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Assessment of the Impact of an EC Directive on Priority Substances under the WFD on the Current Regulation of Contaminated Sites

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Contents

Summary and conclusions

A proposal for an EC Directive on Priority Substances under the Water Framework Directive was put forward by the European Commission in July 2006. An initial assessment has been carried out on whether one or more of the priority substances (PS) can be expected to constitute a risk of exceeding the Environmental Quality Standards (EQSs) in surface waters due to losses from contaminated sites and soils.

Furthermore, an assessment has been carried out on which of the priority hazardous substances (PHS), in relation to soil and groundwater contamination, need to be handled if it should be decided to stop losses of PHSs to the aquatic environment completely.

In the final version of the Daughter Directive proposal (COM(2006)397 final), EQSs are also established for a group of eight substances called "other pollutants" (Annex I, Part B). These substances have been included in the initial assessment.

In continuation of these, an estimate on types and number of sites of relevance was given.

The assessment on relevant priority substances is based on a screening of the following:

- Use and production - both present and historical
- Physical-chemical properties
- Toxicity
- Common practice including quality standards such as Groundwater Quality Standards (GQS), to answer the question: Will the contaminations be detected in the framework of common practice and legislation

The following substances were screened out as their use volume was less than 1 ton/year: Hexachlorobenzene, hexachlorobutadiene, pentachlorobenzene, isodrin, aldrin, C_{10-13}-chloroalkanes, chlorfenvinphos, chlorpyrifos, 1,2-dichloroethane, dieldrin and endrin.

As endosulfan has only been used in very small amounts (2 tons/year), presumably on very few locations, and has only been produced on one site in Denmark, endosulfan was screened out too. The Priority Hazardous Substances anthracene, pentabromodiphenylether, cadmium and compounds, mercury and compounds pentachlorobenzene and PAH were screened out based on their physical and chemical properties, i.e. low mobility in the soil and groundwater zone. This means that 10 out of 13 of the PHSs were screened out.

Based on the screening, it was assessed that the following 6 priority substances, in case of a soil and groundwater pollution, posed a potential risk of exceeding the EQS in surface waters:

- HCH/lindane
- Nonylphenol
- Octylphenol
- Tributyltin and compounds
- Trichlorobenzene
- Trichloromethane

Of these the following 3 are classified as PHSs:

- HCH/lindane
- Nonylphenol
- Tributyltin compounds.

For each of the 6 substances a necessary dilution factor has been established, in order to comply with the EQSs for surface waters. The dilution factor is established as the relation between an estimated source concentration and EQS. The critical areas have been identified from the dilution factor and the estimated mixture and dilution in the groundwater and surface waters. The number of possible sites which are assessed to pose a risk for unacceptable contamination of surface waters, have been estimated by comparing the critical areas with an estimate of the number and location of area, which might be contaminated with the actual substance.

Major polluted sites in Denmark and waste dumps were included in the estimate.

It was seen that for each of the 6 priority substances except tributyltin compounds, less than 350 smaller sites and a few larger sites were expected. For tributyltin, the number was around 500 larger sites, primarily winter store places for yachts and shipbuilding yards.

Regarding the number of sites contaminated with the PHSs HCH/lindane, nonylphenol and tributyltin compounds, it was estimated that a total of approx. 630 smaller sites and 500 larger sites might need to be remediated in order to stop losses of the PHSs to the environment. As this assessment is based on generalized assumptions and done within a statistical framework, specific investigations or monitoring of surface waters would be necessary in order to evaluate the actual risks posed by these sites.

This document is based on the assumption that losses of the PHS's ought to be stopped. In reality this implies that measures should be taken by Denmark with the purpose of stopping the losses. By aiming to stop the losses through the necessary measures Denmark will fullfill its obligation as stated in the Water Framework Directive.

Sammendrag og konklusioner

EU Kommissionen har i juli 2006 fremsat et forslag om et datterdirektiv til Vandrammedirektivet vedrørende såkaldt prioriterede stoffer. Denne rapport giver en indledende vurdering af, hvilke af de prioriterede stoffer (i rapporten benævnt PS), der i tilfælde af jord- og grundvandsforurening forventes at ville udgøre en risiko for at overskride Kommissionens foreslåede miljøkvalitetskrav (i rapporten benævnt EQS) for overfladevandområder.

Ydermere er der udarbejdet en vurdering af, hvilke af de prioriterede farlige stoffer (i rapporten benævnt PHS) der, i tilfælde af jord- og grundvandsforurening, er behov for at håndtere udsivning af, hvis man ønsker helt at standse tilførslen til vandmiljøet. Dette skal ses i sammenhæng med, at det ifølge vandrammedirektivet er et mål at arbejde for at opnå ophør/udfasning af udledning og tab af prioriterede farlige stoffer til vandmiljøet.

Det endelige forslag fra Kommissionen til datterdirektiv (KOM(2006)397 final) indeholder en gruppe på otte stoffer kaldet "andre forureninger" (Annex I, Part B). Disse stoffer har også indgået i den indledende vurdering.

I fortsættelse heraf er der givet et overslag over typer og antal af områder, der er relevante.

Vurderingen af relevante PS bygger på en screening af følgende:

- Anvendelse og produktion - både nu og historisk
- Fysisk-kemiske egenskaber
- Toxicitet
- Almindelig anvendelse herunder kvalitets standarder såsom GQS, som kan besvare spørgsmålet: Vil forureningen blive opdaget indenfor rammerne af almindelig praksis og lovgivning.

Følgende stoffer blev screenet ud af undersøgelsen, fordi forbruget var under 1 ton/år.: Hexachlorbenzen, hexachlorbutadien, pentachlorbenzen, isodrin, aldrin, C_{10-13}-chloralkaner, chlorfenvinphos, chlorpyrifos, 1,2-dichlorethan, diedrin og endrin.

Da endosulfan kun har været anvendt i meget små mængder (2 ton/år) og formodentlig kun på meget få steder, og kun har været produceret i Danmark ét sted, er den screenet ud. PHS antracen, pentabrom diphenylether, cadmium og forbindelser, kviksølv og forbindelser, pentachlorbensen og PAH er screenet ud baseret på deres fysiske og kemiske egenskaber f.eks. lav mobilitet i jord- og grundvandszonen. Det betyder at 10 ud af 13 PHS' blev screenet ud.

På baggrund af screeningen blev det vurderet, at for følgende 6 PS vil en given jord- og grundvandsforurening kunne give anledning til, at der sker overskridelse af EQS i overfladevandområder:

- HCH/lindane
- Nonylphenol

- Octylphenol
- Tributyltin og forbindelser
- Trichlorbenzen
- Trichlormethan

Af disse er følgende 3 stoffer klassificeret som PHS'er:

- HCH/lindan
- Nonylphenol
- Tributyltin og forbindelser

For hvert af de 6 stoffer er fastsat en nødvendig fortyndingsfaktor, for at EQS kan overholdes i overfladevandområder. Fortyndingsfaktoren er fastsat ud fra forholdet mellem en anslået kildestyrke og EQS. Ud fra fortyndingsfaktoren og antagelse om opblanding og fortynding i grundvand og overfladevand er kritiske områder identificeret. Antallet af mulige lokaliteter, der vurderes at udgøre en fare for uacceptabel forurening af overfladevand, er vurderet ved at sammenholde de kritiske områder med et skøn over antallet og beliggenheden af områder der kan være forurenet med de pågældende stoffer.

For nonylphenol og octylphenol blev det beregnet at kun 1 henholdsvis 2 mindre lokaliteter vil kunne give anledning til overskridelser af HQS. Fokus bør derfor primært rettes mod de resterende 4 PS. For lindan, triclorbenzen og trichlormethan forventedes færre end 350 mindre lokaliteter og nogle få større lokaliteter at kunne give anledning til overskridelser af HQS. For tribultyltin beregnes antallet til omkring 500 større lokaliteter, fortrinsvis bådpladser på land for lystbåde og skibsværfter.

Med hensyn til antallet af områder forurenet med PHS, HCH, nonylphenol samt tribultyltin og -forbindelser, blev det skønnet, at for mindre end 630 mindre og 500 større områder kunne det være relevant at sætte ind med afværgeforanstaltninger, hvis man fuldt ud ønsker at stoppe udsivning af PHS til vandmiljøet som følge af jord- og grundvandsforureninger. Dette skøn er baseret på generelle antagelser og statistiske beregninger, hvorfor en vurdering af den faktiske risiko ved disse lokaliteter forudsætter mere specifikke undersøgelser eller overvågning af overfladevandsområder.

I nærværende notat er det benyttet som forudsætning for vurderingen, at udsivningen af disse stoffer skal ophøre. Dette medfører i praksis , at de af Danmark foretagne foranstaltninger skal have til formål at sikre standsning/udfasning. Danmark skal således tilstræbe at opfylde målet om udfasning gennem de nødvendige foranstaltninger og vil derved opfylde sin forpligtelse efter vandrammedirektivet.

1 Introduction

1.1 Background

The Water Framework Directive (2000/60/EC) was established to provide a new, comprehensive regime for the protection of inland surface waters, transitional waters, coastal waters and groundwater ***inter alia*** through measures towards chemical pollution from priority (hazardous) substances (***Article 1, c***). The WFD ***Article 16*** requires the Commission to bring forward specific proposals on priority substances in surface waters.

The list of priority substances (including proposals for priority hazardous substances) was established already in 2001 by Decision no. 2455/2001/EC of the European Parliament and of the Council. Since then, work has been ongoing in the Commission to prepare the scientific basis for a Daughter Directive of the WFD intended to establish, among others, environmental quality standards (EQS) for the priority substances (PS) identify the substances to be regarded as priority hazardous substances (PHS), and defining the regulatory requirements applying to these substances.

The Daughter Directive proposal (COM(2006) 397 final) by the EC Commission was officially released in July 2006 and the consequences to Denmark of implementing the directive has been assessed in a separate report prepared for the Danish EPA by COWI A/S.

However, the possible importance of losses of PS/PHS from contaminated sites was only briefly touched upon in the report and therefore the Danish EPA decided to initiate a screening exercise regarding significance of soil and groundwater contamination in relation to the requirements of the Daughter Directive and clarifying to what extent achieving compliance with the directive would require further action to be taken by Denmark.

1.2 Objectives

The objective of this study is to make an initial technical assessment of the consequences for Denmark of implementing the Priority Substances Daughter Directive with emphasis on transport ("losses") of the priority substances from soil and groundwater pollution to surface waters. That is:

- Assessing which of the priority substances that are expected to constitute a risk of exceeding the EQSs in the aquatic environment due to losses originating from soil and groundwater pollution

- In continuation of that, give a conservative estimate on the number of sites polluted with the relevant priority substances and constituting a risk of exceeding the EQSs in surface waters.

Assessing which of the priority hazardous substances can be expected to constitute a risk of leaching into surface waters due to losses originating from soil and groundwater pollution
In continuation of that, give a conservative estimate on the number of sites polluted with the relevant priority hazardous substances and constituting a risk of surface water contamination.

1.3 Project scope and delimitation

The study was initiated in September 2006. The study includes soil and groundwater pollution due to contamination from point sources as well as diffuse sources, and includes both known sites and sites that has not yet come to the authorities' knowledge.

1.3.1 Point sources

All point sources will, as a starting point, be part of the project.

Major contaminations such as Høfde 42, Kærgård Plantage, Proms Kemiske Fabrikker and the like, will be handled separately on the basis of the recommendations Danish EPA received from the counties and an assessment of their relevance carried out by Ole Kiilerich, Danish EPA in consultation with COWI.

Regarding discharges from remediation facilities, this can be simplified to the following types:

1. Short-term discharges, e.g. in connection with dewatering of excavations or the like.

2. Long-term discharges, e.g. volume pumpings, demarcation of the contamination flare etc.

Relating to 1
The characteristic of these short-term discharges is that usually the water is so contaminated that it has to be treated before being disposed of to the surface waters. Generally, it needs to be treated before discharge to the sewage treatment plant. Treatment usually comprises active carbon treatment, treatment in an oil separator, if necessary supplemented with natural purification in a treatment plant. The purification is thus based on methods which usually purifies to a higher level than in the discharge demands e.g. Statutory Order 921 (1996). An increase of the discharge demands as a result of the Daughter Directive is not assessed to increase the cost of short-term discharges from contaminated sites substantially.

Relating to 2
The major part of the discharges from remediation facilities are led to sewage treatment plants. Discharges through the sewage system are included in the main report and are therefore not part of this study. Discharges which are led to surface waters are usually treated using methods with a high degree of purifying, and possible extra costs as a result of the implementation of the Daughter Directive are assessed to be negligible.

It is assessed that diffuse percolation from ongoing refuse dumps to surface waters, as a rule, is limited through the refuse dump authorisation and handling of percolate, and thus can be marginalised in the present investigation. Discharges from ongoing refuse dumps are included in the main screening project as they require actual discharge permissions.

With regard to disused refuse dumps, it cannot be ruled out that uncontrolled percolation/seepage of percolate to the groundwater or surface waters takes place. An estimate of disused refuse dumps where substances of relevance have been deposited and the distance to the surface waters thus implies a risk will be carried out.

1.3.2 Diffuse contamination

As a starting point, diffuse contamination is marginalised in the present investigation. This owing to the assessment that the major part of a possible percolation/seepage from diffuse contamination from e.g. roads is collected in drains and thus is part of the rainwater discharge dealt with in the main report. Pesticide residues in e.g. fields and on railway embankments are also covered in the main screening. In addition, it is assessed that spreading of diffuse contamination around source contaminations e.g. neighbouring contamination from major industries or the like to the surface waters will be marginal compared to the percolation/seepage of the source contamination.

The following areas are omitted in consideration of their essentiality:

- Run-off of contaminated material from unpaved areas close to the point source straight to surface waters is marginalised, as it is assessed that this mass flow of contamination is very limited compared to e.g. run-off through the sewage system. Run-off through the sewage system is included in the main report.

- Run-off of contaminated groundwater straight to surface waters through drain systems such as perimeter drain or field drain can locally constitute a potential route of spreading. Though the accumulated run-off of contamination through drains is assessed limited compared to other routes of spreading, the issue will be addressed briefly in section 3.4.

- Particular transport (e.g. colloid transport) of contamination in the groundwater aquifer is left out, as it is assessed limited compared to all other transport of contamination in the groundwater zone.

- Free phase contamination is not explicitly part of the assessment as it is assessed that free phase contamination in relation to surface waters is generally visible and included in the current legislation and practise. It is thus not expected to constitute additional costs in relation to Danish environmental management.

As initial dilutions for e.g. streams, lakes and the like, which are affected by percolation/seepage from soil contamination, are not yet defined, the necessary initial dilution in the surface waters will be estimated.

The geological model comprises two main geological types - a sandy and a clay soil type.

1.4 Project Organisation

The work was carried out by a team of consultants at COWI A/S consisting of Jesper Kjølholt (project manager), Tage Vikjær Bote, Dorte Glensvig and Marlene Ullum.

Ole Kiilerich, project responsible in the Danish EPA, has participated actively during the implementation of the project, in particular in the process of clarifying methodological issues.

2 Methodology

The main objective of the current Danish legislation on contaminated soil and groundwater is to protect human health and groundwater resources. Therefore, measures to protect contamination of surface waters from soil and groundwater pollution are rare. However, protection of surface waters often occurs as a side-effect when measures to protect groundwater resources are implemented.

The objective of this project is to identify substances and types of soil and ground water contamination that can cause pollution of surface waters, without being discovered by the present legislation and administration. At these sites further action can be relevant to ensure that the proposed EQSs for priority substances in surface water are not exceeded. Further action can also be relevant to cease the leaching of priority hazardous substances (PHS).

It is noted that the framework of the project does not permit a detailed assessment, but only an introductory screening of the consequences of implementation of the Directive on 33 priority substances under the Water Framework Directive.

The Daughter Directive proposal also establishes EQSs for a number of "other pollutants" (OP) (Annex I, Part B), i.e. some chemicals that are not priority substances but substances which were previously included in a number of directives that will be repealed by 2013 (Directives 82/176/EEC, 83/513/EEC, 84/456/EEC, 84/491/EEC and 86/280/EEC). These eight substances have been included in this project equally to the priority substances.

