DANMARKS OG GRØNLANDS GEOLOGISKE UNDERSØGELSE RAPPORT 2005/49

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Carsten Suhr Jacobsen, Sebastian R. Sørensen,
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1. Abstract

Danish groundwater is the source for almost all drinking water production in Denmark. Groundwater monitoring is thus important in order to ensure the custumer with clean drinking water. During the last decades the numbers of analysis has keept increasing – reflecting an increased knowledge and concern over important contaminants. However some analysis has also been removed from the analysis program often reflecting that the contaminant only very infrequently has been detected. Finally, the expences connected with the total number of contaminants being analysed should be constantly minimised.

The present report can be seen as an attemt to review scientific litterature and other relevant sources to get a list of likely contaminants of Danish groundwater – not presently beeing monitored. Danish autorities has working groups concluding which contaminants to include on the list of analysed contaminants. Such "emerging contaminants" can be broadly defined as any synthetic or naturally occurring chemical or any microorganism that is not commonly monitored in the environment but has the potential to enter the environment and cause known or suspected adverse ecological and (or) human health effects. In some cases, release of emerging chemical or microbial contaminants to the environment has likely occurred for a long time, but may not have been recognized until new detection methods were developed. In other cases, synthesis of new chemicals or changes in use and disposal of existing chemicals can create new sources of emerging contaminants.

The report points out that some pesticides and degradation products could be considered to be included in the Danish monitoring system. Four degradation products from triazine herbicides that have not been analysed in the Danish monitoring system have been found in US groundwater. Further metabolites from the herbicides bromoxynil and ioxynil have been found to be persistant in Danish soils, and might be mobile in soil.

Estrogens originating from livestock manure has been shown to leach trough Danish fractured soil at concentration many times the effect level of estrogen on fish. This estrogen source relating to specialised livestock production is not – like its human ancestor – passed through a sevage plant with efficient estrogen degrading microbial communities.

A Danish study on presence of fecale indicator bacteria in private wells shows that 25% of all wells has high concenrations of these fecale indicator bacteria. Patogenic microorganisms has not been monitored for in Danish groundwater, but field trials in Ireland have demonstrated significant leaching of patogenic bacteria following deposition of live stock manure om farmland. Other animal breeded patogens, like cryptosporium or giardia, are frequently found outside Denmark in drinkingwater based on surface water. This group of patogens is frequently present in livestock manure but has not been monitored for in Denmark with the exception of pinpoint analysis to validate methods.

Pharmaceuticals are present in large amounts in most livestock manure but their degradation and movement in soils is not well described. 8 different pharmaceuticals have been identified as the most likely contaminants originating from manure. Among different human related pharmaceuticals 3 compounds are identified.

Finally several other industrial compounds like antibacterial compounds and synthetic musk products have been detected in surface water, but no measurements have been attempted in groundwatersamples.

In the future the use of genetically modified plants that produce compounds like pharmaceuticals or Bt toxin should be considered in relation to groundwater contamination. Presently no such production has been started and the compounds are thus not risk assessed.

2. Introduction to emerging contaminants

Optimization of efforts spend in monitoring of drinking water quality calls for constantly considering the compounds and microorganisms being analyzed. The present GEUS report is seen as a review of recent scientific literature and searches in foreign governmental databases and homepages to possibly point at maybe important areas not currently being considered in the Danish priority list.

The report will first give a brief overview in chapter 3 of sources to get knowledge of which compounds and microorganisms that today are being analyzed. The following chapters 4 - 10 deals with the various areas of potential interest. Finally, chapter 11 gives a shortlist of what we are considering as “emerging contaminants” in Danish drinking water.

2.1 Definition and background

Groundwater is the major source of drinking water in Denmark, with more than 90% of the produced drinking water based on groundwater. The groundwater quality is high and drinking water in Denmark is generally only given a very mild treatment in the water production plants. This treatment includes aeration and passage through a sand filter, but no further filtration or chemical safeguarding is used. Denmark is a land heavily impacted by pesticide use. Degradation product from 2 groups of soil applied herbicides is particular responsible for the extensive close down of more than 40% of the water production pipes (GEUS grundvandsovervågning).

