Journal of Cleaner Production 87 (2015) 675-682

Contents lists available at ScienceDirect

Journal of Cleaner Production

journal homepage: www.elsevier.com/locate/jclepro



Substitution of hazardous offshore chemicals in UK waters: an evaluation of their use and discharge from 2000 to 2012

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ARTICLE INFO

Article history: Received 7 June 2014 Received in revised form 12 September 2014 Accepted 15 September 2014 Available online 7 October 2014

Keywords: Chemical substitution Offshore oil and gas OSPAR Chemical management

ABSTRACT

The offshore oil and gas industry will use and discharge large quantities of chemicals into the marine environment during operational activities, with some of those chemicals considered hazardous. Chemical substitution, as part of the environmental regulatory regime, has been advocated as a simple and effective tool to reduce inputs of hazardous substances to the environment. In 2007 the UK National Plan was introduced, to prioritise into four groups and subsequently phase out in stages the most hazardous substances used and discharged during offshore oil and gas operations. Level 1 substances categorised for phase out in 2010 were virtually eliminated from discharge between 2006 and 2012 and there was a significant decline in discharge of substances at Level 2 to 4 over the same period. The discharge of substitutable substances had been reduced to less than 5 tonnes at most production installations by 2012. More than 91% of this discharge is contributed by corrosion inhibitor, scale inhibitor, demulsifier and water clarifier formulations. The discharge of corrosion inhibitors accounted for the largest contribution to UK National Plan Level 2 substitutable substance discharges, and they appear to be the type of product with the fewest options found for substitution. This implies that a finite discharge of substances from these groups will continue to require formal justification beyond the target date, as occurred for Level 1 substances after the 2010 target date. The overall figures for substitutable substance discharges from 2006 to 2012 suggest that the introduction of the UK National plan with prioritisation of substances for substitution and ongoing encouragement of operators and, indirectly, suppliers to work towards reduction goals for substitutable substances is resulting in a reduction in discharges and contributing to their ultimate phase out. The next few years will be particularly challenging as the deadline for the phase-out of discharges of substitutable substances included in OSPAR Recommendation, 2006/3 is 1 January 2017 and, in addition, by 2018 all chemical substances used offshore will need to have been registered under the EC REACH Regulation. The approach described in this paper illustrates the benefits of a prioritised strategy for chemical substitution and an ongoing dialogue between the industry and regulator. A continuing case by case dialogue with offshore operators and suppliers will be essential to ensure that alternative technical solutions are trialled and options for substitution are investigated at the earliest stage.

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1. Introduction

The amount of man-made chemical substances increased enormously during the twentieth century, with the total global production of chemicals growing from 1 million tonnes/year in 1930 to 500 million tonnes/year in 2005 (The Danish Ecological Council, 2006). There are chemicals that are known to possess hazardous properties and to present human and environmental health risks, whilst the hazards and risks posed by many others have never been assessed (The Danish Ecological Council, 2006). The most common legislative approach to elimination of the use of hazardous substances is the substitution principle (Hansson et al., 2011). Although several definitions of the principle exist in environmental legislation (Lofstedt, 2013) for the purposes of this review it will be regarded as 'the substitution of hazardous substances by less hazardous, or preferably non-hazardous, alternatives where such alternatives are available' (European

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http://dx.doi.org/10.1016/j.jclepro.2014.09.053

Commission, 2001). The basis of this definition is the hazard associated with each substance, which is related to its inherent properties.

Methods used to promote substitution on the basis of chemical hazard have been highlighted in various documents (Hansson et al., 2011; Lohse and Lißner, 2003). These include bans, lists of unwanted chemicals, positive lists and substitution plans (Hansson et al., 2011). Examples of lists of unwanted and dangerous substances are the OSPAR List of Chemicals for Priority Action (LCPA), OSPAR List of Substances of Possible Concern (LSPC), REACH Substances of Very High Concern (SVHC) and the Directive 2013/39/EU priority substance list. Positive lists of acceptable substances, or substance group/classes, include the OSPAR Pose Little Or No Risk (PLONOR) to the environment list, the REACH Annex IV list and the Swedish BASTA system.