The screening of the priority substances and contamination situations is divided into two steps:

- Step 1: Identification of substances (PS, PHS and OP) used in Denmark and types of contaminated sites where these substances are/were handled (Chapter 3).

- Step 2: An assessment of the number of sites in Denmark contaminated with the identified substances of relevance and constituting a risk of exceeding the EQSs in surface waters or risk of priority hazardous substances (PHS) leaching into surface waters (Chapter 4)

Based on step 1 and 2, an assessment of the need for further action to be taken by Denmark to ensure that the EQSs are not exceeded due to soil and groundwater contamination will be carried out (Chapter 5). The assessment also includes the need for action if Denmark decides completely to cease the leaching of hazardous substances (PHS) from polluted sites to surface waters.

2.1 Step 1

Step 1 is based on five elements:

- Use and production in Denmark
- Substance characteristics
- Will the contamination be detected in the framework of common administration of soil and groundwater pollution?
- Types of contamination situations of concern
- An overall assessment of substances and types of contaminated sites of relevance based on the previous four elements

For every element in the screening, the substances are divided into two to five groups, depending on whether or not we assess the substances to be of interest in relation to the objective. At the final assessment, the result of each element is used in an overall assessment of substances of concern. In the following, the five elements are briefly described.

2.1.1 Use and production in Denmark

The basis for the data is the PS screening project (2005), expert knowledge contributed by Jesper Kjølholt, Tage Bote and Dorte Glensvig and general knowledge available in COWI. This means that further collection of use and production data has not taken place.

Substances which have not been used or produced in Denmark were screened out. Furthermore, only limited focus has been given to substances which have only been used or produced on a small scale in Denmark.

2.1.2 Substance characteristics

The county of Copenhagen was contacted for information on the prioritization system GISP with the purpose of assessing the hazardousness of the individual substances towards the groundwater resource, as an indicator of how easily they spread in the water environment.

Substances which are rather or relatively immobile in the groundwater environment were screened out and the substances which are moderately or highly mobile were singled out.

2.1.3 Will the contamination be detected in the framework of normal practice/legislation?

Legislation and practice have been described as a starting point for assessing which contamination situations are expected to be managed in the framework of environmental legislation.

Basically, it has assumed that as long as the substances are covered by common practice and legislation, they do not pose a risk or need for further actions or increased environmental costs. In other words, if investigations of the substances in relation to soil and groundwater are generally carried out, additional actions for implementing the Daughter Directive are not expected, and the combination of location and substance are screened out. An exception is the situation where the limit values in the Daughter Directive (EQS) are lower than the limit values normally used (groundwater quality criteria

(GQC)). In these situations the combination of location and substance were singled out.

A comparison of the groundwater quality criteria (GQC) and the proposed EQS values have therefore been carried out. Depending on the difference between GQC and EQS a prioritizing of the substances were carried out.

Only a limited number of substances will be detected during normal groundwater monitoring and investigations of contaminated sites, causing a risk that some prioritized substance will not be detected or remediated.

The laboratory Eurofins Danmark A/S was contacted regarding how frequently ground water analysis includes the priority substances. This has been used as an indication of how often common practice includes the priority substances in investigations of soil and groundwater contamination.

2.1.4 Types of contaminated sites and spreading of contamination

A number of conceptual models for contamination of soil and groundwater and run-off to surface waters have been established. Estimates on natural dilution in both the groundwater zone and when the groundwater contamination reaches the surface waters were carried out. As initial dilution factors for non point releases to the surface waters were not available, the need for natural dilution to reach the EQSs in the surface waters have been estimated and evaluated based on expert knowledge.

2.1.5 An overall assessment of substances and contaminated sites of relevance

Based on the results of the previous four elements an overall assessment of substances and types of contaminated sites of relevance is carried out: which of the 41 substances and which types of contaminated sites are expected to constitute a risk of exceeding the EQSs in surface waters.

Priority hazardous substances are specifically included in the assessments.

2.2 Step 2

In step 2, results from step 1, especially the fifth element regarding substances and types of contaminated sites of relevance, is used as the starting point of identifying a realistic number of sites constituting a risk of exceeding the EQSs in surface waters and thus requires further action to be taken by Denmark to ensure that the EQSs are not exceeded.

Furthermore an assessment of the number of sites contaminated with the priority hazardous substances is given.

2.3 Need for further action

Based on step 1 and 2 an overall assessment is carried out. The assessment is based on the need for further action to ensure that none of the priority substances (PS) and other pollutants (OP) exceed the proposed EQSs, and to meet the aim of ceasing the leaching of priority hazardous substances (PHS) into surface waters.

3 Step 1 - Substances and types of contaminated sites of relevance

3.1 Present and historical uses of the 41 substances

In the following chapter, an assessment of substances of relevance regarding use and production has been conducted. The assessment is based on the assumptions and delimitations mentioned in chapter 2.

Table 3.1 summarizes data from Kjølholt et al (2005) on present and historical production and uses of the 33 priority substances under the Water Framework Directive and the 8 other pollutants. The data in the table are based on the PS screening project regarding present use and on fingertip knowledge regarding historical use, as the framework of this project does not include further detailed investigation into e.g. production sites in Denmark, handling methods or investigation of contaminated sites.

Table 3.1
Present and historical uses of the 33 priority substances and 8 other pollutants under the Water Framework Directive. Priority Hazardous Substances (PHS) are marked in **bold**. Other pollutants (OP) are marked with a # .
Data source: PS Screening Project (Kjølholt et al., 2005) + DK Pesticide Statistics.

Name of substance (No., WFD Annex X)	**Amounts (ton) per year**	**Present and historical uses**
Alachlor	28.3-18.6 (1981-1983)	Herbicide used in oilseed rape. Registered for use in Denmark from 1972 (maybe earlier) until 1986. Not produced/formulated in Denmark.
Aldrin#	<1	Insecticide used in small amounts before 1963. Not produced/formulated in Denmark.
Anthracene	Unknown	PAH substance. Main intended use as component in creosote for industrial wood preservation until 1989.
Atrazine	15.4, 105.8, 42.6 (1974, 1985, 1993)	Herbicide used until 1994 (banned) in maize fields, forests and uncultivated areas. Produced/formulated in DK by NAB, and probably also KVK and Esbjerg Kemi
Benzene	22,500 (2004)	Main amount as component of gasoline. Solvent used in paints, wood preservatives, degreasing agents and as raw material in organic synthesis
Pentabromo diphenylether *	30-120 (1997) (all PBDEs)	Flame retardant in epoxy, polyester, polyurethane and textiles
Cadmium + compounds	43-71 (1996)	Main use in batteries, but is also found in toys and other plastics, and as an impurity in zinc, fertilizers, cement etc.
Carbon tetrachloride#	1 (2000, 2001)	Solvent widely used in the start of the 20. Century. Through the 20. Century the solvent has been phase out, end it was banned in Denmark in 2001.Use in polymer technology as reaction medium, catalyst; in organic synthesis for chlorination of organic compounds eg. CFC's; in soap perfumery and insecticides. Solvent for laboratory use.
$C_{10\text{-}13}$-chloroalkanes	< 1 (2004)	Primary use as cooling/lubricating agent in metal work industries, but (maybe) also in fillers/sealant and hardeners

Name of substance (No., WFD Annex X)	Amounts (ton) per year	Present and historical uses
Chlorfenvinphos	1.4, 0.16 (1988, 2001)	Insecticide, primarily for use in cabbage and for indoor cultivation of ornamental plants. Last year of use was 2001. Probably never produced or formulated in DK
Chlorpyrifos	<0.1, 0.5-0.9 (-1987, 1999-2004)	Insecticide. Main uses for indoor control of cockroaches, ants and vermin. Produced in DK by Cheminova
DDT[#]	35-40 (1956-69) 1 (1970-84)	Insecticide. Registered for use in Denmark from 1956 (maybe earlier) until 1984. It was banned for agricultural use in 1970 and totally in 1984. Not produced/formulated in Denmark.
1,2-Dichloroethane	0.05 (2004)	Main use as intermediate in the production of PVC (no such production in DK). Solvent in glues, paints, degreasing agents etc.
Dichloromethane	450-500 (1995)	Solvent and extraction agent with a wide range of applications e.g. removal of paint/lacquers, cleaning (degreasing), pharmaceuticals, lab chemical
Dieldrin[*]	0.8 (average for a period of 29 years)	Insecticide used against crawling insects but not outdoors, and against pests in wood. Registered for use in Denmark from 1956 (maybe earlier) until 1988. Not produced/formulated in Denmark. In 1992 it was banned in Denmark.
Di(2-ethylhexyl)phthalate	>5,000 (2004)	Main use as plasticizer in soft PVC, but also in other polymers, rubber, glue, sealants, textile prints etc. etc.
Diuron	20-30	Herbicide used in horticulture, new plantations in forests, plant nurseries. Also important use as anti-fouling agent. Unknown, if production or formulation in DK has taken place
Endosulfan	2.0 (1994)	Insecticide, primarily used in oilseed rape. Used in Denmark until 1994. Formulated earlier in DK by NAB
Endrin[*]	<1	Insecticide used in small amounts before 1963. Not produced/formulated in Denmark
Fluoranthene	Unknown	PAH substance. No intended use in DK, but a component of creosote
Hexachlorobenzene	0 (2004)	Historical use as fungicide (wheat, onions). Probably never used in DK, but if so, the use dates more than 30 years back
Hexachlorobutadiene	0 (2004)	Intermediate in synthesis of rubber. Probably never used in Denmark
γ-HCH	12.3 (1994)	Insecticide. Used in Denmark until 1994, mainly in oilseed rape and plantation of spruce trees (including Christmas trees). Produced/formulated earlier in DK by NAB and possibly others (e.g. KVK)
Isodrin[*]	0	Insecticide, has never been used or produced in Denmark
Isoproturon	up to 540 (1997)	Herbicide used in cereal crops (mainly winter cereals). Banned in 1999. Not produced or formulated in DK
Lead + compounds	15,000-19,000 (2000)	Main consumption is for use in batteries (52 %) and materials for buildings (roofs etc.). Also in various alloys, component in glass and PVC etc. etc.
Mercury + compounds	1.4-1.9 (intended) (2001)	Main intended use is for tooth filling, but also e.g. for thermometers, various electrical equipment and certain batteries
Naphthalene	46,500 (2004)	Production of roofing felt and related products, constituent of tar and creosote
Nickel + compounds	5,400-7,800 (1992)	Main use is stainless steel (more than 80 %). Also for other alloys and metal products, and as impurity in coal, oil, fertilizers, cement etc.
Nonylphenol	300-800 (2004)	Previously, considerable use of NPE in washing and cleaning products, and in pesticides. Today, mainly in certain hardeners, paints and fillers

Name of substance (No., WFD Annex X)	Amounts (ton) per year	Present and historical uses
Octylphenol	16 (2002)	Probably same types of uses as NPE, but much lower consumption
Pentachlorobenzene	0 (2004)	Uncertain, if the substance has ever been used in Denmark. Impurity in the fungicide quintozene (which has been used in DK)
Pentachlorophenol	0 (2004)	No use in DK today except when occurring in imported textiles etc. Earlier (until 1977) also used in DK as preservative for wood, textiles, leather etc.
PAH	Unknown	Various tar products including creosote for preservation of wood, carbon black. Most important source today is as combustion by-product
Simazine	20 (typically)	Herbicide used in Denmark until 2003. Mainly used on uncultivated areas and in horticulture, forestry and plant nurseries. Produced/formulated in DK by NAB, and probably also KVK and Esbjerg Kemi
Tetrachloroethylene*	740-800.000 (1995)	Solvent widely used in DK: The main use is in dry-cleaning but also used for production of pharmaceuticals, for graphical production, and as degreasing solvent for metal working.
Tributyltin compounds	13-16 (1994)	Only marginal use today. Earlier, extensive use as anti-fouling agent and also (before 1999) as wood preservative
Trichlorobenzene	10-60 (1988)	No use in DK today, but earlier used in the production of pesticides and also in electronic equipment
Trichloroethylene*	690-870.000 (1995)	Main use is as a degreasing solvent for metal working. Plastic and rubber manufacturing , cleaning and glue processes.
Trichloromethane	8.3 (2004)	Main uses in DK (no production): Pharmaceutical, solvent, lab chemical
Trifluralin	up to 67 (1996)	Herbicide used in a range of crops until 1998. Probably formulated earlier in DK by NAB

As it appears from table 3.1, it is assessed that some substances have not been used or produced in Denmark. These are:

- Hexachlorobenzene
- Hexachlorobutadiene
- Pentachlorobenzene
- Isodrin

Furthermore, certain substances are expected only to have been used in Denmark in limited quantities and are therefore not expected to be of relevance regarding the objective of the project. Using 1 tons/year as a limit, these are:

- Aldrin
- C10-13-chloroalkanes
- Chlorfenvinphos (as an average)
- Chlorpyrofos
- 1,2-dichloroethane
- Dieldrin
- Endrin

In table 3.2 below (only showing the pesticides among the 41 substances in table 3.1), an assessment of the risk of a point source of pesticide in soil and groundwater is given. Based on the delimitation in chapter 2, the assessment does not include diffuse contamination such as pesticide residues in e.g. fields and on railway embankments due to spreading of pesticides.

The assessment is based on the following principles:

- If the pesticide has only been used in a small amount, and have not been produced in Denmark, it has been screened out as not relevant regarding point sources

- If the pesticide has only been produced in Denmark, but has not been used, it has been assessed as relevant regarding point sources.

If the pesticide has been produced in Denmark, the production company is mentioned in brackets.

Table 3.2
An assessment of the risk of point source of pesticides based on data in table 3.1 and expert knowledge from Jesper Kjølholt. [1:] Amount used in agriculture and not including possible Danish production

Name of substance (No., WFD Annex X)	Amounts (ton per year)[1]	Assessment of relevance as point source contaminant
Alachlor	28.3-18.6 (1981-1983)	Not relevant
Atrazine	15.4, 105.8, 42.6 (1974, 1985, 1993)	Relevant (has been produced by NAB, Kemisk Værk Køge and Esbjerg Kemi)
Chlorfenvinphos	1.4, 0.16 (1988, 2001)	Not relevant
Chlorpyrifos	<0.1, 0.5-0.9 (-1987, 1999-2004)	Relevant (only production by Cheminova)
DDT#	35-40 (1956-69) 1 (1970-84)	Relevant (production by Cheminova)
Diuron	20-30	Probably relevant, but mostly because of the use as anti-fouling biocid in ship paint
Endosulfan	2.0 (1994)	Relevant (Only produced by NAB)
Hexachlorobenzene	0 (2004)	Not relevant
γ-HCH	12.3 (1994)	Relevant (Produced by NAB and presumably Kemisk Værk Køge)
Isoproturon	up to 540 (1997)	Not relevant
Simazine	20 (typically)	Relevant (Produced by NAB, Kemisk Værk Køge and Esbjerg Kemi)
Trifluralin	up to 67 (1996)	Relevant (Only produced by NAB)

It is seen from table 3.2, that 4 out of 12 pesticides have been assessed not relevant. An overall assessment is made in chapter 4.

3.2 Physical-chemical properties

In table 3.3, the physical and chemical properties of the 41 substances under the Water Framework Directive are summarized.

Table 3.3
Environmental characterization of the 41 priority substances and other pollutants under the Water Framework Directive based on their physical-chemical properties and degradability in soil. Priority Hazardous Substances (PHS) are marked in **bold**. Other pollutants are marked vith a #.
Data source: PS Screening Project (Kjølholt et al., 2005).