The chemical compounds being analyzed for today represent a small fraction of the chemicals that occur in the environment. The same is true with microorganisms – or rather the analysis is in the best case following indicator microorgansims, but are not specifically towards the interesting pathogens.

The two areas, chemical compounds and microorganisms, contain emerging contaminants. The definition of emerging is however imprecise in that an emerging contaminant could be

1) contaminants which recently is being introduced in the environment and consequently not beforehand could have been a threat to the environment
2) contaminants which have not been possible to analyze – at least not in a robust and cost-effective way

This report can not be considered a fully covering listing of what we need to analyze in the future, but rather be a listing of likely ideas which should be considered further by the Danish EPA. Its likely relevant to repeat the structured survey of litterature and monitoring-programs to search for emerging contaminants with regular intervals – every second or third year.

3. Current status of Danish groundwater contaminants

The Danish groundwatermonitoring program is providing a yearly report of the concentrations of groundwater polutants. The monitoring program can be reached via the following URL:
http://www.geus.dk/publications/grundvandsovervaagning/grundvandsovervaagning.htm
The detailed report is in Danish but a short Englism summary is given. From this summary the following main conclusions regarding inorganic trace elements and organic micropollutant including pesticides and their degradation products is given:

Maximum Admissible Concentration (MAC) of many inorganic trace elements has been exceeded in all elements of the groundwater monitoring programme. From 1998-2003, the MACs have been exceeded in 32% of screens in the monitoring areas. In agricultural watershed catchment areas, where young and shallow groundwater is surveyed in areas with intensive agriculture, results are conspicuous with many high nickel, zinc, lead and arsenic values. Within groundwater monitoring areas and in water abstraction wells, arsenic in particular was found in high values. In major water works with effective sand filters, inorganic trace elements will partly precipitate and will not necessarily have a negative effect on drinking water quality. However, in smaller water supplies without water treatment facilities, they may form a water quality problem.

Organic micro pollutants have been found in 92% of well screens in groundwater monitoring areas from 1993-2003. By excluding anionic detergents (due to a non-specific method of analysis), organic micro pollutants are detected at least once in 63% of well screens. The percentage for agricultural watershed catchment areas is 56 and approximately 20% for water abstraction wells (also without anionic detergents). However, the concentration of these compounds is below the MAC for drinking water in most groundwater abstraction wells, as well as in most well screens in groundwater monitoring areas.

The percentage of well screens with **pesticides** and/or their **metabolites** in groundwater monitoring areas was approximately 27 in 2001, 2002 and 2003. The percentage of well screens with concentrations above the MAC for drinking water (0,1 µg/l) was about 8.5 in both 2001 and 2002, but increased to about 10% in 2003. Pesticides or their metabolites were detected in more than 40% of well screens sampled from 1998 until 2003, and the share above MAC was about 15%.

The metabolite 2,6-dichlorbenzamide (BAM), a degradation product of chlorthioamide and dichlobenil, and triazins and their metabolites, notably deethylisopropylatrazine, are the most commonly detected compounds. The detection of deethylisopropylatrazine has increased to 9% of wells sampled. This metabolite was detected in more than 30% of monitoring at shallow depth below agricultural watershed catchment areas. The metabolite was detected in about 3% of analysed water supply wells. Only about 200 water supply wells were analysed for this metabolite, and it is anticipated that detection will increase as analyses are performed on an increasing number of water supply wells.

Groundwater abstraction wells are still severely affected by pesticides or metabolites. During the period from 1998-2003, the percentage of detections was approximately 26; 6% exceeded MAC. During the same period, the annual percentage of wells with concentrations exceeding MAC, declined from 10 to 5%. In 2003, pesticides or their metabolites were detected in about 27% of the wells.