The substitution principle is most often applied on the basis of hazard (Hansson et al., 2011; Lofstedt, 2013) but it is noted that alternative approaches exist based on risk, which in addition to the inherent properties take into account public and environmental exposure to the substance, in part determined by usage. It has also been proposed that, although it is possible to rank chemicals in order of their hazard properties, a risk-based approach is more appropriate in order to select a safer alternative (UK Royal Society of Chemistry, 2007, Hansson et al., 2011 and Lofstedt, 2013). Hansson et al. (2011), stated that all decisions on chemical substitutions should be based on the best available evidence, and it is generally accepted that the evidence can be sufficient to warrant a substitution even if it only consists of hazard information and it is not possible to undertake quantitative risk estimates.

This review focuses on chemicals used in offshore oil and gas exploration on the UK continental shelf (UKCS) and the trends in the use and discharge of hazardous substances by this sector. The UKCS has been exploited for hydrocarbons for over 40 years, during which time more than 3300 million tonnes of oil and 2,600,000 million cubic metres of gas have been produced (DECC UK monthly production data). The extraction of these reserves has required considerable use of chemicals, both during the exploration phase, primarily related to the use of complex drilling fluids, and during the subsequent production phase, where chemicals are required to assist gas, condensate, oil and water separation, to protect equipment from corrosion and to ensure safety. After use, many of these chemicals are discharged into the sea, creating a potential risk to the marine environment.

In the UK, the risks from such activities are controlled through the Offshore Chemical Regulations 2002 (as amended) which are based upon internationally-agreed principles set out in OSPAR Decision, 2000/2 (as amended by OSPAR Decision, 2005/1) on a harmonised mandatory control system for the use and reduction of the discharge of offshore chemicals (HMCS). The regulations are administered and enforced by the Department of Energy and Climate Change (DECC) and require operators to perform an environmental risk assessment of the use and discharge of chemicals as part of a permit application process.

In order to obtain a permit, the operator must select only chemicals that have been registered and their hazards assessed by Cefas (the Centre for Environment, Fisheries and Aquaculture Science), acting on behalf of DECC. One of the key components in the registration process is pre-screening, and it is at this stage that substances that are candidates for substitution, i.e. substitutable substances (SSs), are identified. The pre-screening is conducted according to OSPAR Recommendation 2010/4, which examines chemicals based upon the persistence, bioaccumulation potential and toxicity (PBT) of their component substances. Those chemicals that contain components qualifying as particularly hazardous are

identified as SSs and are flagged in the lists of registered substances with a substitution warning.

In 2006, OSPAR Recommendation, 2006/3 invited Contracting Parties to develop National Plans to establish a time frame for the potential cessation of the discharge of SSs from offshore installations. In response, the United Kingdom National Plan (UKNP) was developed and published in 2007.

The essential elements of the UKNP are summarised in Table 1. Under the plan, chemical products (formulations consisting of many substances or composed of a single substance) are assigned to one of four levels 1–4, with level 1 denoting the highest priority for substitution. Where a product contains multiple SSs of differing UKNP levels, the product is assigned the UKNP level of its highest priority component substance. All four levels were assigned a recommended phase-out target, which was 2010 for UKNP level 1 substances, and extended to 2016 for UKNP level 4 substances.

Presented here are the results from a study which examined changes in the use and discharge of SSs, and the substitutable products (SPs) containing them, during UKCS offshore oil and gas production operations between 2000 and 2012. This time frame includes the ten years that followed the introduction of the Offshore Chemicals Regulations, and the period immediately before that introduction, and the six years that followed the implementation of OSPAR Recommendation, 2006/3. Temporal and spatial trends of SSs and SPs are discussed, and their causes analysed. Finally, the future outlook for substitution is considered.

2. Methods

The chemical usage and discharge data was collated in two stages; the first stage conducted in 2006 collated data for the years 2000–2005 prior to the formation of the UKNP levels. The second stage conducted in 2013 collated data for the years 2006–2012. The method used to obtain data at both stages was the same, the method below outlines how the data was collated for 2006 to 2012.

