                                     | <u>√¹</u>  | 1,29 س   | √ 1,29  | <u>x</u>   |
|   | Heat treatment increases<br>oleophillotty  | See Note 1.  | Enhanced by drying to<br>expel water from internal<br>spaces  |  |
| Sphag-Sorb 37                                     | ✓¹   | 1,29 س   | ✓ 1, 29   | ×  |
|   | Heat treatment increases<br>ofeophilicity  | See Note 1.  | Enhanced by drying to<br>expel water from internal<br>spaces  |  |
| Oclan-Sorb 39                                     | <b>√</b> !   | 1, 20  | √ 1,29  | x  |
|   | ·  | See Note 1.  | Enhanced by drying to<br>expel water from internal<br>spaces  |  |
| Ocian-Sorb Plus <sup>au</sup>                     | √1   | <b>√</b> 1.29  | √ 1.29  |  |
|   | ·  | See Note 1.  | Enhanced by drying to<br>expel water from internal<br>spaces  | Via supplement of oil-<br>degrading microbes and<br>microbe-stimulating<br>nutrients |
| Other   |  |  |   | •  |
| products<br>Petrol Rem <sup>39</sup>              | Adsorbency arises from the hydrophobicity and oleophilicity of waxes 1,15, 17,27. In Petrol Rem, it is exploited to bring oil- | Physical structure of  Petrol Rem breaks down in contact with oil to  release oil-degrading  backeria and nutrients. | Physical structure of  Petrol Rem breaks down  in contact with all to  release oil-degrading  bacteria and nutrients. | Via supplement of oil-<br>degrading microbes and<br>microbe-stimulating<br>nutrients |
| <u>.</u>  | degrading bacteria in<br>close proximity to the oil<br>rather than to trap it.   |  |   |  |

Use of sorbents in the field: techniques of deployment and environmental interactions

All products for which we obtained manufacturers' information are supplied in loose form, so are suitable for deploying on spilt oil without subsequent recovery (the method of use envisaged by AMSA for spills in remote and sensitive coastal environments). There are no instructions specific to particular sorbents, except that sorbents be deployed in quantities proportional to their efficiency in retaining specific oils (this recommendation is somewhat fatuous given the paucity of information supplied by the manufacturers). The different methods proposed for deploying loose sorbents included manual dispersal, aerial drop (via airplane, helicopter, crane or boat boom), or mechanical spraying using some form of compressed air blower. There was no information to



suggest that these different methods are not equally applicable to all of the sorbent products discussed here.

All the sorbents investigated from manufacturers' product-information are reportedly biodegradable. No additional information on the mechanisms or rates of degradation of particular sorbents was available. *Oclan-Sorb Plus* <sup>38</sup> and *Petrol Rem* <sup>39</sup>, which are supplemented with oil-degrading microbes and nutrients, reportedly undergo more rapid degradation in combination with oil than would occur in the absence of these supplements.

None of the sorbents discussed here was reported to leach oil if deployed in quantities proportional to their efficiency in retaining specific oils (again, this is a fatuous comment given the lack of detailed information on the interaction of particular sorbents with particular oils).

None of the manufacturers of the sorbents discussed here provided information on the actual or potential biological/ecological consequences of using them on oil spilt in marine habitats.

Reported advantages and disadvantages of different sorbent materials

Information from manufacturers indicated that none of the sorbents had any unique advantageous or disadvantageous properties.

## Costs

Information on current costs (as of mid-2000) was provided for only three sorbent products: Sea-Sweep  $^{34}$ , Absorbent  $W^{35}$  and Spill-Sorb  $^{36}$ . The details are as follow.

Loose Sea-Sweep  $^{34}$  is sold in bulk units weighing ~908 kg comprising either lots of 80 x 11.34 kg bags, costing Aus\$ 8, 017, or lots of 400 x 2.27 kg bags, costing Aus\$ 12, 350. Loose Absorbent  $W^{35}$  is available in either 50 l bags, costing Aus\$ 36.30 each, or 10 l bags, costing Aus\$ 9.50 each. Loose Spill-Sorb  $^{36}$  is sold in double-compressed bags, each weighing 25 kg and costing \$US 95.00,

Costs for Absorbent W and Spill-Sorb in the form of various sorbent devices (booms, pillows, etc.) were also provided and are summarised in Appendix 4.