Name of substance (No., WFD Annex X)	Solubility (mg/L)	Vapour pressure (Pa)	Log Kow (Log Koc)	Aerobic degradability in soil (T½)
Alachlor	135-247	1.3-2.9 x 10-3	2.5-3.6 (2-2.5)	<30 d
Aldrin#	0.018	0.016	6.5	>200 d
Anthracene	0.032-0,085	0.8 x 10-3	4.2-4.6 (3.4-5.1)	?
Atrazine	33-70	4 x 10-5	2.2-2.5 (1.8-2.0)	60-150 d
Benzene	1,800	99,700	1.6-2.2 (1.3-3.0)	30 d
Pentabromo diphenylether	<0.001-0.0024	2.9-7.4 x 10-7	6.6-7.0 (> 4.7)	slow
Cadmium + compounds	-	-	-	-
Carbontetrachloride#	780	11,940	2.64	-
C_{10-13}-chloroalkanes	practically insoluble	0.02-1.9	4.4-8.7 (2.3-2.7)	?
Chlorfenvinphos	3-145	2.5 x 10-6 1-37 x 10-3	3.9-3.2 (2.0-2.7)	40 d
Chlorpyrifos	0.36-1.1	1.0-3.4 x 10-3	4.7 (4.7-5.3)	20-50 d
DDT#	0.0017	2.13x10-4	6.91	>200 d
1,2-Dichloroethane	8,500-9,000	8,500-8,700	1.5-1.8 (1.0-2.3)	9 d
Dichloromethane	13,700	47,500	1.3	7 d
Dieldrin#	0.195	0.00078	5.4	>200 d
Di(2-ethylhexyl)phthalate	3-4.5	3.4 x 10-5	4.9-7 (4.8-5.9)	<50 d
Diuron	35-42	1.1 x 10-6	2.7 (2.5)	>90 d
Endosulfan	0.3-0.5	7.5-17 x 10-6	3.5	?
Endrin#	0.25	0.0004	5.2	>200 d
Fluoranthene	0.22-0.27	0.7-1.3 x 10-3	4.7	slow
Hexachlorobenzene	0.005-0.006	2.3 x 10-3	3.0-6.9 3.5-5.3)	slow
Hexachlorobutadiene	2-4	20-36	4.8-4.9 4.0-4.5)	slow
γ-HCH(	7.8	4.4-21 x 10-3	3.9 (2.8-3.8)	several months
Isodrin#	0.2	?	5	?

Isoproturon	65	3.3 x 10-6	2.3 (1.7-1.9)	12-29 d
Lead + compounds	-	-	-	-
Mercury + compounds	-	-	-	-
Naphthalene	22-34	10.5	3.0-3.7 (2.6-3.5)	15-30 d
Nickel + compounds	-	-	-	-
Nonylphenol	3-6	0.3-100	4.2-4.7 (3.6-3.7)	slow
Octylphenol	3-5	0.07	5.3-5.5 (3.5-4.3)	inherent
Pentachlorobenzene	0.2-1.3	0.86-4.8	4.8-5.2 (3.5-5.1)	slow
Pentachlorophenol	14	4-15 x 10-3	3.3	?
PAH (data for BaP)	3.4-4.5	7 x 10-7	6.0 (6.3-6.7)	slow
Simazine	5.0-6.2	2.9 x 10-6	2.1-2.4	50 d
Tetrachloroethylene#	260	2,466	3.4	slow
Tributyltin compounds (data for TBTO)	30	1 x 10-3	3.2-3.8	4-5 months
Trichlorobenzene	36-49	22-36	3.9-4.2 (3.1)	inherent
Trichloroethylene#	1,180	9,199	2.42	slow
Trichloromethane	7.5-9.3	21,300	2.0 (2.3)	?
Trifluralin	0.18	9.5 x 10-3	5.3 (3.8-4.1)	3-18 weeks

For each of the 41 substances, an assessment of the ability of the substance to spread from a soil or groundwater contamination to surface waters has been carried out. The assessment is based on the prioritizing system GISP (1996) and an assessment of the mobility and degradability of the substances.

The following principles are used in the screening of substances of relevance:

- The mobility of the substances is evaluated regarding solubility and affinity to particular matter (Log Kow). The evaluation of solubility and affinity is based on the principles in GISP.

Solubility		Log K_{ow}	
>1,000 mg/l	High	<3	High
1 - 1,000 mg/l	Medium	3 - 4	Medium
<1 mg/l	Low	>4	Low

- The assessment of degradability of the substances is based on the aerobic degradability of the substances in groundwater measured as the half time constant (T½). The degradability of the substances often changes with different redox-conditions. Aerobic degradability has been chosen for the assessment due to the fact that most shallow groundwaters are aerobic.

Aerobic degradability T½	
>60 days	Slow
15 - 60 days	Medium
<15 days	Fast

- Substances will be screened out if they are relatively immobile in the groundwater environment or if the substances are moderately mobile and highly degradable.

- Substances will be singled out if they are highly mobile or if the substances are moderately mobile and slowly degradable.

The assessment is given in table 3.4.

Table 3.4
Assessment of the ability (risk) of substances to travel from a soil and groundwater contamination to surface waters of the 41 substances under the Water Framework Directive based on their physical-chemical properties and degradability in soil. The assessment is furthermore based on the principles in GISP and the data in table 3.3.

Name of substance (No., WFD Annex X)	Risk of transport based on solubility		Risk of transport based on affinity to particular matter		Aerobic degradability in groundwater		Assessment (risk of transport of substance from soil and groundwater pollution to surface waters)
	(mg/L)	Score	Log Kow (Log Koc)	Score	(T½)	Score	
Alachlor	135-247	medium	2.5-3.6 (2-2.5)	medium/ high	<30 d	slow	**high risk**: (medium mobility, but slow degradability)
Aldrin#	0.018	low	6.5	low	>200 d	slow	low risk: (low mobility, but slow degradability)
Anthracene	0.032-0.085	low	4.2-4.6 (3.4-5.1)	low	?	slow	low risk: (low mobility, but slow degradability)
Atrazine	33-70	medium	2.2-2.5 (1.8-2.0)	high	60-150 d	slow	high risk: (high/medium mobility, slow degradability)
Benzene	1,800	high	1.6-2.2 (1.3-3.0)	high	30 d	medium	high risk: (high mobility, and medium degradability)
Pentabromo diphenylether	<0.001-0.0024	low	6.6-7.0 (> 4.7)	low	slow	slow	low risk: (low mobility, but slow degradability)
Cadmium + compounds	-	-	-	-	-	non	low risk: (low mobility, but no degradability)
Carbontetrachloride#	780	medium	2.64	high	-	non	high risk: (high/medium mobility, low degradability)
C10-13-chloroalkanes	practically insoluble	low	4.4-8.7 (2.3-2.7)	low	?	slow	low risk: (low mobility, but slow degradability)
Chlorfenvinphos	3-145	medium	3.9-3.2 (2.0-2.7)	medium	40 d	medium	medium risk: (medium mobility, and medium degradability)
Chlorpyrifos	0.36-1.1	medium	4.7 (4.7-5.3)	low	20-50 d	medium	low risk: (low/medium mobility, medium degradability)

Name of substance (No., WFD Annex X)	Risk of transport based on solubility		Risk of transport based on affinity to particular matter		Aerobic degradability in groundwater		Assessment (risk of transport of substance from soil and groundwater pollution to surface waters)
	(mg/L)	Score	Log Kow (Log Koc)	Score	(T½)	Score	
DDT#	0.0017	low	6.91	low	>200 d	slow	low risk: (low mobility, but slow degradability)
1,2-Dichloroethane	8,500-9,000	high	1.5-1.8 (1.0-2.3)	high	9 d	fast	high risk: (high mobility, but fast degradability)
Dichloromethane	13,700	high	1.3	high	7 d	fast	high risk: (high mobility, but fast degradability)
Dieldrin#	0.195	low	5.4	low	>200 d	slow	low risk: (low mobility, but slow degradability)
Di(2-ethylhexyl) phthalate	3-4.5	medium	4.9-7 (4.8-5.9)	low	<50 d	medium	low risk: (low mobility, and medium degradability)
Diuron	35-42	medium	2.7 (2.5)	high	>90 d	slow	high risk: (high mobility, and slow degradability)
Endosulfan	0.3-0.5	low	3.5	medium	?	slow	medium risk: (low/medium mobility, but slow degradability)
Endrin#	0.25	low	5.2	low	>200 d	slow	low risk: (low mobility, but slow degradability)
Fluoranthene	0.22-0.27	low	4.7	low	slow	slow	low risk: (low mobility, but slow degradability)
Hexachlorobenzene	0.005-0.006	low	3.0-6.9 3.5-5.3)	medium/ low	slow	slow	low risk: (low mobility, but slow degradability)
Hexachlorobutadiene	2-4	medium	4.8-4.9 4.0-4.5)	low	slow	slow	medium risk: (low/medium mobility, but slow degradability)
-HCH	7.8	medium	3.9 (2.8-3.8)	medium	several months	slow	medium risk: (low mobility, but slow degradability)
Isodrin#	0.2	low	5	low	?	?	low/medium risk: (low mobility, but unknown degradability)
Isoproturon	65	medium	2.3 (1.7-1.9)	high	12-29 d	medium	medium risk: (medium high mobility, medium degradability)
Lead + compounds	-	-	-	-	-	non	low risk: (low mobility, but no degradability)
Mercury + compounds	-	-	-	-	-	non	low risk: (low mobility, but no degradability)
Naphthalene	22-34	medium	3.0-3.7 (2.6-3.5)	medium	15-30 d	medium	medium risk: (medium mobility, medium degradability)
Nickel + compounds	-	low	-	-	-	non	low risk: (low mobility, but no degradability)

Name of substance (No., WFD Annex X)	Risk of transport based on solubility		Risk of transport based on affinity to particular matter		Aerobic degradability in groundwater		Assessment (risk of transport of substance from soil and groundwater pollution to surface waters)
	(mg/L)	Score	Log Kow (Log Koc)	Score	(T½)	Score	
Nonylphenol	3-6	medium	4.2-4.7 (3.6-3.7)	low	slow	slow	medium risk: (medium/low mobility, medium degradability)
Octylphenol	3-5	medium	5.3-5.5 (3.5-4.3)	low	inherent	slow	medium risk: (medium mobility, slow degradability)
Pentachlorobenzene	0.2-1.3	low	4.8-5.2 (3.5-5.1)	low	slow	slow	medium risk: (low mobility, but slow degradability)
Pentachlorophenol	14	medium	3.3	medium	?	slow	medium risk: (medium mobility, slow degradability)
PAH (data for BaP)	3.4x10-5-4.5 x10-5	low	6.0 (6.3-6.7)	low	slow	slow	low risk: (low mobility, but slow degradability)
Simazine	5.0-6.2	medium	2.1-2.4	high	50 d	medium	medium risk: (medium/high mobility, slow degradability)
Tetrachloroethylene#	260	medium	3.4	medium	slow	slow	medium risk: (medium mobility, slow degradability)
Tributyltin comp. (data for TBTO)	30	medium	3.2-3.8	medium	4-5 months	slow	medium risk: (medium mobility, slow degradability)
Trichlorobenzene	36-49	medium	3.9-4.2 (3.1)	medium	inherent	slow	medium risk: (medium mobility, and slow degradability)
Trichloroethylene#	1,180	high	2.42	high	slow	slow	high risk: (high mobility, but slow degradability)
Trichloromethane	7.5-9.3	medium	2.0 (2.3)	high	?	slow	high risk: (medium/jigh mobility, and slow degradability)
Trifluralin	0.18	low	5.3 (3.8-4.1)	low	3-18 weeks	medium/ slow	low risk: (low mobility, and medium/slow degradability)

Substances are screened out if they are relatively immobile in the groundwater environment or if the substances are moderately mobile and highly degradable.

The following 16 substances have been screened out:

- Aldrin
- Anthracene
- Pentabromo diphenylether
- Cadmium + compounds
- C10-13-chloroalkanes
- Chlorpyrifos
- DDT
- Dieldrin
- Di(2-ethylhexyl) phthalate
- Endrin

- Fluoranthene
- Lead + compounds
- Mercury + compounds
- Nickel + compounds
- PAH
- Trifluralin

An assessment of the risk of the substance to spread from a soil or groundwater contamination to surface waters has been supplemented with an assessment of the toxicity of the substances stated as the Environmental Quality Standard (EQS) of the substances. In the assessment, the following principles have been used:

- The principles of graduating the Groundwater Quality Criteria (GQC) from GISP is used on the EQS:

Toxicity	
EQS	Assessment
<1 µg/l	High
1 - 10 µg/l	Medium
>10 µg/l	Low

- The daughter Directive on priority substances includes two types of Environmental Quality Standards (EQS); for "Inland surface waters" and for "Other surface waters". A few substances have the lowest EQS value for "Other surface waters", but for most of the substances the EQSs are identical. Whether EQS are used for "Inland surface waters" or for "Other surface waters", the score for toxicity in Table 3.5 are the same.

The assessment is given in table 3.5 and is combined with the results from table 3.4 using the following principles:

- If both risk of spreading of substance from soil and groundwater to surface waters and high score on toxicity, the overall assessment is high risk for surface waters.

- If low risk on spreading of substance from soil and groundwater to surface waters the overall assessment is low risk independent of the toxicity.

Table 3.5
Assessment of the toxicity of the 41 substances under the Water Framework Directive based on GISP and Environmental Quality Standards (EQS) for inland surface waters. The toxicity assessment is combined with the risk assessment from table 3.4 regarding risk of spreading from soil and groundwater contamination to surface waters.

Name of substance (No., WFD Annex X)	Risk of transport of substance from soil and ground water pollution to surface waters	EQS µg/l	Toxicity Score	Assessment
Alachlor	high risk	0.3	high	High risk: (high mobility and highly toxic)
Aldrin#	low risk	0,01	low	Low risk: (low mobility)

Name of substance (No., WFD Annex X)	Risk of transport of substance from soil and ground water pollution to surface waters	EQS µg/l	Toxicity Score	Assessment
Anthracene	low risk	0.1	high	Low risk: (low mobility)
Atrazine	high risk	0.6	high	High risk: (high mobility and highly toxic)
Benzene	high risk	10	medium	Medium risk: (high mobility and medium toxicity)
Pentabromo diphenylether	low risk	0.0005	high	Low risk: (low mobility)
Cadmium + compounds	low risk	0.08	high	Low risk: (low mobility)
Carbontetrachloride#	high risk	12	low	Medium risk: (high mobility and low toxicity)
C10-13-chloroalkanes	low risk	0.4	high	Low risk: (low mobility)
Chlorfenvinphos	medium risk	0.1	high	Medium risk: (Medium mobility and highly toxic)
Chlorpyrifos	low risk	0.03	high	Low risk: (low mobility)
DDT#	low risk	0,002	high	Low risk: (low mobility)
1,2-Dichloroethane	high risk	10	low	Medium risk: (High mobility and low toxicity)
Dichloromethane	high risk	20	low	Medium risk: (High mobility and low toxicity)
Dieldrin#	low risk	0,01	high	Low risk: (low mobility)
Di(2-ethylhexyl) phthalate	low risk	1.3	medium	Low risk: (low mobility)
Diuron	high risk	0.2	high	High risk: (high mobility and highly toxic)
Endosulfan	medium risk	0.005	high	Medium risk: (medium mobility and highly toxic)
Endrin#	low risk	0,005	high	Low risk: (low mobility)
Fluoranthene	low risk	0.1	high	Low risk: (low mobility)
Hexachlorobenzene	low/medium risk	0.01	high	Medium risk: (low/medium mobility and highly toxic)
Hexachlorobutadiene	medium risk	0.1	high	Medium risk: (medium mobility and highly toxic)

Name of substance (No., WFD Annex X)	Risk of transport of substance from soil and ground water pollution to surface waters	EQS µg/l	Toxicity Score	Assessment
-HCH	medium risk	0.02	high	Medium risk: (medium mobility and highly toxic)
Isodrin#	low/medium risk	0.005	high	Medium risk: (low/medium mobility and highly toxic)
Isoproturon	medium risk	0.3	high	Medium risk: (medium mobility and highly toxic)
Lead + compounds	low risk	7.2	medium	Low risk: (low mobility)
Mercury + compounds	low risk	0.03	high	Low risk: (low mobility)
Naphthalene	medium risk	2.4	medium	Medium risk: (medium mobility and medium toxicity)
Nickel + compounds	low risk	20	low	Low risk: (low mobility)
Nonylphenol	medium risk	0.3	high	Medium risk: (medium mobility and highly toxic)
Octylphenol	medium risk	0.1	high	Medium risk: (medium mobility and highly toxic)
Pentachlorobenzene	medium risk	0.007	high	Medium risk: (medium mobility and highly toxic)
Pentachlorophenol	medium risk	0.4	high	Medium risk: (medium mobility and highly toxic)
PAH (data for BaP)	low risk	0.002-0.05	high	Low risk: (low mobility)
Simazine	medium risk	1	high	Medium risk: (medium mobility and highly toxic)
Tetrachloroethylene#	low/medium risk	10	medium	Medium risk: (low/medium mobility and medium toxic)
Tributyltin compounds (data for TBTO)	medium risk	0.0002	high	Medium risk: (medium mobility and highly toxic)
Trichlorobenzene	medium risk	0.4	high	Medium risk: (medium mobility and highly toxic)
Trichloroethylene#	high risk	10	medium	high risk: (high mobility and medium toxic)
Trichloromethane	high risk	2.5	medium	High risk: (medium/high mobility, and slow degradability)
Trifluralin	low risk	0.03	high	Low risk: (low mobility)

Substances will be singled out if they are 1) highly mobile or if the substances are moderately mobile and slowly degradable and 2) considered highly toxic. The following four substances are singled out:

- Alachlor
- Diuron
- Trichloromethane
- Atrazine
- Trichloroethylene

Please see table 3.10 for an overall assessment on transport and toxicity of the substances in the soil and groundwater environment.