Data was collated from the Environmental Emissions Monitoring System (EEMS) returns submitted by offshore operators. EEMS is the environmental database maintained by DECC for the UK oil and gas industry that provides measured and calculated data relating to emissions (including discharges to sea) from offshore installations and some associated onshore terminals (Oil and Gas: EEMS database). The reported year, product names, registration numbers, installation names and reported use and discharge data in EEMS were imported into a Microsoft Access database that was linked to a live copy of the offshore chemical registration database maintained by Cefas, and the EEMS data was analysed using information on the products and substances (e.g. PBT data, CAS numbers, and product function) held on the Cefas database. For the

| Table 1 | |
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UK National Plan level criteria and interim target dates.

| UK national plan level | Ecotoxicological properties | Phase out date |
|---------------------------|--|-------------------|
| Level 1 | Organic substances that are highly persistent, bioaccumulating and toxic | End December 2010 |
| Level 2 | Organic substances that are: moderately persistent, bioaccumulating and toxic; or highly persistent and bioaccumulating; or highly persistent and toxic | End December 2012 |
| Level 3 | Organic substances that are: moderately persistent and bioaccumulating; or moderately persistent and toxic; or bioaccumulating and toxic | End December 2014 |
| Level 4 | Organic substances that are highly persistent; or inorganic substances with toxicity <1 mg/l | End December 2016 |

purpose of this review the components of the offshore chemical products were separated into three groups: PLONOR, substitutable and non-substitutable.

A database query run on the 16th October 2013 returned information on the composition of offshore chemical products, including the product function; product substitution warning status; product UKNP level; component substances, percentage composition data; substance substitution warning status; and substance UKNP level for the years 2006–2012. This 'snapshot' of information on chemical composition and current substitution status was compared to data for the years 2000–2005, since it is not uncommon for chemical registration information and substitution status to change over time due to the availability of additional data being submitted by the chemical manufacture or supply company. For 2006–2012 the substitution status of the chemical was classified based on the data available on 16th October 2013, in order to ensure consistency over this period.

Where appropriate, trends in the data thus obtained were then subjected to statistical analysis, and a linear model for analysis of covariance was used to evaluate the relationship between discharges against time. Details of the statistical analysis are provided in the Supplementary Data appended to this paper.

It should be noted that the data used for this study concerns chemicals that have been used and discharged during production operations only, since these are responsible for most of the discharges of SSs. Chemicals are also discharged in the course of other offshore activities (e.g. drilling operations, well intervention/workover/abandonment operations, pipeline operations and decommissioning operations) but these are not included. Drilling discharges generally comprise relatively benign chemicals (Sheahan et al., 2007), whilst the quantities of SSs involved in the other operations are small by comparison.

3. Results and discussion

3.1. Temporal trends in the use and discharge of offshore chemicals 2000–2012

Between 2000 and 2012 overall UK oil production fell (DECC Monthly Oil Production Data), as a result of production decline from ageing reservoirs and an increase in the number of uneconomic fields that had ceased production, which was exacerbated by extended shutdowns for repair of the infrastructure used by fields that are still operational.

Although these factors contribute to reduced chemical use, they are balanced by the fact that chemical use increases as exploited fields age (Igunnu and George, 2013) and new fields were developed during the period. The net effect is that chemical use and discharge cannot be predicted from the production figures. The overall pattern of use and discharge of offshore chemicals between 2000 and 2012 is shown in Fig. 1, indicating that after peaking in 2005, the quantity of chemicals discharged during 2012 was similar to that recorded for 2000, at 26,899 and 28,817 tonnes respectively.