## DISCUSSION AND RECOMMENDATIONS

The purpose of this report is to advise AMSA on suitable, naturally-degrading sorbents for potential use in the clean-up of oil-spills in sensitive and/or remote coastal habitats. Recommendations follow searches of the scientific literature (using computer data-bases) and from approaches to manufacturers of sorbents identified on the WWW. Recommendations for suitable sorbents are based on key attributes stipulated by AMSA. These are:

- their effectiveness in sorbing and retaining a range of oils;
- their degradability and their effects on the degradability of sorbed oil;
- their methods of deployment, recovery and disposal;
- their requirements for storage and shelf-lives;
- their environmental side-effects when deployed and, finally,
- their costs.



The following overview of sorbents provides recommendations for discriminating amongst them (according to each of the key attributes identified by AMSA). In addition to identifying potentially suitable sorbents, we also assess the nature of the available information and identify important areas where relevant information is lacking. This critique is based mainly on AMSA's requirements for information, but we have also provided our assessment of the kinds of information needed to inform decision-making. These opinions arise from our role as experts in environmental conservation and experimental marine ecology.

# Overview of the range of different naturally-degrading oil-sorbents

Sorbents considered here differed enormously in composition and physical form. The most important contrasts for classifying the different sorbents are:

- sorbents of plant versus animal origin;
- loose materials versus materials formed into sorbent structures (booms, pillows, etc.);
- unprocessed or 'raw' natural materials versus materials refined or treated to improve sorbent properties;
- fibrous versus granular sorbents (N.B.; these represent extremes of a continuum) and
- sorbents enhanced with oil-degrading bacteria and/or nutrients to stimulate their action versus sorbents without such bacteria and/or nutrients.

At most, 41 different kinds of natural oil-sorbents were discovered. Many appeared very similar and were possibly identical. Thirty three of the 41 were made from readily available and cheap plant materials. The majority of sorbents (33 of 41) were plant-based sorbents made from wastematerials. The following types of plant-based sorbents were generally distinguished: (i) raw, non-woody fibres from the stems, leaves or seeds of plants; (ii) raw, woody material; e.g. sawdust, woodchips, etc.; (iii) refined and/or treated plant fibres; (iv) peat moss.

Most of the animal-based sorbents were also made from readily available and relatively cheap materials (wool <sup>4, 14, 17, 27, 33</sup>, feathers <sup>2, 15, 32</sup>, crab-shells <sup>2</sup>, *etc.*), but one (Petrol Rem <sup>39</sup>) was made from beeswax, which is probably more scarce and expensive.

Only two of the sorbents we evaluated (1 plant based (Conwed <sup>31</sup>) and 1 animal based (Seaclean <sup>32</sup>)) were woven or formed into sorbent devices, the remainder were loose granules (e.g. chitin, peat, sawdust, etc.), or fibres of various lengths (e.g. cotton, coconut fibres (coir), wool, pine needles, etc.).

In many cases, particularly with the purpose-made sorbents, raw plant and animal materials were treated in some way to improve their sorbent properties <sup>3, 25, 31, 32, 33, 34, 35, 36, 37, 38</sup>. This generally involved drying and/or chemical treatment to increase the sorbents' affinity to oil and repellency to water. Note that, for some materials, notably feathers <sup>15</sup>, wool <sup>4, 17, 27</sup> and cotton <sup>14</sup>, the raw state was recommended, because excessive refinement might strip surface chemicals that were important for the adsorption of oil.

Five sorbents contained supplements to enhance the degradation of sorbed oil. Of these, three (keratin, chitin and chitosan <sup>2</sup>) were supplemented with oil-degrading Pseudomonas bacteria, one (Petrol Rem <sup>39</sup>) was supplemented with nutrients to stimulate naturally-occurring bacteria and one (Oclan-Sorb Plus <sup>38</sup>) contained both nutrients and bacteria (of unknown species).