The most commonly detected compounds in water abstraction wells are BAM, atrazine and triazine-metabolites as well as mechlorprop and dichlorprop. From 1998-2003, pesticides or their metabolites have been detected in more than 50% of sampled shallow (0-20 mbgs) groundwater abstraction wells. Like in groundwater monitoring areas, occurrences decrease with increasing depth.

The metabolite BAM often appears in combination with other pesticides and metabolites in shallow aquifers, and can, accordingly, be used as an indicator for other pesticides, for example in small private dug or drilled wells, as these often abstract shallow groundwater.

In the Novana program: http://www.dmu.dk/Overv%C3%A5gning/NOVANA/
Detailed listing of number of contaminants measured within defined groups, the used time-span between repeated analysis, and the storage and data analysis can be found (also in Danish).

4. Metals

Metals constitute limited group of compounds which may be a treat to the groundwater resource. In water the metals will be at ionic forms as halo- oxo- or hydroxylated compounds. It is not all forms that constitute a treat to the groundwater, as some species are less toxic than other species. Also the solubility and the sorption of the individual species are different, parameters both affecting the leaching of the compounds towards the groundwater. Routine measurements of groundwater corporate all forms of the individual metals in one analysis and do not distinguish between the different metallic species. Within the last decades focus has been on the heavy metals due to their negative effects on humans and the environment. For lead and mercury plans for reduction in their use has been initiated and therefore increased findings in groundwater is not expected. In the Danish Groundwater Monitoring Programme (GRUMO) several metals are as a routine measured, but only nickel, arsenic, aluminium, and zinc are found in concentrations above the limits set for drinking water to a larger extend (table 1; GEUS 2004). Arsenic is found naturally especially in reduced aquifers and if the water recovery from such aquifers is increased e.g. due to pollution of the upper oxidised groundwater, then increased problems with arsenic may be expected. Similar to arsenic the concentration of nickel will depend on the

Table 1: Analysis of metals in the Danish Groundwater Monitoring Programme (GRUMO) in the period 1998-2003 (GEUS, 2004).

	Limit concentration for drinking water µg/l	Wells having more than one sample above the limit %
Aluminium	100	12
Antimony	2	<1
Arsenic	5	15
Barium	700	<1
Lead	5	1
Boron	1000/100[1]	1/3
Cadmium	2	<1
Chromium	20	0
Cyanide	50	<1
Copper	100	<1
Mercury	1/0.1[1]	0/1
Molybdenum	-	-
Nickel	20	6
Selenium	10	<1
Silver	10	0
Tin	10	0
Zinc	100	6

[1]Limit concentration/recommended concentration

pattern of water recovery. In anaerobic aquifers nickel may be bound as sulphuric nickel. Increased water recovery, however, will lower the water table and the reduced sediments may be aerobic. At the aerobic conditions the free nickel will be released and be a treat to the groundwater resource. Aluminium is also found in groundwater, probably due to the general acidifying of the environment. At lower pH chalk and eventually clay minerals will dissolute and aluminium will be released to the water. Zinc is also found, but at present the source is not known.
Recently the Danish EPA published a report about the fate and effect of 11 metals in the environment. The metals were so called 'second rank' elements with regard to use pattern and consumption in Denmark. The elements were antimony, beryllium, bismuth, boron, gallium, indium, lithium, molybdenum, palladium, platinum, and vanadium (Kjølholt et al., 2002). Either of the metals is estimated to be a treat to the groundwater resource.
A web of science based search of the international literature reports no metals not already measured as emerging contaminants.

5. Pesticides and their persistent degradation products

Brüsch and Felding, 2000, compared pesticides found in Danish and foreign ground water in a state of the art project. This project was based on reviewed literature, so-called grey literature, on down loading databases from web sites and on direct contact with institutions responsible for ground water monitoring. The juxtaposition of more than 50 databases and chemical ground water data from monitoring programs were compare with approximate 550 pesticides and metabolites, where the parent pesticides were used in Denmark in the period 1956 – 1998. To identify new upcoming pesticides the most relevant web sites used by Brüsch and Felding, 2000, were revisited, and the data collected were compared with the results from the state of the art project.