3.3 Present administration and legislation

This section presents an assessment of which priority substances there may be a need for further action by Denmark. The assessment is based on the assumptions and delimitations mentioned in chapter 2.1.3.

3.3.1 Acts and orders

Soil and groundwater contamination and subsurface run-off of pollutants such as the priority substances to surface waters are regulated by several acts and ministerial orders. Regarding the objective of the project, the most relevant ones are:

- ENVIRONMENTAL PROTECTION ACT, part 4 includes administration of pollution of surface waters, both subsurface run-offs from contaminated sites and sewage waters.

- CONTAMINATED SOIL ACT, Act no. 370 of 2 June 1999, which does not specifically address surface waters. It states in part 1 that the act shall apply to soil which due to human impact may detrimentally affect the groundwater, human health, and the environment. Furthermore it states, that this act shall not apply to soil affected by the spreading of sludges, fertiliser, and pesticides, etc. for agricultural purposes.

These acts and orders constitute the basis for all environmental investigations and assessments carried out in Denmark. From the list above, it should be expected that inland surface waters, transitional waters and coastal waters would be fully and comprehensively included in all investigations and assessments except for those few exceptions mentioned above, such as pollution on agricultural areas. In practice, however, risk assessment of inland surface waters, transitional waters and coastal waters due to contaminated sites is only carried out in a limited number and are generally superficial/introductional.

In the following chapter, a brief overview on quality standards used on surface waters as well as a summary on environmental practice in Denmark regarding contaminated sites and surface waters is given.

3.3.2 Quality Guidelines

As mentioned in the previous chapter, several types of quality standards are used in risk assessing the effect of subsurface run-off from contaminated sites to surface waters such as inland surface waters, transitional waters and coastal waters.

- Groundwater quality standard (GQS): Standards defined by the DANISH EPM and valid for the primary reservoir. Groundwater quality standards for the secondary water body above the primary reservoir are typically defined as 10 times GQS based on expert knowledge.

- Environmental quality standard (EQS) listed in the proposal for Daughter Directive to the Water Framework Directive (WFD) addressing priority substances in the aquatic environment.

3.3.3 Practice on environmental investigations and assessments

As the acts and orders mentioned above leaves room for the Ministry of Environment or the counties to prioritise the effort, the reality is that the environmental investigations and risk assessments are focused primarily on drinking water interest. This means that in case of a polluted site, investigations and risk assessments towards surface waters are either not relevant or only carried out as a superficial view.

Common practice on environmental investigations and assessments regarding contaminated sites and surface waters are described below.

- Since the ratification of the Contaminated Soil Act, investigations have primarily been focusing on "Particularly valuable water abstraction areas" large enough to ensure the future supply of pure drinking water. Presently, these cover 34 % of the area of Denmark (DANISH EPM 2006), see figure 3.1. As a consequence, most investigations have been carried out at a distance from transitional waters and costal waters. This means that the knowledge on number of sites close to coastal and transitional waters contaminated with e.g. priority substances, is limited.

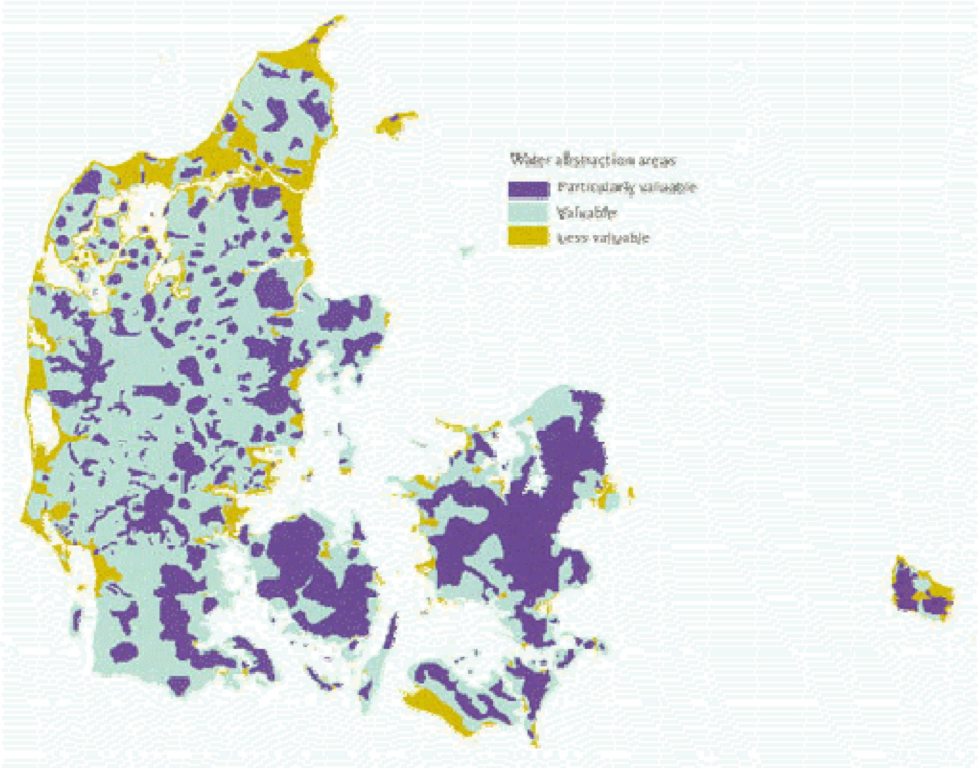

Figure 3.1:
Water abstraction areas. From Danish EPM's homepage (Danish EPA 2006).
Particularly valuable waters cover app. 34% of the area of Denmark, valuable waters cover app. 53%, and less valuable waters cover app. 13%..

- When planning an investigation on a potentially contaminated site, practice is that if use of a certain substance on the site has been limited compared to other relevant substances which are known to pose a risk of groundwater contamination, the lesser used substance will not necessarily be included in the investigation.

- If a substance - such as a metal or a PAH - is not expected to travel easily in the groundwater aquifer it will not be included in groundwater investigations.

- Basically, surface waters are not investigated unless the surface water is located right next to the contaminated site or if there is visual evidence of contamination in the surface waters such as free phase contamination.

- National surface water quality standards (WQS) are generally not included in the investigation or the risk assessment unless the site is located right next to costal waters. Even in cases where sites are located right next to surface waters, WQS have seldom been used. Instead GQS have been used.

- If inland surface waters or transitional waters are located closer than approx. 100 m from a contaminated site, risk assessment regarding these waters generally use groundwater quality standards GQS as bench markers for the risk.

- If inland surface waters or transitional waters are located more than approx 100 m from a contaminated site, risk assessment regarding these waters is not carried out.

3.3.4 Acts, orders and practice in relation to project objective

It is expected that, in general, the present administration of groundwater and soil contamination will handle contamination with any of the 41 substances under the Water Framework Directive. This is owing to the administrative practice that all types of contaminants can be included both in investigations and in remediation. However, experience on general practice shows that including a substance in an investigation is on the condition that the substance has been used or produced in a significant quantity and that it is supposed to constitute a substantial part of the contamination. In general, this means that including a priority substance in an investigation on a site, presupposes that the amount of the priority substance is several per cent of the total use of chemicals per year. As an example - atrazine will not automatically be included in the investigations if the yearly use is up to 100 kg atrazine compared to 10 tons of chlorinated solvents such as PCE (AVJ 1997).

As it can be seen from table 3.1, the use or production of several of the priority substances are less than a few tons per year. The production amount is probably distributed to 1-2 sites in Denmark, whereas the amount used in Denmark should be distributed to several sites, indicating that the amount used on a site can be very low. It is therefore expected that several of the priority substances will not automatically be included in investigation, as common practice is today, and thus potentially poses a risk of non-compliance with the EQSs. As the amount of substance used per year often is low, it is expected that any risk of non-compliance with EQSs will be very local.

3.3.5 Identification of substances of concern regarding quality standard scenarios

A comparison of GQS and the EQSs for Inland surface waters proposed by the Commission is listed in table 3.6. As mentioned earlier the EQS for "Other surface waters" are mostly the same as EQS for "Inland surface waters", but for some substances the EQS for "Other surface waters" are the lowest. However the conclusions based on table 3.6 will not be changed when using "Other surface waters" instead of "Inland surface waters". The following principles have been used:

- GQS/EQS ratios are calculated.

- If EQS is smaller than GQS (GQS/EQS >1), this indicates that there is a risk, and that a contamination with the priority substance is not detected through general administrative practice regarding soil and groundwater contamination.

- If EQS is larger or equal to than GQS, is it assumed that a contamination with the priority substance is detected and handled through general administrative practice.

Table 3.6
A comparison of GQS (Ground water quality standard) and EQS (Environmental quality standard for indland surface waters) proposed by the Commission.

Name of substance (No., WFD Annex X)	GQS µg/L	EQS µg/L	GQS/EQS
Alachlor	0.1	0.3	0.333
Anthracene	0.2	0.1	2.0
Atrazine	0.1	0.6	0.167
Benzene	1	10/8	0.1
Pentabromo diphenylether		0.0005/ 0.0002	0.0
Cadmium + compounds	0.5	0.08/0.2	6.3
C_{10-13}-chloroalkanes		0.4	0.0
Chlorfenvinphos	0.1	0.1	1.0
Chlorpyrifos	0.1	0.03	3.3
1,2-Dichloroethane	1	10	0.1
Dichloromethane	8	20	0.4
Di(2-ethylhexyl) phthalate	1	1.3	0.8
Diuron	0.1	0.2	0.5
Endosulfan	0.1	0.005/ 0.0005	20
Fluoranthene	0.2	0.1	2.0
Hexachlorobenzene	0.1	0.01	10
Hexachlorobutadiene		0.1	0.0
γ-HCH	0.1	0.02/ 0.002	5.0
Isoproturon	0.1	0.3	0.3
Lead + compounds	1	7.2	0.1
Mercury + compounds	0.1	0.03	3.3
Naphthalene	1	2.4/1.2	0.4
Nickel + compounds	10	20	0.5
Nonylphenol	20	0.3	67
Octylphenol	20	0.1/0.01	200
Pentachlorobenzene		0.007 0.0007	
Pentachlorophenol	0.15	0.4	0.4
PAH (data for BaP)	0.2	0.002	100
Simazine	0,1	1	0,1
Tributyltin compounds (data for TBTO)		0.0002	
Trichlorobenzene		0.4	
Trichloromethane	1	2.5	0.25
Trifluralin		0.03	

Name of substance (No., WFD Annex X)	GQS	EQS	GQS/EQS
	µg/L	µg/L	
DDT	0.1	0.025	0.025
The "drins" (aldrin, dieldrin, endrin and isodrin)	0.03	0.01/ 0.005	3.0
Carbontetrachloride	1	12	0.083
Tetrachloroethylene	1	10	0.1
Trichloroethylene	1	10	0.1

It appears from table 3.6 that 18 out of 41 of the substances have EQS larger than GQS. It is assessed that soil and groundwater contamination with these substances will be managed through the existing administrative system, and ensuring compliance with the EQSs will therefore not require further action to be taken by Denmark. However, it should be noted that sites located in vulnerable areas are usually prioritized higher than other sites in the existing administrative system. The substances are:

GQS/EQS smaller than 1:

- Alachlor
- Atrazine
- Benzene
- Chlorfenvinphos
- 1,2-Dichloroethane
- Dichloromethane
- Di(2-ethylhexyl) phthalate
- Diuron
- Isoproturon
- Lead + compounds
- Naphthalene
- Nickel + compounds
- Pentachlorophenol
- Simazine
- Trichlormethane
- Carbontetrachloride
- Tetrachloroethylene
- Trichloroethylene

For some of the priority substances is it assessed, that since the EQS is smaller than GQS, there is a risk that contamination with the priority substances will not be detected in the investigation, as they are managed under the present administrative system. This indicates that this does not exclude the possibility and need for further action to be taken in Denmark to ensure compliance with the EQSs. The substances are:

GQS/EQS larger than 1:

- Anthracene
- Cadmium + compounds
- Chlorpyrifos
- Endosulfan
- Fluoranthene
- Hexachlorobenzene
- HCH/lindane
- Mercury + compounds
- Nonylphenol
- Octylphenol
- PAH (benzo[a]pyren)
- PAH (benzo[b + k]fluoranthen)
- PAH (benzo[g,h,i]perylen +indeno[1,2,3-cd]pyren)
- Trichloromethane
- Trifluralin
- DDT
- Cyclodiene pesticides:
  (aldrin, dieldrin, endrin, isodrin)

No Danish groundwater quality standards (GQS) have been established for the substances:

- Pentabromo diphenylether
- Hexachlorobutadiene
- Tributyltin compounds
- C10-13-chloroalkanes
- Pentachlorobenzene
- Trichlorobenzene

3.3.6 Substances of concern regarding practice on analysis

Based on an interview with Nis Hansen, Eurofins Danmark A/S, it is assessed that the major part of groundwater analyses are carried out in the framework of:

1. Water supply and unfiltered water monitoring
2. NOVANA groundwater monitoring
3. Groundwater investigations in connection with contaminated sites.

Comparison of analysis programmes for 1) and 2) is found in table 3.7. From this it appears that several priority substances are not part of the analysis programmes.