# Recommendations based on the different sorbents mechanisms of action and effectiveness in sorbing and retaining oil

There are three primary mechanisms by which sorbents capture oil:

- adsorption to the surface of the sorbent material;
- absorption into air-spaces among aggregated granules or fibres of the sorbent material (primary absorption);
- absorption into spaces *within* individual granules or fibres of the sorbent material (secondary absorption).

Most of the sorbents covered in this review capture oil by more than one of these mechanisms (Tables 3, 6 and 17). There were virtually no quantitative data and little qualitative data to discriminate amongst sorbents based on the amount of oil captured via each mechanism. In this circumstance, it is only possible to describe the properties of sorbents that facilitate each of these mechanisms and provide examples of the various mechanisms.

Adsorption is facilitated by a large external surface area and surface-coatings that are eleophilic. Most of the sorbents have a large surface area, but precise information was not provided, although 'one gram of feathers has a greater surface area than any of the known sorbent materials' <sup>32</sup>, but the latter were not identified. In general, sorbents with the greatest surface area will be those made of relatively small granules or fine fibres and those with surfaces that support structures such as hairs, pits, scales, *etc.* 

For most sorbents, there was no information about chemical oleophilicity, but several sorbents were noted to have chemical coatings with great affinity for oil, e.g. wool 4, 17, 27, feathers 15, heattreated wood 3, 25 and the plant fibres kapok 4, milkweed 7, 30, and unbleached cotton 14, 28. In discussing chemical affinity for oil, one sorbent requires special mention. Petrol Rem comprises various nutrients (to stimulate oil-degrading bacteria) micro-encapsulated in spheres of beeswax. Being waxy, Petrol Rem has a great chemical affinity for non-polar compounds such as oils. In fact, the affinity is so great that the beeswax actually dissolves in oil. Thus, Petrol Rem is not a sorbent in the normal sense. The prime purpose of the beeswax in Petrol Rem is to provide an efficient delivery-mechanism for the nutrients within.

The sorbents that provide the greatest capacity for primary absorption of oil are those formed from long fibres. Good examples include wool <sup>4, 14, 17, 27, 33</sup>, cotton <sup>5, 7, 8, 10, 13, 14, 17, 22</sup>, coconut fibres (coir) <sup>11, 13</sup>, milkweed, kapok, sisal <sup>11</sup> and refined cellulose fibres <sup>31</sup>. These are the best kinds of sorbents for recovering oil because they can be woven, or, if deployed as loose fibres, will naturally form tangled 'mats'. Sorbents comprising woven or tangled fibres have greater structural integrity than aggregations of particulate sorbents, so they are better at retaining oil in their interstices when recovered from the shore.

Sorbents with good secondary absorption characteristics include peat moss <sup>1, 6, 15, 16, 18, 19, 20, 21, 29, 32, 36, 37, 38</sup>, cotton <sup>5, 7, 8, 10, 13, 14, 17, 22</sup>, kapok <sup>4, 8, 9, 10, 11, 12, 14</sup> and milkweed <sup>4, 7, 14, 24</sup>. The common characteristic of these sorbents is great internal porosity. Drying of sorbents (via heat or chemicals) can improve secondary absorption by driving water out of internal spaces. This treatment is most commonly used for peat-based sorbents <sup>32, 36, 37, 38</sup>.

The best quantitative data for discriminating amongst sorbents in terms of their ability to capture oil were in the reports by Environment Canada 31, 32, 33. These cover most of the different kinds of



sorbents discovered. Capture of oil was quantified using initial oil pick-up (IOP; Table 8) and maximal oil pick-up on re-use (MOP; Table 9). There was no attempt to quantify the relative contributions of adsorption, primary absorption and secondary absorption. MOP is an important consideration where the aim is to recover and re-use the sorbent. Each sorbent was tested with a range of oils of widely differing viscosities.

A wool-based sorbent, *Wool Kmop* <sup>33</sup>, stood out as having the greatest IOP and MOP for the greatest range of oils. *Wool Kmop* performed well for oils as different in viscosity as cyclohexane and 7-day Crude (Tables 8 and 9). Other sorbents that performed well in terms of IOP and MOP were the *Conwed* sorbent blanket (refined cellulose) and *Verdyol* treated vegetable fibres <sup>32</sup>.