USA		Europe		Denmark , national monitoring system		Denmark, all analytical programs	
Avg. Frequency		Avg. Frequency		Avg. Frequency		Avg. Frequency	
Atrazine	1,3	Atrazine	2	2,6-dichlorbenzamide	1	2,6-dichlorbenzamide	1
Deethylatrazine	2,5	Deethylatrazine	2	Deethylatrazine	4,3	Deethyldeisopropylatrazine	2
Simazine	3	2,6-dichlorbenzamide	2,5	Deisopropylatrazine	4,3	Deethylatrazine	6
Prometon	3,8	Bentazone	4	Atrazine	5	Deisopropylatrazine	7
Metolachlor	5	Simazine	5,3	Bentazone	6,7	Bentazone	8
Tebuthiuron	6,5	Diuron	5,5	Mecoprop	7,7	Atrazine	9
Alachlor	8,3	Isoproturone	6,5	Dichlorprop	8	Simazine	12
Carbofuran	9,3	Atrazine, deisopropyl-	7	MCPA	8	Dichlorprop	13
Cyanazine	9,3	Mecoprop	7,7	Simazine	9,5	Ethylenthiurea(ETU)	14
Metribuzin	10,3	Dichlorprop	8	Hydroxyatrazine	10	Mecoprop	15

Table 2. The 10 most frequently found pesticides and metabolites in ground water in USA, Europe and Denmark. Avg. frequency – A low number indicate, that the substance has been found most frequently in the monitoring programs used as background material. A top 10 list for the individual programme has been calculated. Summing up al top 10's and dividing by the number of programs give an average frequency. E.g. 2,6-dichlorbenzamide has a value "1" in the column "Denmark, al analytic programs" indicating that 2,6-dichlorbenzamid was detected most frequently in al the programs. From Brüsch and Felding,, 2002.

Information about more than 550 pesticides and their metabolites used in Denmark from 1956 to 1998 has been collected, Brüsch and Felding, 2000, and the results from Europe and USA have been processed in a database (8). Approximately 300 pesticides and metabolites have been analysed in water samples from ground water and 140 have been found. A minor number of substances are only reported as "found" (9) and no information

about number of analyses or circumstances were reported. In monitoring programs where only few parameters are analysed it is normal to find all compounds, while it is common to find only some of the analysed parameters in large programs. But a trend is: Increasing number of parameters in the analytic program → increasing number of parameters will be found. Obvious other limiting factors also could be detection limits, well type, analytic methods, area use (agricultural, urban, roads or railways) and monitoring purpose.
The results have been used to improve the national Danish analytic ground water monitoring program. Results from the Danish pesticide leaching assessment programme have also contributed to update of the national monitoring programme, for example frequent findings in high concentrations of the metabolites desamino-diketo-metribuzin and diketo-metribuzin. These substances are now incorporated in the new ground water monitoring programme (NOVANA) and probably these two metabolites will be found frequently in groundwater under areas where metribuzin has been used in agriculture. Metribuzin has also been found frequently in surface water in USA, draining agricultural areas, Martin, Crawford and Larson, 2004.

In table 2 pesticides and metabolites detected in monitoring programs in the US, Europe and in Denmark are compared. Only frequently analysed pesticides have been included: Pesticides analysed more than 100 times in monitoring programs, pesticides analysed more than 200 times in larger compiled programs and pesticides analysed in more than 2-3 programs.
From table 2 it can be seen, that the metabolite BAM (2,6-dichlorbenzamide) is found frequently in Denmark, while atrazine and metabolites are detected most frequently in Europe and in the US. BAM has often been found in urbane areas and not in young ground water samples from agricultural areas. In Europe bentazone, simazine, diuron, isoproturon and two phenoxy acids have also been frequently detected. Ethylen-thiourea (ETU) has been found in Denmark, but it should be noticed that the detection's originated from ground water sampled in selected wells. Also – it has been found that BAM may be a good indicator for contamination as other contaminants are often together with other compounds.