Table 3.7
Comparison of analysis programmes for 1) Water supply and unfiltered water monitoring and 2) NOVANA groundwater monitoring. If the substance is included in surface waters monitoring and/or if it is common practice to include the substance in groundwater investigations in connection with contaminated sites, it is noted in the comments

Name of substance (No., WFD Annex X)	Water supply monitoring	NOVANA groundwater monitoring	Comments
Alachlor	Yes	No	
Anthracene	No	No	Also included in surface water monitoring
Atrazine	Yes	Yes	Included in surface water monitoring
Benzene	Yes	Yes	
Pentabromo diphenylether	No	No	
Cadmium + compounds	Yes	Yes	Included in surface water monitoring
$C_{10\text{-}13}$-chloroalkanes	No	No	
Chlorfenvinphos	Yes	No	
Chlorpyrifos	Yes	No	
1,2-Dichloroethane	Yes	No	Included in groundwater investigations in connection with contaminated sites
Dichloromethane	No	No	Included in groundwater investigations in connection with contaminated sites
Di(2-ethylhexyl) phthalate	No	Yes	Included in groundwater investigations in connection with contaminated sites. Also included in surface water monitoring
Diuron	Yes	Yes	Included in surface water monitoring
Endosulfan	Yes	No	
Fluoranthene	Yes	No	Included in surface water monitoring
Hexachlorobenzene	No	No	Included in groundwater investigations in connection with contaminated sites.
Hexachlorobutadiene	No	No	Included in groundwater investigations in connection with contaminated sites.
γ-HCH	Yes	No	
Isoproturon	Yes	Yes	Included in surface water monitoring

Name of substance (No., WFD Annex X)	Water supply monitoring	NOVANA groundwater monitoring	Comments
Lead + compounds	Yes	Yes	Included in surface water monitoring
Mercury + compounds	Yes	No	Included in surface water monitoring
Naphthalene	Yes	Yes	Included in groundwater investigations in connection with contaminated sites. Also included in surface water monitoring
Nickel + compounds	Yes	Yes	
Nonylphenol	No	Yes	Included in groundwater investigations in connection with contaminated sites. Also included in surface water monitoring
Octylphenol	No	No	
Pentachlorobenzene	No	No	Included in groundwater investigations in connection with contaminated sites.
Pentachlorophenol	No	Yes	Included in groundwater investigations in connection with contaminated sites.
PAH	Yes	No	Included in surface water monitoring
Simazine	Yes	Yes	Also included in surface water monitoring
Tributyltin compounds (data for TBTO)	No	No	Included in coastal waters monitoring
Trichlorobenzene	No	No	Included in coastal waters monitoring
Trichloromethane	Yes	Yes	Included in groundwater investigations in connection with contaminated sites.
Trifluralin	Yes	No	

Name of substance (No., WFD Annex X)	Water supply monitoring	NOVANA groundwater monitoring	Comments
DDT	Yes	Yes	
Aldrin Dieldrin "Eldrin" "Isodrin"	No	Yes	Also included in surface water monitoring
Carbontetrachloride	Yes	Yes	Included in surface water monitoring
Tetrachloroethylene	Yes	Yes	
Trichloroethylene	No	Yes	

Eurofins Danmark A/S informs that at present, a few of the substances have no standardized method of analysis in Denmark.

Regarding 3) groundwater analyses in connection with contaminated sites, it is the impression of both Eurofins Danmark A/S and COWI that a large number of priority substances never or rarely form part of groundwater analyses. This applies to, among others, PAH's and heavy metals. This situation is assessed due to the fact that, generally, groundwater analyses are not carried out for substances with low mobility in the groundwater zone and that the other priority substances are not analysed unless they are assumed to constitute a significant part of the source contamination. This presupposes, other things being equal, that information on whether these substances have been used to a certain extent on the property, are available.

3.4 Types of contaminated sites of concern

Contamination of soil and ground water and run off of pollutants to surface waters can happen in many ways, in many places and can be distributed in many ways. Typical conceptual models for contamination and spreading of pollutants are described by, among others, Danish EPA (1996).

Please see chapter 2 regarding which type of sites and ways of dispersal are included in the project.

In this chapter, only properties of the site such as geology, hydrogeology, size of point source and distance to surface waters are included. Physical-chemical properties are only included in relation to an estimate of the initial concentration leaving the point source.

Contaminated water leaching from point sources is subjected to dilution when it flows towards the surface waters. The resulting concentration of contaminants in the surface waters is dependent on many parameters, see box 3.1, of which geology, recharge and travel distance are among the most important.

Box 3.1: Factors defining the concentration of contaminants leaching from a point source to surface waters

- Horizontal size of point source
- Concentration of contaminants in water leaching from point source
- Water permeability in soil, depending on e.g. geology and porosity
- Infiltrating precipitation in the area, depending on among other things the paved surface in the area
- Distance from point source to aquifer (secondary or primary groundwater body)
- Potential gradient in the aquifer defining the transport from the point source to the surface water
- Distance from point source to surface water
- Connection between aquifer and surface water
- Initial dilution of contaminated water leaching in the aquifer when leaching into the surface water

To make the assessments more functional, rough estimates of dilution factors in the aquifer in different scenarios are calculated in section 3.4.1. Dilution factors are here the reduction of the initial concentration at the point source to the edge of the surface water. In section 3.5, initial dilution of the contaminated groundwater in the surface water will be addressed.

As the framework of this study only permits an introductory approach, a simplified system with several assumptions has been chosen. When choosing the simplified system, the starting point has been to find general systems, which can describe a large part of Denmark and therefore gives a realistic indication of dilution factors.

A conceptual model for transport of contaminants from a contaminated site to surface waters appears from figure 3.2.

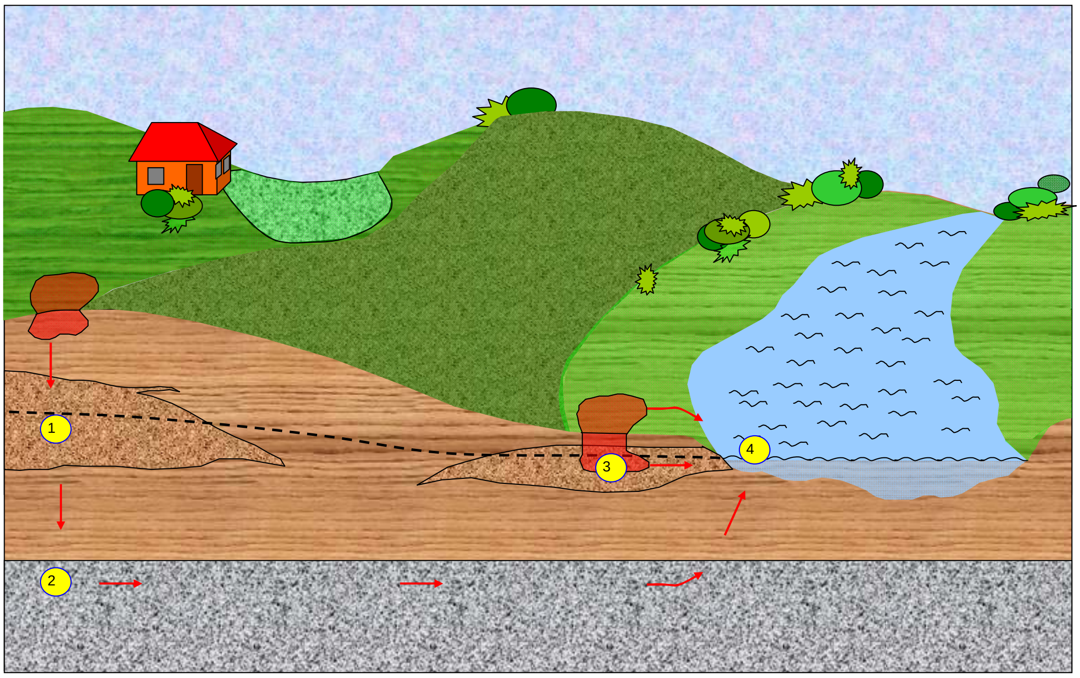

Figure 3.2:
Conceptual model for the dilution of contamination from point source to edge of surface water and initial dilution in the surface water. Abbreviations in the figure are described in the text in section 3.4.1.

3.4.1 Dilution of contaminated water leaching from point sources

Rough estimates of dilution factors in different scenarios can be deducted from mass balance equations. The approach and resulting dilution factors are described below.

The mass balance equation is defined for a given area and can be described by fluxes entering and leaving the specified area combined with the concentration of the contaminant in these fluxes. The concentration entering the area C_{in} is the concentration in the leaching water from the point source. The concentration leaving the area and entering the recipient is called C_{out}. The water flux out of the area is the sum of water fluxes entering the area, assuming a negligible storage of water in the area. Finally, the flux entering the area is the sum of three different fluxes; the flux leaching from the point source q_{cont}, the recharge $q_{recharge}$ (infiltrating precipitation) and the groundwater flux q_{gw} entering the area upstream of the point source. The mass balance equation is then written as:

$$V_{cont} \cdot C_{in} + V_{recharge} \cdot 0 + V_{gw} \cdot 0 = (V_{cont} + V_{recharge} + V_{gw}) \cdot C_{out}$$

where generally $V = q \cdot A$. The equation implies that there is no contamination of the groundwater and the infiltrating precipitation. The dilution factor F is then described by:

$$F = C_{in} / C_{out} = (V_{cont} + V_{recharge} + V_{gw}) / V_{cont}$$

The volumes are described as the fluxes multiplied with the contributing area for the individual flux:

$$F = (A_{source} \cdot q_{recharge} + W_{source} \cdot L_T \cdot q_{recharge} + W_{source} \cdot D_{mixing} \cdot q_{gw}) / A_{source} \cdot q_{recharge}$$

where the area of the point source is expressed by a length L_{source} and a width W_{source}. The travel distance from the point source to the recipient is called L_T and the mixing depth D_{mixing}.

The three terms in the equation depend on many different parameters and they contribute differently in different scenarios. According to the conceptual figure there are only two distinct scenarios depending on the pathway to the recipient. It is therefore assumed that lateral flow and transport through till and clayey soil is negligible compared to flow in higher permeable soils such as chalk and sand.

One scenario reflects a point source close to a receiving surface water body, where the contaminated water leaches to a secondary groundwater body. This body is in hydraulic contact with the receiving surface water body and has a limited and unknown size upstream of the point source. Thus, the dilution from the groundwater can be small and must be omitted from the mass balance equation when the contaminated water travels to the recipient in a secondary groundwater body. The dilution factor in a secondary water body will then only depend on the travel distance.

In the other scenario, the contaminated water has reached the primary groundwater body. In a sandy soil, it is assumed that there are no secondary groundwater bodies above the primary reservoir. In Denmark, this applies to the area west of "hovedstilstandslinien"[1]. In the rest of the country, local secondary groundwater bodies are often found above the primary groundwater body. The contaminated water leaches to both water bodies, but is mainly transported to the surface waters through the primary reservoir. The primary groundwater body is mainly sandy layers, but it some areas the primary reservoir consists of fractured chalk.

In order to quantify every term in the equation, the following assumptions are made:

- The recharge $q_{recharge}$ (L/T) is the same whether it is through the soil outside the point source or it describes the leaching from the point source. Thus, there is no pavement inside the area of interest.

- The transverse dispersion are neglected in the lateral direction

- The transverse dispersion in the vertical direction is assumed to result in a mixing depth of 0.25 m below the point source. The depth of the mixing zone increases with the travel distance, and it is assumed that the depth of the mixing zone is 10 times greater than the initial depth at a travel distance of 100 m. These assumptions are based on experience from the field and from calculations in JAGG.

- The area of the point source A_{source} is described by a length L_{source} and a width W_{source}. Because the transverse dispersion in the lateral direction is neglected, the water balance is reduced to a two dimensional system, the width can remain unknown. The length of the point source L_{source} is assumed to be 10 m.

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[1] main ice limit

- The groundwater flux into the system is described by Darcy's equation, thus the flux is expressed by the potential gradient over the travel distance multiplied by the hydraulic conductivity of the soil.

- The thickness of the reservoir is greater than the mixing depth for all travel distances.

- It is assumed that within the first 100 m from the point source, the primary part of the transportation of contaminants happens in the secondary groundwater body. Beyond 100 m from the point source the major part of the transportation of contaminant happens in the primary groundwater body.

- If there is a secondary groundwater body above the primary reservoir, the concentration entering the primary reservoir is reduced by a factor 10.

Based on these assumptions, dilution factors can be estimated for different geographical and geological settings. The involved parameters vary across the country and with the hydrogeology present at the actual site of interest. The parameters are, however, assumed to vary within the intervals listed in table 3.8 below.

Table 3.8:
Parameter values used in the water balance equation

Infiltration	Potential gradient	Hydraulic conductivity sand	Hydraulic conductivity chalk
0.5-2 mm/d	1-10 ‰	10^{-3} - 10^{-5} m/s	10^{-4} - 10^{-6} m/s

By combining the parameters, a dilution factor F can be estimated. The dilution factor depends on the travel distance from the point source to the recipient and the four different scenarios based on variation in the pathway and in the geology.

Table 3.9:
Estimated dilution factors F

Locations	West of "Hovedstilstandslinien"	Sporadic areas		East of "Hovedstilstandslinien"	
Geology	Sandy soil with transport in a primary water body	Chalk with transport in a secondary water body	Chalk with transport in a primary water body consisting of chalk	Till and clayey soils with transport in secondary water body	Till and clayey soils with secondary water bodies present, but with transport in underlying primary water body
Estimated part of Denmark	23 %	5 %		72 %	
Travel distance (m)	Dilution factors F				
10	2-20	2-4		2	
50	5-60	5-10		5	
100	10-100	10-20		10	
200	20-200		200-400		200-2,000
500	50-500		500-1,000		500-50,000
1000	100-1,000		1,000-2,000		1,000-10,000

It can be seen from table 3.9 that within the first approx. 100 m from the point source, the dilution factor is often no more than 20.

At a distance of more than 100 m from the point source, the dilution factor is typically more than 100 and more than 1,000 at a distance of more than 1,000 m.

3.4.2 Dilution trough drainage systems

As stated in chapter 2, the focus in this report is on leaching of contaminated groundwater from a point source to surface waters via primary or secondary groundwater bodies. It has been chosen not to include leaching via drainage systems, that is drainage systems leading directly to surface waters such as land-drain, perimeter drain etc. The reason for this is further explained in this section.

Leaching of contaminated water via draining systems can potentially be dominating in areas near surface waters. As it will appear from section 4.1.1, areas near to surface waters are defined as areas closer than 100 m to inland surface waters and closer than 500 m from coastal waters. In areas close to surface waters, the leaching of contaminated water primarily happens through the secondary groundwater bodies, where the dilution generally will be relatively limited.

If the leaching happens through drains, the dilution in the groundwater bodies will be marginalized. A certain dilution is expected in the drainage system as the draining effect often covers an area which is larger than the area of the point source. The expected dilution in the drainage system is assessed to be of the same magnitude as the dilution in the secondary groundwater body.

In traditional cases of soil and groundwater pollution, leaching through drainage systems is generally considered to be, environmentally speaking, a more vulnerable way of spreading contaminants. This is due to the fact that the amount of sorption and degradation of contaminants is supposed to be higher in the groundwater body than in the drainage system. This is again based on comparison of retention time in drainage systems and groundwater bodies respectively.

In this report, it has been chosen to examine leaching of contaminants as an overall view on conservative dilution. The effect of sorption and degradation of contaminants is only included in the assessment for relatively immobile substances, and substances that are highly degradable and moderately mobile. These substances are considered to be of low risk regarding groundwater transportation, but also transportation via drainage systems will be limited for substances with these characteristic. The assessment of the leaching via drainage systems and via secondary groundwater bodies is therefore almost identical.

On this background, it has been decided not to examine leaching through drainage systems more detailed, but to assume that leaching through drainage systems regarding the effect on the surface waters can be covered by the description of dilution in the groundwater bodies near surface waters.

3.5 Substances constituting a risk of exceeding EQSs

Based on the result in section 3.1-3.4, an overall assessment of substances constituting a risk of exceeding the EQSs is carried out.

3.5.1 Relevant substances

For every substance, an assessment of whether the substance is relevant regarding the objective of this study is carried out. Substances are screened out if they are either not used or produced in Denmark, if the physical/chemical characteristics will not lead to spreading to the surface water or if the EQS is larger than the GQS. In table 3.10 below, an assessment of the substances is summarized.

As shown in table 3.10, five substances have not been screened out. These are: HCH, nonylphenol, octylphenol, tributyltin compounds and trichlorobenzene.

The five mentioned substances will be examined in the following chapters. In table 3.12, an assessment of the typical types of contaminated sites for the five substances is listed.

Table 3.10
Assessment of the 41 substances under the Water Framework Directive based on the principles described in chapter 3. 1: As endosulfan has only been used in very small amounts (2 tons/year), presumably on very few locations and has only been produced at one site in Denmark, it has been screened out.