Fig. 2A shows the annual quantities of substances discharged in each of the three groups (defined in Section 2) between 2000 and 2012. The most notable trend is the decline of SSs discharged, which fell from a total of ~2700 tonnes in 2000 to <800 tonnes in 2012: less than half of the initial quantity. Most of the decline is observed between 2006 and 2012, with the total decreasing steadily by a total of 1664 tonnes, despite a 6 tonne increase in 2010. A clear decrease in the proportion of the total that is constituted by SSs is also apparent, with SSs represented around 10.2% of the total of all substances discharged in 2000 and ~2.8% in 2012, whilst the discharge of the non-substitutable substances and PLONOR remained fairly constant over time. The net result has been



Fig. 1. Total use and discharge of offshore chemicals between 2000 and 2012.

an overall shift in chemical discharge in favour of less hazardous substances, and this is further emphasised by Fig. 2B, which shows the extent to which the proportion of SSs in the overall tonnage has fallen between 2000 and 2012.

Further analysis of the data is presented in Fig. 3, which shows the trends in the discharges of SPs (Fig. 3A) and SSs (Fig. 3B) between 2006 and 2012, broken down by UKNP level (this analysis is not possible for products registered before 2006, when the use of substance-level data for chemical registration became mandatory). The linear model for analysis of covariance indicated that the decline of discharges versus time is statistically significant with 95% confidence for UKNP levels 2, 3 and 4. There was no statistical significance for UKNP level 1 products and substances from 2006 to 2012, but the discharge of these substances had already been virtually eliminated.

Whilst the observed reductions are a welcome trend, it does however indicate that the complete elimination of discharges from UKNP levels 2, 3 and 4 is unlikely to materialise before the relevant targets proposed by DECC, which fall outside the period covered by this review. This implies that a finite discharge of substances from these groups will continue to require formal justification beyond the target date, as occurred for UKNP level 1 substances after the 2010 target date. In the case of those substances, the small quantities discharged (<1 tonne on average) reflected isolated instances where the need for a product featuring such substances had been justified by the operator and permitted by DECC. It should also be noted that, in 2011, the discharge of only one UKNP level 1 product was permitted, at a single installation, and no discharges were recorded for 2012.

3.2. Spatial distribution of the use and discharge of substitutable substances and products

The location and total amount of SSs discharged at offshore oil and gas installations on the UKCS are shown in Fig. 4. Comparison of the data between 2006 and 2012 illustrates where significant reductions in SS discharges have occurred during that period. Significant improvements are indicated for the most northerly installations, but no other regional trends are apparent. The majority of installations (74%) discharged less than 5 tonnes of SSs in 2012. Most installations which discharged 25–75 tonnes and >75 tonnes of SSs in 2006 had reduced their discharges to less than 25 tonnes in 2012 and, at some installations, to less than 5 tonnes in 2012. Fig. 4 shows there were six instances of SS discharges of >75 tonnes in 2006, and only one in 2012.

Fig. 4 also indicates that the installations that discharge the most SSs are generally located in the northern North Sea, whilst the



Fig. 2. Top Figure: Discharges of PLONOR, substitutable and non substitutable substances present in production chemicals between 2000 and 2012. Bottom Figure: Discharges of substitutable substances as a percentage of the total discharge.

installations in the southern North Sea discharge much smaller quantities. This regional trend reflects the prevalence of gas extraction activities in the southern North Sea, which are relatively undemanding in terms of chemical requirements compared with oil extraction activities. Thus, installations in areas off the east coast of Scotland and Shetland, in the central and northern North Sea, involved in both oil and gas extraction, have higher discharges of SSs and SPs. These discharges often relate to the use of inhibitors for waxes and asphaltenes, as the deposit of these substances would reduce the efficiency of the extraction of the crude oil.

3.3. Chemical functions of substitutable products

Between 2000 and 2012 over a million tonnes of products (substitutable, non-substitutable and PLONOR) were used as part of offshore oil, condensate and gas production operations. Between 2006 and 2012 the total amount used was 541,442 tonnes with by far the largest contributor being 155,758 tonnes of gas hydrate inhibitors (Figure S1 in the Supplementary data). However, although gas hydrate inhibitors accounted for more than a quarter of the entire tonnage of chemical products used between 2006 and 2012,

gas hydrate inhibitors are generally relatively low-risk chemicals (e.g. alcohols) and the total use of these inhibitors only contributed to less than 10 kg of SS discharge during the same period.