In determining MOP, Environment Canada were also able to determine the maximal number of effective re-uses for each sorbent. The sorbents that showed the greatest re-usability with the greatest range of oils were, in no particular order, the *Seaclean* <sup>32</sup> (feather pillow), *Verdyol* <sup>32</sup>, *Wool Kmop* <sup>33</sup> and *CAP Cork* <sup>33</sup> (cork granules; Table 10).

Other relevant actions evaluated in the Environment Canada reports were initial water pick-up (IWP) and maximal water pick up on re-use (MWP). Great affinity for water is an undesirable feature for an oil-sorbent, because it directly interferes with the capture of oil and could eventually cause the sorbent to sink. Sorbents that exhibited little IWP generally also showed little MWP. The sorbents which showed the least IWP and MWP with the greatest range of oils were, in no particular order, *CCD Woodchips* <sup>33</sup>, the *Seaclean* sorbent pillow <sup>32</sup> and *Verdyol* <sup>32</sup> (Tables 11 and 12).

The Environment Canada reports also provided a more qualitative evaluation of sorbents in terms of their behaviour following 48-hours exposure to oil on water. The main object of this test was whether sorbents would continue to float after prolonged exposure. Most of the sorbents previously recommended based on their affinity for oil and repellence to water performed well in these tests. Exceptions were the *Seaclean* sorbent pillow, which sank with most oils and Verdyol, which sank with the less viscous oils (Table 13).

## Degradability of sorbents and effects on degradability of sorbed oil

There is very little information to discriminate amongst sorbents based on their degradability or their effect on the degradability of oil. Degradability was not measured for any of the sorbents but sorbents made from woody material, wool or feathers would probably take the longest to biodegrade. Sorbents made from non-woody plant material (e.g. peat, cotton, milkweed) or refined cellulose fibres would probably degrade more quickly. The beeswax-based sorbent *Petrol Rem* would be expected to degrade quickest of all because it dissolves in oil without leaving a solid residue. How quickly it would degrade in the absence of oil is unclear.

In terms of effects of sorbents on the degradability of oil, supplements of oil-degrading bacteria and/or nutrients to stimulate them appear to be effective. Commercially available examples of supplemented sorbents include *Petrol Rem* <sup>39</sup>, which contains nutrients and *Oclan-Sorb Plus* <sup>38</sup>, which contains both nutrients and bacteria.

## Recommendations for deploying sorbents

Virtually nothing can be said about the relative ease of deployment of the different sorbents. All of the loose, particulate sorbents should be amenable to manual deployment or deployment via blower or air-drop. Structures formed from sorbents (mats, booms, pillows, etc.) generally need to be manually deployed in the places they are most needed (Table 14).



There have been no substantial evaluations of the performance of natural sorbents in actual oil-spills that can be used to provide recommendations.

Recommendations based on the leachability of oil from the different sorbents

The 48-hour submersion tests in the Environment Canada reports (Table 13) provided some qualitative information on leaching from the different sorbents. Of sorbents of value on other grounds, Conwed 31, Seaclean 32, Verdyol 32, CCD Woodchips 33, CAP Cork 33 and Wool Kmop 33, only Seaclean and Verdyol cause problems of leaching (seen as discolouration of the oil-water mixture). No other information was available to discriminate among sorbents in terms of leaching.

Recommendations based on environmental side-effects of the different sorbents

There is virtually no information about the different sorbents in terms of their possible environmental side-effects. Most sorbents were reported to be non-toxic, but, more often than not, this was the only information given. No sorbent was reported as being toxic. Where details of toxicity tests were provided, the tests were typically simple 'lethal dose' tests done on single species under laboratory conditions. These kinds of tests are far too simplistic and abstracted from reality to provide any real indication of potential ecological impacts in natural habitats (Underwood, 1995).

One environmental recommendation is, however, that AMSA avoid using sorbent materials harvested from nature. Peat moss, one of the most frequently-cited natural sorbents, has traditionally been extracted from natural peat bogs. There are real concerns about the environmental sustainability of the peat extraction industry because it involves the wholesale removal of habitat. In terms of source, the most environmentally sound sorbent would be some form of waste or renewable material. For example, wool has valuable properties and can be produced sustainably.