Name of substance (No., WFD Annex X)	Overall evaluation	Risk based on use and production (see table 3.1)	Risk of point source of pesticides (see table 3.2)	Risk based on physical and chemical properties and toxicity (see table 3.4)	Risk based on comparison of GQS and EQSs (see table 3.6)
Alachlor	Screened out		Not relevant		Not relevant
Aldrin#	Screened out	Use less than 1 t/y		Not relevant	
Anthracene	Screened out[3]			Not relevant	
Atrazine	Screened out		Not relevant		Not relevant
Benzene	Screened out				Not relevant
Pentabromo diphenylether	Screened out[2]			Not relevant	
Cadmium + compounds	Screened out[3]			Not relevant	
Carbontetrachloride #	Screened out				Not relevant
C10-13-chloroalkanes	Screened out[3]	Use less than 1 t/y		Not relevant	
Chlorfenvinphos	Screened out	Use less than 1 t/y			Not relevant
Chlorpyrifos	Screened out	Use less than 1 t/y		Not relevant	
DDT#	Screened out[3]			Not relevant	
1,2-Dichloroethane	Screened out	Use less than 1 t/y			Not relevant
Dichloromethane	Screened out				Not relevant
Dieldrin#	Screened out[3]	Use less than 1 t/y		Not relevant	
Di(2-ethylhexyl) phthalate	Screened out			Not relevant	Not relevant
Diuron	Screened out				Not relevant
Endosulfan	Screened out[1]	Use less than 2 t/y			
Endrin#	Screened out	Use less than 1 t/y		Not relevant	
Fluoranthene	Screened out			Not relevant	
Hexachlorobenzene	Screened out[2]	Not used	Not relevant		
Hexachlorobutadiene	Screened out[2]	Not used			
-HCH					
Isodrin#	Screened out[2]	Not used			
Isoproturon	Screened out		Not relevant		Not relevant
Lead + compounds	Screened out			Not relevant	Not relevant
Mercury + compounds	Screened out[3]	Use less than 2 t/y2		Not relevant	
Naphthalene	Screened out				Not relevant
Nickel + compounds	Screened out			Not relevant	Not relevant
Nonylphenol					
Octylphenol					

Name of substance (No., WFD Annex X)	Overall evaluation	Risk based on use and production (see table 3.1)	Risk of point source of pesticides (see table 3.2)	Risk based on physical and chemical properties and toxicity (see table 3.4)	Risk based on comparison of GQS and EQSs (see table 3.6)
Pentachlorobenzene	Screened out[2]	Not used			
Pentachlorophenol	Screened out				Not relevant
PAH (data for BaP)	Screened out[3]			Not relevant	
Simazine	Screened out				Not relevant
Tetrachloroethylene#	Screened out				Not relevant
Tributyltin compounds (data for TBTO)					
Trichlorobenzene					
Trichloroethylene#	Screened out				Not relevant
Trichloromethane	Screened out				Not relevant
Trifluralin	Screened out			Not relevant	

[2]:The hazardous substances hexachlorobenzene and hexachlorobutadiene are screened out because they have not been used in Denmark. he hazardous substances hexachlorobenzene and hexachlorobutadiene are screened out because they have not been used in Denmark.
[3] Priority Hazardous substances antracene, pentabromo diphenylether, cadmium and compounds, mercury and compounds pentachlorobenzene and PAH have been screened out based on their physical and chemical properties.

As shown in table 3.10, 9 substances were screened out solely based on comparison of GQS and EQS. However for sites located in some areas without groundwater resources (less vulnerable areas), the GQS are not necessary used in risk management. These less vulnerable areas are mostly located near or in coastal areas. Therefore water quality standards (WQS, from Statutory Order 921) have often been used instead of GQS.

Table 3.11 gives a comparison of WQS and EQS for the 9 substances. For most of the substances the EQS is identical with or larger than the WQS. Only pentachlorophenol and trichloromethane have an EQS smaller than the WQS. Therefore these two substances will be examined in the following chapters along with five that were singled out (see table 3.10).

Table 3.11:
Estimated need for dilution for the 9 substances that were screened out solely based on comparison of WQS and EQS .

Substance	WQS µg/L	EQS µg/L	WQS/EQS
Benzene	2	10	0.2
Dichloromethane	10	20	0.5
Diuron	-	0.2	-
Naphthalene	1	2.4	0.42
Pentachlorophenol	1	0.4	2.5
Simazine	1	1	1
Tetrachloroethylene	10	10	1
Trichloroethylene	10	10	1
Trichloromethane	10	2.5	4

3.5.2 Need for dilution to comply with the EQS

When looking at the spreading of contaminants in the groundwater body, the starting point is the concentration in the leaching water from the point source C_{in}. As free phase pollution is marginalized in this study the maximum concentration of interest is the solubility. Generally, the initial concentration in the point source does not reach the solubility. Based on the experience in COWI, it is estimated that the maximum concentration in the leaching water from the point source as a maximum is approximately 75 % of the solubility and. More realistic is C_{in} 10 % of the solubility, this value will be used unless other experience is inconsistent with this assumption.

In table 3.12 estimations on the leaching concentration Cin are summarized together with an estimate on the need for dilution, as both dilution in the groundwater body and initial dilution in the surface water are necessary to ensure compliance with the EQS.

Table 3.12:
Estimated need for dilution for the five substances that were singled out and the two additional substances (pentachlorophenol and trichloromethane, see section 3.5.1). The estimated leaching concentration Cin from point sources is compared with the EQS1.

Substance	Solubility mg/L	C_{in}^{1} µg/L	EQS µg/L	Need for dilution C_{in}/EQS (approx.)
HCH/lindane	7.8	780	0.02	39,000
Nonylphenol	*3-6*	*600*	0.3	*2,000*
Octylphenol	*3-5*	*500*	0.1	*5,000*
Tributyltin compounds	*30*	*3,000*	0.0002	*15,000,000*
Trichlorobenzene	*36-49*	*4,900*	0.4	*12,000*
Pentachlorophenol	*14*	*1,400*	*0.4*	*3,500*
Trichloromethane	*7.5-9.3*	*930*	2.5	*372*

1: Cin is 10 % of the solubility.

It is seen from table 3.12, that the need for dilutions to comply with the EQSs is high, especially, for HCH, tributyltin compounds and trichlorobenzen. The results will be discussed further in the next chapter.

3.6 Phase out of hazardous priority substances

In section 3.5.1, an assessment of all 41 substances including the 13 hazardous priority substances (PHSs) has been carried out. Substances are screened out if they are either not used or produced in Denmark, if the physical/chemical characteristics will not lead to spreading to the surface water or if the EQS is larger than the GQS. The assessment is summarized in table 3.10.

An assessment of the priority hazardous substances (PHS) also needs to be carried out regarding the cessation of losses to the environment. The assessment is almost the same as in chapter 3.5.1. Substances are screened out if they are either not used or produced in Denmark, or if the physical/chemical characteristics implies that spreading to surface waters will not take place.

As seen in table 3.10, hexachlorobenzene and hexachlorobutadiene are screened out because they have not been used in Denmark. As endosulfan has only been used in very small amounts (2 tons/year), presumably at very few locations, and has only been produced at one site in Denmark, it has also been screened out. Anthracene, pentabromodiphenylether, cadmium and compounds, mercury and compounds pentachlorobenzene and PAH are screened out based on their physical and chemical properties. It is believed that none of these substances will be appear in surface waters due to losses from contaminated soil or groundwater.

4 Step 2 - Number of sites in Denmark constituting a risk

4.1 Geographic distribution of areas near surface waters

Facts about Danish area and surface water are shown in box 4.1.

Denmark has a total area of 4,308,000 Ha equivalent to 43,080 km²
The farmed land covered approximately 65 %, forest, marsh land, dunes etc. 23 %, urban areas approximately 4 % and built-up areas and road etc. outside the urban areas approximately 8 %[1].
The area west of 'hovedstilstandslinien' constitutes approximately 23 % (equivalent to the area of Ribe County, Ringkøbing County and half of Sønderjyllands County)[2].
In 1982, Denmark had approximately 30,000 km water courses[1]. Public controlled/re-aligned water courses constitute approximately 22,300 km equivalent to approximately 75 %. Water courses protected by the Nature protection Act § 3, have a total length of 20,300 km equivalent to approximately 65 %.
Water courses west of 'hovedstilstandslinien' constitute approximately 7,100 km equivalent to approximately 23.5 %.
At a survey in the 1980'ies, Denmark had 7,200 lakes with a total area of 470 km² 1. The average size of a lake is thus 0.07 km².
The total Danish coast line is approximately 7,300 km.

Text box 4.1
Facts about Danish area and surface waters. Data have been collected from [1]: Danish EPA (1994) and [2]: DST (2006).

As shown in section 3.4, Denmark is divided into three parts, geologically viewed:

- West of 'hovedstilstandslinien'
- Areas with high situated limestone
- Remaining areas east of 'hovedstilstandslinien'.

The area west of 'hovedstilstandslinien' is characterised by consisting mainly of glacial water deposits.

The area constitutes, cf. text box 4.1, approximately 23 % of the total Danish area. Text box 4.1 also states that the total length of water courses west of 'hovedstilstandslinien' is also approximately 23 %. On the basis of this, it is assumed that water courses, lakes and coastal areas are evenly distributed. The area east of 'hovedstilstandslinien' is characterised by mainly being composed of moraine/till sediments. The area constitutes the remaining part of Denmark i.e., approximately 72 % of the total Danish area.

4.1.1 Areas close to surface waters

Areas close to surface waters are in this report defined as areas closer than 100 m to inland waters and closer than 500 m to costal waters. The total area close to surface waters can therefore be calculated as follows:

The areas close to water courses are approximately 4,000 km². The total length of water courses included in the nature protection act is approximately 20,000 km². On both sides of the water course, is a border of 100 m.

$$Areal_{Waterc.} = (20.000km \cdot 100m) \cdot 2 = 4{,}000km^2$$

The areas close to lakes are approximately 2,250 km². If it is presumed that a lake has the shape of an ellipse where the shortest radius is 100 m and the longest radius is 200 m, then the area of the 100 m wide border near the lake can be calculated as an ellipse with the shortest radius being 300 m and the longest 400 m, minus the area of the lake of 0.07 km².

$$Areal_{Lakes} = (\pi \cdot (100m + 2 \cdot 100m) \cdot (200m + 2 \cdot 100m) - 0{,}07) * 7.200 = 0{,}3km^2 \cdot 7{,}200 = 2{,}250km^2$$

The areas close to the coastline can be calculated as the total coastline (7,300 km) multiplied by 500 m, which is equivalent to 3,650 km².

The total of the areas close to the surface waters can be calculated as approximately 9,900 km², which is equivalent to approximately 23 % of the total Danish area.

4.2 Geographical distribution of sites

The geographical distribution of contaminated sites (V2) and potentially contaminated sites (V1) in Denmark depends on where the activities leading to the contamination or potential contamination have taken place. Furthermore our present knowledge depends just as much on, where and how we trace these sites. In Denmark, the regional authorities started tracing contaminated sites in the beginning of the 1980'ies. Then, it was primarily waste dumps, gasworks and larger industrial sites that was mapped by the authorities. The mapping was thus carried out according the type of activity and not the geographical location of the site. In the 1990'ies, the mapping mostly included smaller companies. The authorities started to select and prioritize geographical areas inside which, the tracing was carried out. The selection of the geographical areas was primarily founded in a wish to protect the groundwater resource, and the last approximately 10 years, the authorities have thus primarily traced sites which are critical in relation to the groundwater resource, and where the substances used are assessed to constitute a hazard to the groundwater resource, se also section 3.3.3-3.3.4.

The geographical distribution of the sites which the authorities at present (2006), know about, are not representative in relation to an assessment of where the total number of sites are located. Areas which are critical in relation to the groundwater resource will be over-represented, while other areas e.g. coastal areas will be represented to a lesser degree.

Figure 4.1 shows the geographical distribution of mapped contaminated sites in 1997 (DMU 2006). It is assessed that the distribution of sites in 1997 gives a better estimate of the geographical distribution of the total number of sites, as the intensive tracing of sites in the groundwater sensitive areas only to a limited extent is included in the 1997 statement.

As shown in figure 4.1, the sites are evenly distributed across the country, with a tendency of the largest number of sites being in densely populated areas. This is both due to the fact these areas have most of the contaminating activities and also, that in these areas more building and construction activities are carried out, with a major probability of hitting the contamination. The assessment of the contaminated sites location in relation to surface waters is, however, independent of these circumstances.

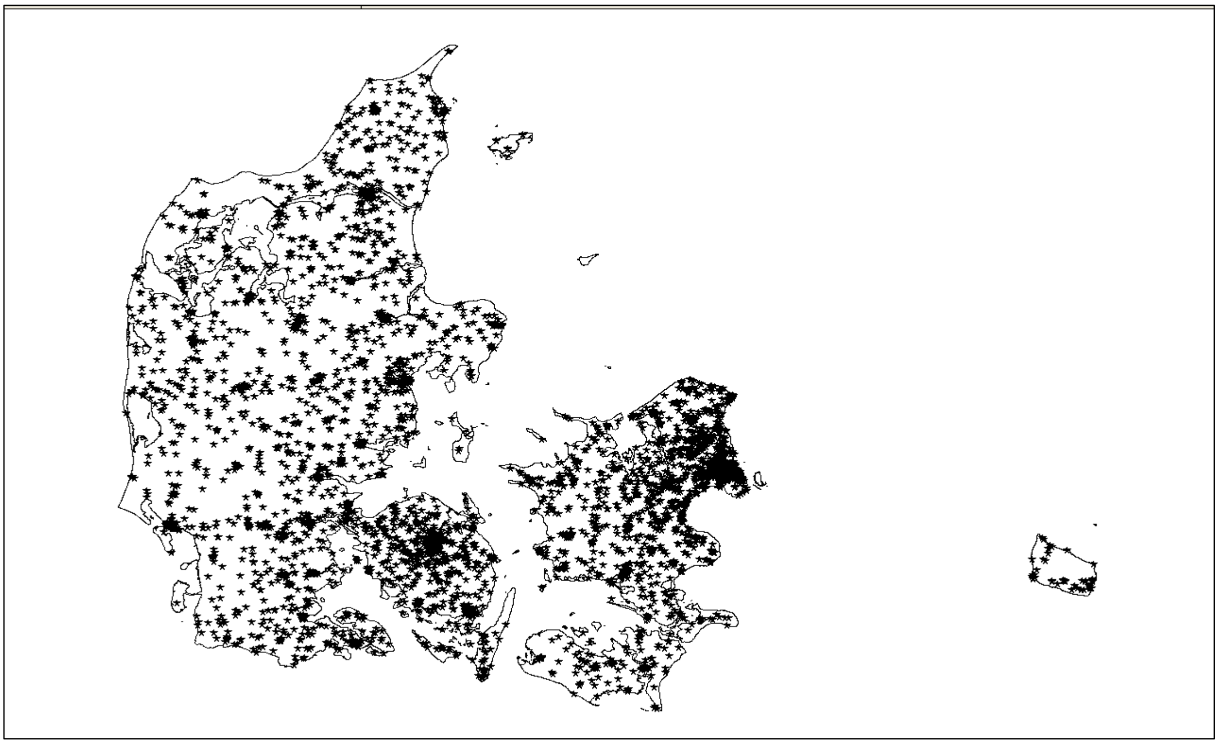

Figure 4.1
Geographic distribution of sites in 1997 (DMU 2006)

In 1997, the regional authorities had mapped approximately 4,677 contaminated sites. In connection with reporting to the Danish EPA, the regional authorities have assessed that approximately 750 sites or approximately 16 % pose a potential contamination risk in relation to surface waters. The total number of contaminated sites located close to surface waters is probably higher, as sites located close to surface waters contaminated with immobile substances are not included in the 750 sites.

As stated in the previous section, it was assessed that areas close to surface waters constitutes approximately 23 % of the total area of Denmark. This should be compared to the assessment that approximately 16 % of the mapped sites pose a threat to surface waters, and that the number of contaminated sites close to surface waters is probably higher. On this basis, it is assessed to be acceptable to regard the contaminated sites as evenly distributed in relation to surface waters, and that approximately 23 % of the sites are located close to surface waters.