A recent study made at GEUS has demonstrated that possible persistent transformation products can be formed from bromoxynil and ioxynil (Nielsen et al 2005). This finding is highly relevant in relation to the search for possible emerging contaminants in Danish groundwater. Irrespective that bromoxynil and ioxynil not has been used for total weed control in uncropped areas as dichlorobenil, the structure and degradation pathways are very similar to the well known dichlorobenil degradation product BAM, that has been found in 19% of 5000 samples of Danish groundwater.

Kolpin and Martin, 2003, have summarised preliminary Results from Cycle I of the National Water Quality Assessment Program, Pesticides in ground water and Pesticides in Surface Water of the United States. The data has been subdivided in ground water and surface water from areas with agricultural land use, mixed land use (major aquifer surveys), undeveloped land use and urban land use. The ground water findings show only few pesticides and metabolites not measured in Denmark. Dieldrin has been found in 1% of 1438 wells under agricultural areas, in 8,5% of 2717 wells in major reservoirs and in 5.1% of 823 wells in urban areas. Dieldrin has also been found in surface water. Dieldrin has not been moni tored frequently in Denmark and dieldrin has been used from 1956 to 1988 in rather small amounts. Occurrence of Pesticides in Shallow Ground Water of the United States, Kolpin, Barbash, and Gilliom, 1998, also show findings of dieldrin in ground water. It is possible that findings of dieldrin in Denmark could occur in wells situated near urban areas. U.S. Geological Survey, 1999, has show that dieldrin persists in shallow urban ground water and that the presence of dieldrin in ground-water several years after being banned indicate dieldrins persistence in soils and ground water and its potential to be a problem in some wells. The data from Kolpin and Martin, 2003, include app. 80 pesticides and metabolites and there is no other findings of "new" substances.

Sulfonylurea, Sulfonamide, Imidazolinone, and Other Pesticides, U.S. Geological Survey, 2004, have been monitored in streams and in ground water. At least one SU, SA, or IMI herbicide was detected in 6 of 8 reservoir samples and flumetsulam, imazethapyr, and imazaquin were each detected in 5 samples. At least one SU, SA, or IMI herbicide was detected in 5 of 25 ground-water samples. Imazethapyr was detected most frequently followed by flumetsulam and imazaquin. These pesticides have not been sold in Denmark but similar low doses pesticides are used in increasing amount and it can not be exclude that some similar pesticides can be found i Danish ground water.

Barbash et al, 1999, have evaluated Distribution of Major Herbicides in Ground Water of the United States and reported findings of several triazine metabolites. Most are also analysed in different Danish monitoring programmes but didealkyl-atrazine, deethyl-hydroxy-atrazin, deisopropyl-hydroxy-atrazin and didealkyl-hydroxy-atrazin are not analysed in Danish ground water and the metabolites are not included in the danish monitoring system. Al the substances have been analysed and found in ground water in US, as well as the more common metabolites like deethyl-atrazine, deisopropyl-atraxine which have been found both in Denmark and in USA. The metabolites deethyl-atrazine and deisopropyl-atrazine are included in the Danish monitoring system.
The hydroxy metabolites have a better sorption in relation to clay and other minerals compared with the other triazine metabolites, but some investigations show a rather large detection frequency. Barbash et al, 1999, also mention that a large number of metabolites from alachlor have been found, but the total consumption of alachlor in Denmark have been small and therefore it would be unlikely to find alachlor metabolites on a countrywide basis.
Organochlorine and organophosphate pesticides occurrence and distribution in surface and ground water of the United States have been investigated, by Scribner, et al 2003 and Hopkins et al, 2004. The organophosphorus pesticides studied are azinphos-methyl, chlorpyrifos, diazinon, disulfoton, ethoprop, ethyl-parathion (parathion), fonofos, malathion, methyl-parathion, phorate, and terbufos. Azinphos-methyl, chlorpyrifos, diazinon, ethyl-parathion (parathion) and malathion have been sold in Denmark. Diazinon was found in 1,2% of the analysed ground water samples, while the others were found less frequently. Malathion, parathion and diazinon have been sold in rather large amounts in Denmark, while the other substances are sold only in small amounts. It can probably be expected to find these substances locally in Danish ground water.