Costs, requirements for storage and shelf-lives of sorbents

The available information about storage and shelf-life identifies only that all the potentially useful sorbents have simple storage requirements and long shelf-lives. Dry conditions were stipulated for many sorbents, but this is probably a sensible precaution for all sorbents. All the sorbents considered are organic, so they will all be more or less prone to natural processes of decay due to fungi and bacteria, organisms which are most active when damp. Moreover, exposure of sorbents to moisture during storage would be likely to reduce their affinity for oil when deployed. Yet again, no information was provided that would allow us to recommend any particular sorbent.

There was no accurate, current information on costs with which to compare the sorbents that have been considered thus far.

#### Recommendations on sorbents

Several sorbents appear to be more or less suitable for AMSA's needs. Even for these, however, recommendations must be tentative because much of the information necessary to form secure recommendations was not available. For the most part, recommendations are based on the sorbents' effectiveness in capturing oil. There was little information to discriminate among



Table 18. Recommended sorbents. The order of sorbents in this table is not significant.

| Recommended sorbent  | Notable positive atmoutes   | Notable negative attributes   | Manulacturer /<br>distributor  |
|--|---|---|--|
| Raw fibres of either cotton,<br>kapok, colr, sisal or milkweed | Great oil-pickup with a range<br>of oils  Good for immobilising and<br>recovering spilt oil   | The information given for these sorbents does not allow precise comparison with others listed here  | None specific  |
| Wool Kmop (small beads of matted wool)                         | Lanolin promotes adsorption of oil  Great oil-pickup with a range of oils  Good for immobilising and recovering spilt oil                             | None specific   | (Distributor) Wool Research<br>Organisation of New Zealand<br>Inc., Private Bag, Christohurch,<br>New Zealand        |
| Conwed (sorbent blanket of treated cellulose fibres)           | Can be re-used several times  Great oll-pickup with a range of oils  Good for Immobilising and recovering spilt oil  Can be re-used several times     | May disintegrate with repeated re-use Must be manually deployed   | (Distributor) CIL Inc., P.O. Box<br>836, Edmonton, Alberta,<br>Canada, TSJ 284                                       |
| Verdyol (treated vegetable fibres)                             | Great dil-pickup with a range<br>of oils<br>Little water pick-up<br>Good for immobilising and<br>recovering spilt oil<br>Can be re-used several times | May sink in oils of low-<br>viscosity   | (Distributor) Verdyol Plant<br>Research Ltd., R.R. 1,<br>Cookstown, Ontario, Canada<br>LOL 1LO                       |
| CCD Woodchips (treated woodchips)                              | Little water pick-up  | Large surface area allows only moderate oil pick-up Probably slow to degrade Less effective for Immobilising and recovering oil than fibrous sorbents | (Distributor) Carbontec Ind,<br>Inc., 400 East Broadway,<br>Bismark, North Dakota, USA,<br>58501                     |
| Feathers; e.g. the Seaclean sorbent pillow                     | Large surface area for adsorption  Good for Immobilising and recovering split oil  Can be re-used several times and stays intact                      | Tends to sink under prolonged exposure to oil on water  Some leaching of oil in water Must be manually deployed                                       | (Distributor) Sea Clean Inc.<br>7000 SW 62 Avenue, Suite<br>555, Miami, Florida USA, 33143                           |
| CAP cork (cork granules)                                       | Moderate oil pickup with a range of oils, but can be re-<br>used several times  | Works with a range of oits,<br>but oil pickup is relatively low<br>Less effective for<br>immobilising and recovering<br>oil than librous sorbents     | (Distributor) Sevenson<br>Environmental Products Inc.,<br>2749 Lockport Rd., Niagra<br>Falls, New York USA, 14302    |
| Ocian Sorb Plus (based on treated peat moss)                   | Contains nutrients and oil-<br>degrading bacteria   | Less effective for<br>immobilising and recovering<br>oil than fibrous sorbents  | (Manufacturer) Hi-Point<br>Industries Ltd., P.O. Box 2535,<br>Poetal Station M, Calgary,<br>Alberta, Canada, T2P 2N6 |
| Petrol Rem (nutrients micro-<br>encapsulated in beeswax)       | Has nutrients to stimulate oll-<br>degrading bacteria. Degradas<br>in oil leaving no solid residue  | Not strictly a sorbent<br>Cannot be used to recover oil.<br>Non-re-usable   | (Manufacturer) Petrol Rem Inc.,<br>USA. (contact via<br>www.petrofrem.com)   |



sorbents based on their degradability, ease of deployment/recovery/storage, costs and, most importantly, their environmental and ecological consequences.