4.3 Number of major sites

Based on the annual reports to Danish EPA concerning major contaminated sites, the Danish EPA has summarized the following data: Approximately 87 larger contaminated sites have been reported of which 11 were major such as Høfde 42 and Kærgaard Plantage.
In 31 % of the cases, it has been stated that they might pose a risk to the surface waters. It is not known how far from the surface waters they are, but many of the major ones are very close to a recipient (e.g. Proms Kemiske

Fabrikker, Stålvalseværket, Høfde 42, Kærgaard Plantage and Collstrup grunden).

The substances which in particular appear on the contaminated sites with potential risk to surface waters are (the number in brackets indicates the percentage of major sites with risk to surface waters, where the substance is present):

  - Tar including PAH and phenols (35 %)
  - Heavy metals (32 %)
  - Oil (32 %)
  - Chlorinated solvents (29 %)
  - Cyanide (26 %)
  - Petrol (16 %)
- The remaining approx. 10 %: chlorinated phenols, pesticides, barbiturates, phenyl acetic acid.

The above mentioned substances are typically part of the reason why remediation is carried out on major contaminated sites e.g. in consideration of the groundwater interests. Based on the reports, it can be established that, typically, remediation is not carried out on major contaminated sites in consideration of the surface waters.

Based on the percentage mentioned above, it can be calculated that:

- 8 major sites are contaminated with chlorinated solvents and are posing a risk to surface waters (87·31%·29% = 8).

- 3 major sites are contaminated with "other subtances" and pose a risk to surface waters (87·31%·10% = 3).

Of the 6 identified priority substances, it is assessed that there are less than 2 major sites contaminated with trichlorobenzene or trichloromethane and less than 2 sites contaminated with HCH (as lindane), nonylphenol, octylphenol and tributyltin compounds and posing a risk of exceeding the EQS in surface waters. Furthermore, in these cases the 6 identified priority substances are not expected to be the major contaminants and are therefore not defining the dimensions of the major remediation. Instead it is expected that contamination with any of the 6 identified priority substances to a large degree is remediated by the remediation methods used on the major contaminants.

4.4 Number of minor sites

In Chapter 3 (Section 3.5.2) seven (5 + 2) substances were singled out for further examination. Table 4.1 is a list of the typical types of contaminated sites for the seven substances. The list is based on the data in table 3.1 and 3.2.

Table 4.1:
Types of contaminated sites of relevance based on data in table 3.1 and 3.2 together with the following references:

Identified substances of concern	Typically used or found in	Types of contaminated sites
HCH/Lindane	Insecticide used until 1994 mainly in oilseed rape and plantations of spruce trees (incl. Christmas trees). Produced earlier by NAB and possibly others (e.g. Kemisk Værk Køge)	Spills while handling, e.g. near place of storage, mixing or buried packaging on agricultural farms and associated companies. Pesticide production sites (NAB and evt. Kemisk Værk Køge) Refuse dumps
Nonylphenol	From decomposition of alkylphenolethoxylates, used in washing, cleaning and dry-cleaning agents[2] and in pesticides. Mainly in certain hardeners, paints and fillers, e.g. water based wall-paint[3] Nonylphenol is used more than octylphenol	Paint production sites Washing and dry cleaning shops Production sites of washing and dry cleaning agents Waste dumps with refuse from paint production and cleaning/washing packaging
Octylphenol		
Tributyltin compounds	Antifouling in paint for ships, produced in Denmark Used in PVC Before 1999, used in wood preservative Found in diapers, plastic toys and articles for everyday use, vinyl floorings, ear plugs etc.[1]	Winter places for yachts Paint production sites PVC production sites Waste dumps
Trichlorobenzene	Not used in DK today. Earlier used in the production of pesticides, as solvent in chemical manufacturing, dyes and intermediates and Component in synthetic transformer oil, lubricants, heat-transforming medium[4]	Pesticide production sites Dye-works Transformers and condensers Waste dumps
Pentachlorophenol	No use in DK today except when occurring in imported textiles etc. Earlier (until 1977) also used in DK as preservative for wood, textiles, leather etc.	Leather and textile tanning and other facilities for preparation of leather and textile. Wood preservative.
Trichloromethane	Main uses in DK in pharmaceuticals, as solvent and as lab chemical.[4] No production in Denmark	Spill in laboratories (Testing, R&D etc.) Waste dumps

1: Danish EPA (2006a); 2: Danish EPA (2006b); 3: Danish EPA (2006c),
4: AVJ (2002a), 5. US-EPA (2006)

In table 4.2 below, an estimate of the total number of potential sites in Denmark where use or production of the seven substances have taken place, is listed.

Table 4.2.
Estimate of number of potential sites where use or production of the 7 psingled out substances have taken place.

Substance	Type of point source site	Number of sites in Denmark
HCH/Lindane	Chemical production of HCH/Lindane	2: (NAB and possibly Kemisk Værk Køge) (table 3.1)
	horticulture, fruit farming, forest nursery, landscape gardening, municipal equipment stores and in seed production [1]	Agriculture (total): 1900-1950: 200,000[10] 1993: 74,000[10]
Nonylphenol and octylphenol	Paint production sites	1950: 50 1960: 85 2001: 68[2]
	Production sites for washing/cleaning agents	1960: 20 2000: 60[3]

Substance	Type of point source site	Number of sites in Denmark
	Dry cleaners, washing shops etc. using washing and cleaning agents	1999: More than 300 dry cleaners[4] 2006: Approx. 200 dry cleaners [5]
Tributyltin compounds	Winter places for yachts	121 (Estimated equal to the number of harbours in Denmark)[6]
	Shipbuilding yard	350[6]
	PVC production	1999: approx. 20[7]
	Paint production sites	1950: 50 1960: 85 2001: 68[2]
Trichlorobenzene	Solvent in chemical manufacturing, dyes and intermediates[11]	Unknown
	Component in synthetic transformer oil, lubricants, heat-transforming medium[11]	300 (Estimated approx. 300 in all of Denmark based on knowledge of 60 transformers on Seeland[12])
	Pesticide production[11]	4 (NAB, Kemisk Værk Køge, Esbjerg Kemi, Cheminova)
Pentachlorophenol	Solvent used as softener for leather and textiles,	50 -100[9] tanneries
	and as an biocide for textiles and wood	75 10
Trichloromethane	Laboratories, R&D, testing	Approx. 1,000[9]
	Laboratories, hospitals	8,085[9]
	Pharmacies	978[9]
	Wholesale business with lab- and hospital articles	4,795[9]
All substances	Waste dumps	1,500[10]

1: In AVJ (2000) 2: AVJ (2004a): 3: AVJ (2004b), 4: AVJ (1999),
5: Glensvig (2006), 6: DST (2006) 7: AVJ (2000), 8: Kjølholt (2006),
9: AVJ (2002a), 10: DS (1994): 11: US-EPA (2006); 12. Dahl Jepsen (2006)

The types of contaminated sites are discussed in the following. Waste dumps are addressed in section 4.4.7.

4.4.1 Sites contaminated with HCH/lindane

Of the mentioned types of point sources in table 4.2 it is assessed that production sites (NAB and possible Kemisk Værk Køge) are the major potential point sources for contamination with HCH. As the primary HCH used was lindane, the term lindane will be used in the following.

This is based on the fact that the amount of lindane handled and stored is large compared to the amount handled on agricultural farms. On the other hand, potential spills on farms might be high, though expected to be of a little size. AVJ (2002b) have compiled investigations on point sources of pesticides. The results regarding lindane are listed in table 4.3.

Table 4.3:
Results from investigations of point sources of pesticides (AVJ 2002b). Lindane was part of all analysis programmes in both soil and groundwater.

Trade	Expected use according to AVJ (2000)	Number of sites investigated groundwater/soil	Lindane found in soil (% of sites)	Lindane found in groundwater (% of sites)
Horticulture	Yes	52/38	11	0
Fruit farming	Yes	5/?	0	0
Machine station	No	40/14	14	0
Nursery	Yes	11/?	0	0
Feedstuffs/seed production	Yes	7/?	0	0
Forestry	No	6/?	0	17
Total	-	121/?	-	-

From the table it is seen that lindane is only found in groundwater on forestry sites. It is also interesting that lindane is not found in the groundwater, although it is found in the soil on 11-14 % of the horticulture and machine station sites.

Compared to the total number of investigated sites regarding groundwater (121), lindane was only found in the groundwater in 17 % out of 6 sites (1 site)

In total, the risk of groundwater pollution with lindane on agricultural sites can be estimated to:

- Groundwater: 1·100/125=0.8 %

Regarding the size of a spill, it is assessed that point sources on production sites might be more than 10·10 m and there might be several on every sites. Spills on agricultural sites are supposed to be around or smaller than 10·10m. As an average, it is assumed that the assumption on size of point source in the derived dilutions factors is acceptable.

Based on the data in table 4.2, a rough estimate on the number of relevant sites having used HCH/lindane is approximately 600 (74,000•0,8%).

In table 4.4, the dilutions factors estimated and the estimate on the need for dilution to comply with the EQSs are used to find the "safe" distance between a point source and surface waters. The safe distance is the distance, where EQS theoretically will not be exceeded.

Table 4.4.
Lindane. The shading indicates a risk of exceeding the EQS at the given distance in the given geological area. The area distribution given in per cent is the distribution of area either close to or far from surface waters divided into the different types of geology.

Locations	West of "Hoved-stilstandslinien" 23 %	Sporadic areas 5 %		East of "Hovedstilstandslinien" 72 %	
Geology	Sandy soil with transport in a primary water body	Chalk with transport in a secondary water body	Chalk with transport in a primary water body consisting of chalk	Till and clayey soils with transport in secondary water body	Till and clayey soils with secondary water bodies present, but with transport in underlying primary water body
Close to surface waters (<100 m) 23%	5 % (F<100)	1 % (F<20)		17 % (F<10)	
Far from surface waters (>100 m) 77%	18 % (20<F<1,000)	4 % (200<F<2,000)		55 % (200<F<10,000)	

From table 4.4 it is assessed that point sources of lindane can constitute a risk of exceeding the EQS in surface waters, even from a distance in sandy geology and chalk, whereas it is assessed only to constitute a risk in till or clayey soils at a distance of less than 100 m from the surface waters.

Theoretically, at 45 % of all sites there is a risk that the EQS can be exceeded. Of these, it is assessed that in average 0.8 % of these have groundwater pollution.

Using these numbers, an estimate on the total number of sites having groundwater pollution and constituting a risk for exceeding EQS in surface waters can be calculated:

45%·600 sites=270 sites.

In addition to these smaller point sources, larger point sources from 1-2 production sites are expected.

4.4.2Sites contaminated with nonylphenol/octylphenol

Of the mentioned types of point sources, it is assessed that the site types constituting the largest risk to surface waters are production sites for washing and cleaning agents. This is based on the assessment that the amount of alkylphenol ethoxylates used at primarily dry cleaners and washing shops and secondary paint productions is small compared to the amount handled at production sites for washing and cleaning agents. Neither in AVJ nor Danish EPA, an account of how often production sites of washing and cleaning agents, dry cleaners, washing shops or paint productions are polluted with nonylphenol or octylphenol are given.

Instead a conservative estimate of 1 % for all potential sites is given.

In table 4.5 and 4.6, the dilutions factors estimated (se table 3.9) and the estimate on the need for dilution to comply with the EQSs (se table 3.12) are used to find the "safe" distance between a point source and surface waters. The safe distance is the distance, where EQS will, theoretically, not be exceeded. For nonylphenol and octylphenol a total of 23 and 41% respectively of the area is characterized as at risk of exceeding the EQSs.

Using these data, a conservative estimate of the potential number of sites with point sources that are at risk of exceeding the EQSs for nonylphenol and octylphenol is:

Nonylphenol: ((85+300+60)·1%)·23% = 1 sites

Octylphenol: ((85+300+60)·1%)·41% = 2 sites

As an average it is assumed that the assumption on size of point source (10·10 m) in deriving dilutions factors is acceptable.

Table 4.5.
Nonylphenol. The shading indicates a risk of exceeding the EQS at the given distance in the given geological area. The area distribution given in per cent is the distribution of area either close or far from surface waters divided into the different types of geology.

Locations	West of "Hoved-stilstandslinien" 23 %	Sporadic areas 5 %		East of "Hovedstilstandslinien" 72 %	
Geology	Sandy soil with transport in a primary water body	Chalk with transport in a secondary water body	Chalk with transport in a primary water body consisting of chalk	Till and clayey soils with transport in secondary water body	Till and clayey soils with secondary water bodies present, but with transport in underlying primary water body
Close to surface waters (<100 m) 23%	5 % (F<100)	1 % (F<20)		17 % (F<10)	
Far from surface waters (>100 m) 77%	18 % (20<F<1,000)	4 % (200<F<2,000)		55 % (200<F<10,000)	

Table 4.6.
Octylphenol. The shading indicates a risk of exceeding the EQS at the given distance in the given geological area. The area distribution given in per cent is the distribution of area either close or far from surface waters divided into the different types of geology.

Locations	West of "Hoved-stilstandslinien" 23 %	Sporadic areas 5 %		East of "Hovedstilstandslinien" 72 %	
Geology	Sandy soil with transport in a primary water body	Chalk with transport in a secondary water body	Chalk with transport in a primary water body consisting of chalk	Till and clayey soils with transport in secondary water body	Till and clayey soils with secondary water bodies present, but with transport in underlying primary water body
Close to surface waters (<100 m) 23%	5 % (F<100)	1 % (F<20)		17 % (F<10)	
Far from surface waters (100 m) 77%	18 % (20<F<1,000)	4 % (200<F<2,000)		55 % (200<F<10,000)	

4.4.3 Sites contaminated with tributyltin compounds

It is assessed that both winter storage places for yachts and ship building yards pose the major risk of exceeding the EQS in surface waters. This is based on the fact that the sites are all placed very close to coastal waters, lakes or larger rivers, and that the number of sites is large - 121, see table 4.2. Furthermore, the sites are generally characterized by having no pavement and only few drains and use of lot of water to clean the bottom of the boats. It is therefore assessed that the amount of infiltration of water contaminated with tributyltin compounds is potentially large.

It is expected that point sources of tributyltin compounds on winter storage places for yachts and ship building yards have a size exceeding 10·10 m, probably more e.g. few hundred meters times few hundred meter.

The dilution factors derived in section 3.4 is therefore probably too small for both ship building yards and winter places for yachts.

Paint production sites are also a potential point source, as tributyltin has been used in the production of ship paint. In Denmark, the number of paint production sites has varied between 50 and 85. Only very few of those have produced paints for ships. It is unknown, how many of these production sites that have used tributyltin and compounds, and there are no investigations on how often tributyltin is found on paint production sites. It is expected to be present on some disused production sites. A rough estimate on the number of paint production sites having used tributyltin compounds is 10-20 % of all paint productions sites, i.e. 10-15 sites.

The size of a point source contamination on a paint production site is expected to be approx. 10·10 m and several point sources can be present on every site.

As the need for dilution is a factor of several millions, it is assessed that tributyltin compounds constitute a risk of exceeding the EQS no matter the distance to the surface waters.

It is expected that the number of contaminated sites constituting a risk of exceeding the EQS is at least 121 winter storage places for yachts and 350 ship building yards described as large point sources and up to maybe 10 or 15 paint production sites.

4.4.4 Sites contaminated with trichlorobenzene

As it is seen from table 4.2, trichlorobenzene or TCB has been produced on 4 production sites in Denmark and has been used in dying, as a solvent in electronic production, as component in synthetic transformer oil, in lubricants and as heat-transforming medium.

On the 4 production sites, it is estimated that point sources are realistic and that the point source may have a size exceeding 10·10 m.

Regarding the use of trichlorobenzene in industries, it is unknown in how many places trichlorobenzene has been used. Based on expert knowledge, trichlorbenzene may have been used on approximately 1,000 industrial locations.

In COWI, expect knowledge of more than 30 years of work with all types of industries incl. electronic industries says that trichlorobenzene is seldomly investigated and never pointed out in analyses. Therefore, a conservative estimate of the risk of having a point source on a site is estimated to 5 %.

The average size of point sources of trichlorobenzene is expected to be around 10·10 m. It is therefore assumed that the assumption on size of point source in deriving dilution factors is acceptable, see section 3.4.