The next most widely-used chemicals comprise scale inhibitors (62,473 tonnes), hydrogen sulphide scavengers (59,599 tonnes) and corrosion inhibitors (52,185 tonnes), all contributing over 10% of the total tonnage used between 2006 and 2012 and contributing to the amount of SSs discharged during the same period. However, as indicated in Fig. 5, the extent of the contribution to the discharge, and the associated trends, differ significantly for the three chemical function groups. In the case of hydrogen sulphide scavengers, SSs represent only a small, and declining, proportion of the total discharged. In the case of scale inhibitors, SSs are markedly more abundant, and as a result this chemical function group was responsible for the greatest discharge of SSs in 2006. However, the discharge of scale inhibitors has decreased steadily since 2006 and this chemical function group was only the fourth largest contributor to SSs discharge in 2012. In contrast, SSs discharges attributable to corrosion inhibitors have remained fairly constant since 2007, and this chemical function group is now the most significant source of such discharges.



Fig. 3. Total discharges (tonnes) of products containing substitutable substances (A) and substitutable substances (B) at different UK National Plan Levels discharged offshore between 2006 and 2012.

To function effectively, corrosion inhibitors must provide a protective layer separating a metal surface from the liquid (usually water) with which it is in contact. In order to create such a barrier. the corrosion inhibitor molecule must offer both a polar group that will adhere to the metal and a hydrophobic group (typically a hydrocarbon chain, or "tail") that will prevent penetration by water. This requirement dictates the need for a surfactant component and, unless the surfactant has a molecular weight of >700, this component will be deemed to be potentially bioaccumulative in the absence of suitable data (Dugue et al., 2011). Since metallic surfaces tend to acquire a negative charge when wet (Lomax, 1998), cationic types are most effective, such as imidazolines and quaternary ammonium salts, but cationic surfactants are generally toxic (Lewis et al., 1991). The combination of toxicity and bioaccumulation potential therefore results in a substitution warning. The creation of environmentally friendly corrosion inhibitors is thus seen to be problematic, since the very properties that they require to perform their function will also qualify them as SSs under the OSPAR Prescreening scheme. The chemical industry is nevertheless devoting considerable effort to tackle this challenge, for example one study has explored the optimisation of the length of the alkyl ethoxylates of some corrosion inhibitor molecules, since shorter alkyl chains of the ethoxylated propoxylated polymer offer lower toxicity whilst longer alkyl chains provide better corrosion protection (Donaldson et al., 2011). Another study has considered the potential for polymeric corrosion inhibitors (Hellberg, 2013). However, such developments have yet to have a significant impact in terms of offshore use.

3.4. The UK substitution strategy the future development of substitution in the UK

Although many studies have identified legislation as one of the most powerful drivers for chemical substitution (Reibstein, 2008; Verschoor and Reijnders, 2001), others have shown that environmental legislation alone is not always sufficient to ensure



Fig. 4. The location and total amount of substitutable substance discharge in 2006 (left) and 2012 (right) and a comparison of UK National Plan level substitutable substance discharge in 2006 (bottom left) and 2012 (bottom right). Each dot represents an installation.

that future reduction targets are met, and greater levels of innovation across the chemical supply industry are needed to realise further progress (Lofstedt, 2013). However, chemical substitution is rarely a simple process, and when a substitution is made without an understanding of all the issues involved this has the potential to increase rather than decrease risks (Laden and Gray, 1993; Tickner et al., 2013). The potential to increase risks is due to the multifaceted nature of chemical substitution, encompassing acute or chronic health risks, safety and fire risks, the limited knowledge of the toxicity of chemicals (Gray, 1995), the error associated with incorrect available information (Verschoor and Reijnders, 1998), the possible shift in risks when considering different types of environments (i.e. workplace versus marine or terrestrial environment) (Goldschmidt, 1993; Hoet et al., 1997; Rossi et al., 1991) and the possible shift in risks in relation to specific use scenarios.



Fig. 5. Total substitutable substance discharged by function type between 2006 and 2012 (product function types with total substitutable discharge of less than 50 tonnes are not included).