The sorbents that AMSA should consider in detail are listed below in Table 18 with comments on positive and negative attributes for each sorbent and the names of their manufacturers (or distributors).

# Using naturally-degrading sorbents for the treatment of oil-spills in sensitive and remote coastal habitats

The decision whether or not it is environmentally appropriate to deploy a naturally-degrading sorbent to 'clean-up' oil spilt in remote or sensitive coastal habitats depends on two issues:

- If sorbents were deployed on an oiled or soon-to-be oiled foreshore, is the effect better or no
  worse than the effect of oil alone? Note that adverse effects of may be due to the sorbent
  itself, disturbances during deployment, after sorbents have captured oil, or during removal of
  oiled sorbent.
- Are there significant environmental risks for other areas if a sorbent is not deployed? For example, if oil is not trapped by sorbents on a particular site, it may move elsewhere.

There is little information about environmental consequences of using sorbents in coastal habitats. Before considering issues of deployment and retrieval of sorbents, it is necessary to consider relevant ecological issues in habitats where oil may be spilt.

Oil-spills are not all the same in their potential environmental consequences. This is not just because oils vary in their chemical composition and therefore potential toxicity. Nor is it only because spills vary in amounts of oil-spilled. The primary consideration is the type of habitat(s) affected and therefore the varieties and abundances of animals and plants that may be damaged.

For example, it is known that crude oil spilled on rocky shores in open, coastal environments generally does not cause long-lasting ("press"; Bender et al. 1984) disturbances. The vast majority of the animals and plants affected are patchy in distribution and variable in numbers from time to time. This is a consequence of life-histories involving very numerous, widely dispersing planktonic larvae or eggs. This ecology makes recovery from a disturbance very rapid. Oil-spills are another type of disturbance from those occurring naturally and recovery is usually fast. This is true even where a spill is very large (e.g. Exxon Valdez; Wells et al., 1995).

Exceptions involve mammals and birds, which do not have the same reproductive capacity. Even for these animals, apparently terrible spills, killing many birds, cause mortality well within natural variation (Wiens, 1996).

In complete contrast, oil in mangrove forests can have long-term consequences, lasting many years (Burns et al., 1994). Oil persists and contaminants have effects lasting decades.

Parallel to such ecological issues, animals and plants in various habitats are much damaged by human trampling around them. This is true for rocky shores (Povey and Keough, 1991) and mangrove forests. In soft-sediment habitats (mangroves, salt-marshes, seagrasses, sandy beaches, mud-flats), trampling and similar disturbances in attempts to clean up oil can have deleterious environmental consequences. Not only is disturbance of sediments very disruptive, but it can work oil below the surface and below layers with sufficient oxygen to allow degradation. Such oil then forms a long-term environmental hazard because it leaches back out of sediments long after the spill is apparently resolved (Underwood et al., 1993).



A second issue is whether sorbent material itself has negative ecological consequences. This is likely in some habitats, because loose granular material would smother animals and plants and, as found for sand on rocky shores, could kill filter-feeders, such as barnacles, mussels, tunicates which have hundreds of other species (unpub. data). When full of oil, the sorbent may be a further source of problems because it may delay degradation and detoxification of the oil.

Finally, if, as seems sensible in many habitats, the oil-soaked sorbent should be removed from the field, all of the issues of disturbance to habitats again become relevant. If, in contrast, sorbents are not removed, the oil can continue to leach into surrounding habitat and the complex of oil and sorbent will take up space, preventing recolonization of damaged habitats.

It is against this background of known environmentally-damaging processes that any use of sorbents (or other attempts to clean up oil) should be considered.