In table 4.7, the dilution factors estimated and the estimate on the need for dilution to comply with the EQSs are used to find the "safe" distance between a point source and surface waters. The safe distance is the distance, where EQS will, theoretically, not be exceeded.

Table 4.7.
Trichlorobenzene. The shading indicates a risk of exceeding the EQS at the given distance in the given geological area. The area distribution given in per cent is the distribution of area either close or far from surface waters divided into the different types of geology.

Locations	**West of "Hoved-stilstandslinien"** **23 %**	**Sporadic areas** **5 %**		**East of "Hovedstilstandslinien"** **72 %**	
Geology	Sandy soil with transport in a primary water body	Chalk with transport in a secondary water body	Chalk with transport in a primary water body consisting of chalk	Till and clayey soils with transport in secondary water body	Till and clayey soils with secondary water bodies present, but with transport in underlying primary water body
Close to surface waters 23 %	5 % (F<100)	1 % (F<20)		17 % (F<10)	
Far from surface waters 77 %	18 % (20<F<1,000)	4 % (200<F<2,000)		55 % (200<F<10,000)	

Theoretically, according to table 4.7, 45 % of all sites can constitute a risk of exceeding the EQS. Of these, it is assessed that, in average, no more than 5 % of these has a groundwater or a soil pollution.

Using these numbers an estimate on the total number of sites having groundwater pollution and constituting a risk of exceeding EQS in surface waters can be calculated:

45% · 1,000 sites · 5 %=23 sites.

4.4.5 Sites contaminated with pentachlorophenole

As it is seen from table 4.2, pentachlorophenole has primarily been used in leather and textile tanning and other facilities for preparation of leather and textile. Pentachlorophenole has also been used in wood preservation. Pentachlorophenole has not been produced in Denmark. From table 4.2, it is estimated that the number of sites having used pentachlorophenole is approximately 150.

Possible spills from tanning and wood preservation are assessed primarily to be outside while handling the chemicals or at stock. It has not been possible to find empirical assessments on the risk of soil and groundwater pollution from these type of locations. It is assessed that in less than 10 % of the sites has pentachlorophenol pollution with a size and a strength that can be called a point source constituting a risk to the environment.

As mentioned in chapter 3.5.1 pentachlorophenole has been singled out because EQS is smaller than WQS for this substance, where as EQS are lager than GQS. There fore it is assessed that point sources of trichloromethane can constitute a risk of exceeding the EQS only in "less valuable water abstraction areas"

Theoretically approximately 13 % of all sites will be located in "less valuable water abstraction areas", (e.g. figure 3.1) and therefore can constitute a risk of exceeding the EQS. Of these less than 10 % has a size and strength that can be called a point source constituting a risk to the environment.

Using these numbers an estimate on the total number of sites constituting a risk of exceeding EQS in surface waters can be calculated to less than 2.

13% · 150 sites · 10 %=2 sites.

4.4.6 Sites contaminated with trichloromethane

As it is seen from table 4.2, trichloromethane has primarily been distributed from companies selling laboratory and hospital articles, and used in laboratories (pharmacies, hospitals, R&D and testing). Trichloromethane has not been produced in Denmark. From table 4.2, it is estimated that the number of sites having used trichloromethane is several thousand (approx. 15,000).

Possible spills from laboratories and wholesale businesses are assessed primarily to be outside while handling the chemicals or at stock. It has not been possible to find empirical assessments on the risk of soil and groundwater pollution in laboratories and wholesale businesses. From more than 30 years of working experience in COWI, it is assessed that trichloromethane is found in less than 5 % of the investigations and that less than 1 % has a size and strength that can be called a point source constituting a risk to the environment.

As mentioned in chapter 3.5.1 trichloromethane has been singled out because EQS is smaller than WQS for this substance, where as EQS are lager than GQS. There fore it is assessed that point sources of trichloromethane can constitute a risk of exceeding the EQS only in "less valuable water abstraction areas"

Theoretically approximately 13 % of all sites will be located in "less valuable water abstraction areas", (e.g. figure 3.1) and therefore can constitute a risk of exceeding the EQS. Of these less than 1 % has a size and strength that can be called a point source constituting a risk to the environment.

Using these numbers an estimate on the total number of sites constituting a risk of exceeding EQS in surface waters can be calculated to less than 20.

13% · 15,000 sites · 1.0 %=20 sites.

4.4.7Waste dumps

As mentioned in chapter 2, landfills are excluded in this report. Therefore, only waste dumps will be addressed.

Waste dumps are characterized by being large in total number, but generally relatively small in size. Typically, the filling height is less than 5 m and the total volume of the dump is less than 100,000 m^3.

Generally, all the waste dumps have received waste uncontrolled and there is no environmental control measure or remediation regarding groundwater pollution.

The waste dumps have only seldomly received large amount of chemical waste, but typically only packaging from chemicals.

The waste is generally characterized by mixed waste, which from an environment point of view has the advantage that there is a high level of biologically degradation in the waste as well as in percolate downstream in the groundwater zone. This indicates that contaminants to a great extent are degraded in the plume.

It is therefore the experience that groundwater pollution from waste dumps only constitutes an environmental problem in the area close to the waste dump. Based on expert knowledge, an estimate of the safe distance regarding compliance with the EQS is approx. 500 m.

Using these estimates of safe distance and comparing them with estimates of dilution as a function of the distance to surface waters, it is assessed that the following substances may pose a risk of exceeding the EQSs in surface waters:

- HCH/Lindane (sandy and chalky sites)
- Tributyltin compounds (all geologies)
- Trichlorbenzene (sandy sites)

Experience from Danish research on groundwater contamination from landfills ("lossepladsprojektet") and international research at for example Waterloo in Canada has shown, that the biodegrading within the landfill body and downstream the landfill will minimize the amount of toxic substances leaking from the landfill. Therefore, it is roughly estimated that that pollution with the 3 mentioned substances will only be seen a few percentage of the landfills (1-5%) Of the 1,500 waste dumps known in Denmark, it is estimated that 30 % of these are located less than 500 m from surface waters.

The number of waste dumps constituting a risk of exceeding the EQSs in surface waters can therefore be calculated as:

1,500 · 30% · (1% to 5%) = 5 -25 sites.

4.5 Total estimate on sites of relevance

4.5.1 Sites at risk of exceeding the EQSs

In the following table, the estimated number of sites constituting a risk of exceeding the EQSs is listed.

Table 4.9:
Number of sites constituting a risk of exceeding the EQSs. See previous chapters for further information.

Substance	"Smaller" sites (approx.)	"Larger" sites
Major contaminated sites in focus in Danish EPA		2-4
HCH/lindane	270	1-2
Nonylphenol	1	
Octylphenol	2	
Tributyltin compounds		10-15 Paint production sites 121 winter storage places for yachts 350 shipbuilding yards Total: 486
Trichlorobenzene	23	
Trichloromethane	26	
Waste dumps	5-25	
Total	Less than 350	less than 500

As it is seen from table 4.9, the number of sites of relevance is less than 350 smaller sites and less than 500 larger sites. For the small sites, HCH/lindane constitute more than 75% of the smaller sites, where as tributyltin constitute more than 98% of the lager sites.

4.5.2 Sites of relevance regarding phase-out of PHS

Losses of hazardous priority substances (PHS) to the environment are, according to the water framework Directive, eventually to be ceased. The number of sites of relevance regarding phase-out of hazardous priority substances can be found using the same method as used in section 4.5.1, just assuming that no dilution is accepted.

The number of relevant sites regarding phase-out of the hazardous priority substances HCH, nonylphenol and tributyltin compounds are listed in table 4.10 below.

Table 4.10:
Number of sites constituting a risk of activities regarding phase out of hazardous priority substances. See previous section for information.

Substance	"Smaller" sites (approx.)	"Larger" sites
Major contaminated sites in focus in Danish EPA (pesticides and others)		87·10% =9
HCH/Lindane	74,000·0.8% =600	1-2
Nonylphenol	5	
Tributyltin compounds		10-15 Paint production sites 121 winter storage places for yachts 350 shipbuilding yards Total: 486
Waste dumps	5-25	
Total	less than 630	less than 500

As it is seen from table 4.10, the number of sites of relevance regarding phase-out of the hazardous priority substances is approx. 50 smaller sites and approx. 500 larger sites.

5 Assessing the need for further action

As it is seen from the previous chapters, 6 of the 41 substance studied (33 priority substances (PS) + 8 other pollutants (OP))are assessed to pose a risk of exceeding the EQSs in surface waters due to point sources in soil and groundwater: HCH/lindane, nonylphenol, octylphenol, tributyltin compounds, trichlorobenzene and trichloromethane.

Of these, 3 priority substances are classified as priority hazardous substances (PHS): HCH/lindane, nonylphenol and tributyltin compounds that ought to be phased-out.

It is also seen that the total number of relevant sites posing a risk of exceeding the EQSs are estimated to less than 850 sites in total for all 6 substances. For nonylphenol and octylpheno the number of sites is estimated to only one or two smaller sites and no larger sites. Therefore, the focus should be on sites polluted with trichlorobenzene and trichloromethane (approximately a dozen sites for each substances), HCH/lindane (app. 270 smaller sites and a few lager sites) and to tributyltin compounds (less than 500 larger sites).

The number of sites contaminated with the 3 priority hazardous substances HCH/lindane, nonylphenol and tributyltin compounds is estimated to a total of approx. 650 smaller sites where HCH/lindane constitute the majority of the sites, and les than 500 larger sites where tributyltin compounds constitute the majority of the sites (the number of sites is larger in this situation because the acceptance criterion is more stringent (i.e. "zero")).

Need for further knowledge

As it is seen from section 4.4, for several of the identified substances no accessible information on how often they are found as point sources and even less information on how often they are considered a risk towards surface waters have been available. This means that the estimates in section 4.4 on number of sites constituting a risk of exceeding EQSs are very uncertain. This uncertainty can be overcome by making investigation on 5-10 relevant sites for each substance or making a more intensive compilation of previous investigations.

Despite this uncertainty, it is assessed that for the 6 substances of concern, the number of sites of concern are probably in the right magnitude, though it is stressed that this study is only introductory.

There is one major problem regarding the number of relevant sites: In practice it will be difficult to identify the relevant sites, i.e. those that pose a risk to the environment, as the percentage of the total number of sites actually being contaminated and posing a risk is very little. This means that the effort regarding investigations, analysis and assessments to locate these few sites can be very large.

5.1 General problem or not?

It is assessed that the possible expenses to investigate and possibly remediate sites polluted with tributyltin compounds may be extraordinarily high compared to the other identified substances due to the fact that the contaminations need to be cleaned up, or contained thoroughly to ensure compliance with the EQSs, as the need for dilution is several million times.

Excluding tributyltin and its compounds, and only looking at the other substances and identified sites of concern, it can be discussed whether a few point source sites qualify a problem to be considered a general problem. For many of the sites, other types of contaminations are to be dealt with, and it is the experience in COWI that many of these types of contaminations are indirectly dealt with when major remediation actions are implemented.

It is therefore assessed that especially - if not only - tributyltin compounds among the priority substances may constitute an environmental issue of general character in relation to the Daughter Directive.

6 Conclusions

A proposal for an EC Directive on Priority Substances under the Water Framework Directive was put forward by the European Commission in July 2006. An initial assessment has been carried out on whether one or more of the priority substances (PS) can be expected to constitute a risk of exceeding the Environmental Quality Standards (EQSs) in surface waters due to losses from contaminated sites and soils. The final Daughter Directive also establishes EQSs for a group of eight substances called "other pollutants" (Annex I, Part B). These substances have been included in the analyses and assessments of this study.

Furthermore, an assessment has been carried out on which of the priority hazardous substances (PHS), in case of a soil and groundwater contamination, needs to be handled if it should be decided to stop losses of PHSs to the aquatic environment completely. This document is based on the assumption that losses of the PHS's ought to be stopped. In reality this implies that measures should be taken by Denmark with the purpose of stopping the losses. By aiming to stop the losses through the necessary measures, Denmark will fullfill its obligation as stated in the Water Framework Directive.

The assessment is based on a screening of the following:
- Use and production - both present and historical
- Physical-chemical properties
- Toxicity
- Will the contaminations be detected in the framework of common practice and legislation.

Based on the screening it was assessed that the following 6 priority substances in case of a soil and groundwater pollution were at risk of exceeding the EQS in surface waters:

HCH/lindane
Nonylphenol
Octylphenol
Tributyltin and compounds
Trichlorobenzene
Trichloromethane

Of these the following are classified as PHSs:

HCH/lindane
Nonylphenol
Tributyltin compounds.

Based on an estimate of the need for dilution to comply with the EQSs and assumptions on dilution in the groundwater body together with different types of geology in Denmark, an estimate on type and number of relevant sites polluted with the six priority substances and posing a risk of exceeding the EQSs were given. It was seen that for each of the 6 priority substances except tributyltin compounds less than 30 smaller sites and a few larger sites were expected. For tributyltin the number was around 500 larger sites, primarily winter store places for yachts and shipbuilding yards.

Regarding the number of sites contaminated with the PHSs HCH, nonylphenol and tributyltin compounds it was estimated that a total of approx. 50 smaller sites and 500 larger sites needs to be remediated in order to stop losses of the PHSs to the environment.

Regarding whether the identified substances and types of contaminates are of general problem is was assessed that especially - if not only - tributyltin compounds among the priority substances may constitute an environmental issue of general character in relation to the Daughter Directive. As this assessment is based on generalized assumptions and done within a statistical framework, specific investigations or monitoring of surface waters would be necessary in order to evaluate the actual risks posed by these sites.

7 References

AVJ (1999): Branchebeskrivelse for renserier, nr. 3/1999.

AVJ (2000): Branchebeskrivelse for plastvirksomheder. nr. 4/2000

AVJ (2002a): Kortlægning af brancher, der anvender chlorerede opløsningsmidler, Nr. 4/2002

AVJ (2002b): Erfaringsopsamling - amternes undersøgelser af pesticidpunktkilder. Nr. 2/2002

AVJ (2004a): Branchebeskrivelse for farve- og lakindstrien. Nr. 2/2004

AVJ (2004b): Branchebeskrivelse for virksomheder, der fremstiller sæbe, vaske- og rengøringsmidler. Nr. 6/2004)

Dahl-Jepsen, Jarl (2006): Expert knowledge on 60 investigations of transformerstations on Seeland.

Danish EPA (1994): Numbers of Nature and Environment, 1994. Danish Ministry of the Environment. - Danish Environmental Protection Agency - Danish Forest and Nature Agency, Statistics Denmark.

Danish EPA (1996): Kemiske stoffers opførsel i jord og grundvand, Bind 1 og 2. projekt om jord og grundvand fra Miljøstyrelsen, nr. 20/1996

Danish EPA (2006a): www. mst.dk/kemi/02054208.htm: Organiske tinforbindelser: Miljø og sundhed

Danish EPA (2006b): www.mst.dk/news/09320000.htm: Pollution from dry-cleaning shops will be reduced.

Danish EPA (2006c): www.mst.dk/Maling uden APE - en mere miljøvenlig mulighed.

Danish EPA (2006d): National implementeringsplan. Stockholmkonventionen om persistente organiske forurenende stoffer.

DMU (2006): Areal Informations Systemet (AIS) on the homepage of National Environmental Research Institute (Danmarks Miljøundersøgelsers) http://www.dmu.dk/Udgivelser/Kort_og_Geodata/AIS/

DST (2006): Danmarks Statistik. WWW. DST.dk, bl.a. http://www.dst.dk/Statistik/ags/kit/Areal.aspx

DST (2006): Statistics Denmark homepage

GISP (2006): Interview with Carsten Bagge Jensen Copenhagen County

Glensvig 2006. Expert knowledge, Dorte Glensvig, COWI A/S

Kjølholt 2006. Expert knowledge, Jesper Kjølholt, COWI A/S

Statutory Order 921 (1996): Bekendtgørelse om kvalitetskrav for vandområder og krav til udledning af visse farlige stoffer til vandløb, søer eller havet (· 1). Oct. 8.1996

US-EPA (2006): www.epa.gov/chemfact/tcben-sd.txt