The introduction of the UKNP has established recommended priorities for substitution but, in view of the issues outlined above, the UK accepts that the replacement of SPs may prove to be a technically or financially unsustainable option in some cases. Where this applies, the UKNP allows offshore operators to continue to formally justify the proposed use and discharge of chemicals that are candidates for substitution. Operators are therefore required to compile technical justification documents. which summarise i) the use and/or discharge of the chemical, ii) the reasons why it is necessary to use and/or discharge the chemical, iii) the efforts made to phase out the use or discharge of the chemical, and iv) the reasons why phase out of use or discharge is not currently considered to be feasible (i.e. technical or/and safety reasons). Although it is therefore possible for operators to continue to use and discharge SSs beyond the target deadline, a strong incentive is maintained favouring the replacement of the relevant products.

Looking ahead, the next decade will be one of considerable challenge to industry and regulators alike. The deadline for the phase-out of discharges of SSs included in OSPAR Recommendation, 2006/3 is 1 January 2017 and, in addition, by 2018 all chemical substances used offshore will need to have been registered under the EC REACH Regulation, which presents its own SS definitions and protocols that differ in detail from those currently employed by OSPAR. Whilst OSPAR is committed to the harmonisation of its regulatory framework with that of REACH where possible and where it does not dilute the OSPAR regime, significant obstacles need to be overcome before this can be fully achieved. EU Member States will also be striving to demonstrate compliance with the Marine Strategy Framework Directive, and its associated target of achieving Good Environmental Status by 2020. How these regulatory demands will be reconciled with the continuing demand for oil and gas remains to be seen.

4. Conclusions

Although the quantity of chemical substances discharged from offshore oil and gas production installations did not decrease greatly between 2000 and 2012, the nature of the chemicals discharged shifted towards those of a less hazardous nature. In particular, the proportion of the total comprising of SSs fell significantly during the period 2000-2012 with the most northerly installations showing notable reductions between 2006 and 2012. These outcomes provide evidence that the Offshore Chemical Regulations, introduced in 2002, and the UK National Plan, introduced in 2007, have been effective in promoting the use of less hazardous substances, and that the strategy adopted towards discouraging the discharge of SSs has been successful. However, significant progress remains to be made before the unnecessary discharge of such substances can be eliminated, and fundamental technical obstacles will need to be overcome. Although the discharge of UK National Plan level 1 substances fell to zero in 2012, current trends indicate that SSs at other levels will continue to be discharged beyond the phase-out dates outlined in the UK National Plan, and the industry will need to continue to justify those discharges to the regulatory authorities.

The approach described in this paper illustrates the benefits of a prioritised strategy for chemical substitution and an ongoing dialogue between the industry and regulator. A continuing case by case dialogue with offshore operators and suppliers will be essential to ensure that alternative technical solutions are trialled and options for substitution are investigated at the earliest stage.

Acknowledgements

The authors would like to express their deepest appreciation to Derek Saward and Mark Shields of DECC Oil and Gas and the OCNS team at Cefas Lowestoft for their professional and efficient work in relation to the risk assessment of offshore chemicals. In particular we would like to thank Lynn G. Jones, Steve Supple, Cheryl Moran and Linda M. Hughes for their invaluable help and support with the offshore work.

Acronyms

- CAS **Chemical Abstracts Service** Cefas Centre for Environment, Fisheries and Aquaculture Science DECC Department of Energy and Climate Change EC **European Commission** EEMS Environmental Emissions Monitoring System Harmonised Mandatory Control Scheme HMCS LCPA List of Chemicals for Priority Action LSPC List of Substances of Possible Concern OCNS Offshore Chemical Notification Scheme OSPAR Oslo and Paris Conventions: The Convention for the Protection of the Marine Environment of the North-East Atlantic PBT Persistence, Bioaccumulation and Toxicity PLONOR Pose Little or No Risk REACH Registration, Evaluation, Authorisation and Restriction of Chemicals SPs Substitutable Products SSs Substitutable Substances SVHC Substances of Very High Concern UK United Kingdom UKCS United Kingdom Continental Shelf
- UKNP United Kingdom National Plan

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jclepro.2014.09.053.

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