One final environmental hazard in removal of oil-soaked sorbents is that the process may also remove cues used by larvae to find suitable habitat. Larvae of many marine animals respond to chemical cues, often created by adults of their own species (e.g. Crisp, 1974) or produced by other types of animals or plants (e.g. Morse et al., 1984), to find habitat while they are being washed about in the plankton. Although oil itself may, in fact, remove such cues, there is no published evidence to demonstrate this. In contrast, mechanical damage can remove cues, because it removes remnants of previous adults. So, removal of oil-soaked sorbents could, if not done with extreme caution, cause loss of appropriate environmental cues in areas damaged during retrieval. This would delay – probably for long periods – processes of recolonization and recovery.

# To deploy or not to deploy sorbents

Deployment of sorbents in the field, given current limited knowledge (see below) should only be done where:

- it is possible to be sure that using sorbents to retain oil in a particular area will assist in preventing the oil from moving to an ecologically more sensitive area.
  - Thus, in south-eastern Australia, many sandy-beaches in wave-exposed areas are less likely to be damaged, in terms of biodiversity, by oil than are habitats such as mangrove forests or seagrass beds. This is because the fauna can rapidly recover from disturbance and natural weathering and degradation are likely to be fast in well-oxygenated areas. Sorbents could help retain oil in such habitats rather than letting it be washed into nearby mangroves or mudflats. Of course, some beaches have great social recreational value and some are important habitat for birds to feed or nest, so there can be no universal rule.
- using sorbents, followed by natural degradation of oil-soaked material would do less
  ecological damage than would be done by the oil alone.

This does not seem likely where deployment involves heavy machinery for delivery and dispersal and where deployment will inevitable involve much trampling by work-crews and vehicles. This suggests extreme caution in soft-sedimentary areas (mangroves, salt-marshes, etc.), but may be suitable action on rocky areas (where oil may not do much damage anyway).

Deployment will be extremely less damaging in open habitats, where access can be by boat



and material can be dispersed from boats. Such habitats are open mud-flats, rocky shores, beaches, seagrass areas.

Table 19. Some indications of appropriate use of sorbents in different coastal habitats.

| Habilat               | Disturbance of |                | nt Deploy sorbent or |
|-----------------------|----------------|----------------|----------------------|
|                       | on digite      |                | 11017                |
| Sheltered rocky shore | Small          | Large          | Probably best not    |
| Exposed rocky shore   | Small          | Possibly large | Probably best not    |
| Sandy beach           | Small          | Probably smalt | Possibly             |
| Mud flat              | Large          | ?              | . ?                  |
| Seagrass              | Large          | ?              | 7                    |
| Mangrove              | Large          | 7              | ?                    |
| Saltmarsh             | Large          | ?              | ?                    |

 using sorbents followed by retrieval of oil-soaked material would do less damage than oil alone, or oil plus sorbents left to degrade naturally.

Areas where retrieval of sorbents would inevitably cause problems are seagrass beds, mangrove forests, areas of rocky shore with beds of mussels, tunicates, *etc.* Trampling, mechanical damage to animals, plants and substrata will all be considerable. It is, however, not clear what are the relative potential consequences of leaving the oil, absorbing it, but leaving the sorbent and retrieving oil-soaked sorbents.

Retrieval may, of course, be important for cost-effectiveness, so that sorbent material can be reused. This potential advantage must be considered in relation to potential environmental hazards.

Some indications of possible responses in different types of habitats are in Table 19. These are based on extensive understanding of the literature on the ecology of these habitats. The Table simply indicates current ignorance or uncertainty.

## Reducing uncertainty by filling in gaps in available information

# Sorbents' properties

It was possible to recommend which sorbents may be superior in terms of uptake and retention of oil and other physical and chemical properties. Such recommendations are, however, made uncertain by the lack of coherent comparable information. Only a few of the sorbents examined seemed to offer better prospects than the rest. It would be sensible for AMSA to consult with Environment Canada (EC) to determine whether EC plans to make future comparative assessments strictly comparable. This requires laboratory studies using the same methods (of agitation, timing, etc.) and using precisely comparable oils and conditions of oils.

Alternatively, AMSA should consider commissioning a comparative study of the subset of sorbents they choose. Such laboratory work will provide some more strictly comparable information, using a range of relevant oils and conditions of weathering of oils, re-use, etc.



## Issues about deployment

Information from laboratory studies can, however, only be indicative of *capacity* of particular sorbents. It will provide no help with the problem of which sorbents to use in the field.

There is currently very little to no information about how well sorbents work in the real world. No comparative assessments have been made of ease of deployment and/or retrieval, particularly under poor weather conditions, at night, such as often occur when oil is spilled.

There must be some practical evaluation, in the field, by trained personnel before all of the current uncertainty could be reduced. The design of these field trials will be somewhat complex because it will require assessments under different weather conditions, in various habitats and different oils.

In fact, such trials should not be done unless planned in conjunction with experimental assessments of environmental impacts, as below.

## Environmental issues

The greatest uncertainty in any evaluation of possibly useful sorbents is that no information has been collected about environmental disturbances they may cause, resulting in impacts on flora and fauna. The issues were outlined in the Section on "Using naturally-degrading sorbents for the treatment of oil-spills in sensitive and remote coastal habitats".

It would be contrary to national and international agreements about precautionary principles to proceed with use of sorbents without some assessment of environmental risks.

This assessment can only be done by field experiments (for example, following the rationale in Underwood and Peterson, 1988). The issues for design of such studies are not straightforward (Green, 1979; Underwood, 1994). They are, however, tractable with suitable expertise. It is particularly important to determine what to do under various scenarios because of problems in numerous previous attempts at clean up of oil. This is characterized by a chaotic response to public demand "to do something" without prior plans built on sound understanding of the issues (Paine et al., 1996).

We strongly recommend that AMSA commission and seek funding to implement the necessary field investigations in a range of habitats (mangrove, seagrass, rocky shore would span the range of issues) to determine the relative environmental impacts of leaving oil, using sorbents, using and retrieving sorbents. Provided the logic and rigour of experimental designs are well-conceived (Underwood, 1997), these experimental studies will be able to answer many of the currently unresolved questions.

Such experiments are often not possible because suitable places to do them are not identified. Around Australia's coast, at any given time, there are numerous planned disturbances that are going to destroy large patched of natural habitat. Such areas are perfect for experimental analyses of oil-spills and suitable responses to them because the habitats are going to be destroyed anyway. For example, no-one knows what to do about oil-spilled into seagrass beds – a habitat considered to be particularly important for ecological reasons related to juvenile fish of commercially important species. So, if there is a spill in a seagrass bed (which are in estuaries and therefore close to tankers, shipping and refineries), it is not known whether or not cleaning should be attempted. This is very important for the future of such habitats. When the Third Runway was built in Botany Bay, 12 hectares of seagrass were destroyed. A proposal to use this area, in



advance of construction, to test processes of clean-up was refused on the grounds that it might not be possible to control the experimental release of oil into 10 X 10 m experimental plots under calm weather conditions on a falling tide. The proposal suggested that the release be done by those charged with clean-up.

On the basis of this response, it seems that no-one should be allowed to attempt to clean-up in a sensitive area if it is not possible to control patches of oil over 10 X 10 m under ideal conditions and a planned release! Nevertheless, the principle is a sound one – AMSA should investigate where major infrastructural and other projects are being planned so that areas of suitable habitat can be used before they are sacrificed. The answers are crucial for all of Australia's planned responses to oil-spills.

The types, magnitudes and capacity for recovery from the potential environmental hazards involved in the use of sorbents as part of clean-up are not known for any coastal habitat in Australia. Until they are, in relation to the actual (as opposed to perceived) environmental impacts of oil itself, it is not possible to determine what is an appropriate strategy for response to oil-spills, including whether or not sorbents should be deployed and whether or not they should be recovered afterwards. Precautionary principles will be flouted if planned responses must continue to be made against a background of ecological ignorance.

## **ACKNOWLEDGEMENTS**

We are grateful to Melanie Bishop and Katie O'Donnell for assistance with searches for literature and Bob Hunt and Grant Kaplan for cataloguing the literature we obtained and for summarising the relevant information. Dr Tim Glasby and Dr Mats Lindegarth were involved in the early stages of planning the literature review; Dr Gee Chapman helped in production of the report.



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