Terbuthylazine and deethylterbuthylazine have been found frequently in drinking water from small private water supplies, Brüsch et al, 2004. It should be expected that an increasing number of findings will occur in deeper ground water reservoirs in the future. It should be noted however that both terbuthylazine and desethylterbuthylazine are included in the monitoring system.

A summary from Umweltbundesamt, Abteilung Wasser, 2004 , include 38 pesticides and summarise also reports from water companies in Germany. There is no indication of the number of analysed water samples, and the summary includes water samples from drinking water extracted from surface water and samples from monitoring stations in surface water.

6. Hormones and steroids

6.1 Introduction to compounds

Within the last decade there has been an increasing interest in possible groundwater contamination with compounds that can cause hormone effect in human and biota. Obviously, this group of compounds includes the natural hormones such as the endogenous mammalian estrogen and testosterone. For example, the steroid compounds are a family of substances sharing a similar chemical structure and the steroid hormone testosterone is an example of a natural compound from this group. Also, various drugs have steroid effect. As demonstrated by several toxicological studies many manmade chemicals may cause hormone or hormone-disrupting effects. One mechanism suggested to cause the effects is binding of compounds to endogenous steroid receptors thereby causing either activation or blocking of the receptors Heberer,T. (2002c), Evans,N.P. et al. (2004), Singleton,D.W. and Khan,S.A. (2003), Machala,M. and Vondracek,J. (1998). The result is various effects on endocrine functions and for that reason the compounds of this group are called endocrine disrupting compounds (EDCs). A list of 118 compounds that may have hormone disrupting effects has been published by EU (available at http://www.mst.dk/kemi/01110400.htm) and reviews on compounds and fate studies has been published (Sonnenschein,C. and Soto,A.M. (1998),Sumpter,J.P. (1998),Ying,G.G. et al. (2002).

Examples of manmade compounds are the synthetic estrogen diethylstilbestrol and several chemical substances used in industry as bisphenol-A Ben-Jonathan, N. and Steinmetz,R. (1998) and nonylphenol White,R. et al. (1994). Also, organo-metal compounds such as tributyltin (TBT) has been shown to cause imposex in marine gastropods Bryan,G.W. et al. (1986),Bright,D.A. et al. (1990). Thus, several of the compounds discussed in this chapter are also considered in other contexts elsewhere in this report. In the present chapter the focus is on the aspect of endocrine-disrupting effects in relation to possible emerging groundwater contaminants.

The natural estrogens include 17β-estradiol (estradiol), 16α-hydroxy-17β-estradiol (estriol), and estrone. In general, natural estrogens are more readily biodegraded than synthetic estrogens such as 17α-ethynylestradiol (ethynylestradiol).

In the literature several classical studies has been published describing hormone effects in the environment Colborn,T. (1995), Guillette,L.J., Jr. et al. (1995), Sumpter,J.P. and Jobling,S. (1995), Toppari,J. et al. (1996), Aherne,G.W. and Briggs,R. (1989). The compounds may be present in the environment in very low levels. However, the concentrations needed to cause effects is also relatively low as compared to the levels generally accessed in classical environmental toxicology studies Welshons, W.V. et al. (2003). Since the early start of the research within this area a major concern has been, and remains to be, the combined effect that may result when two or more weak environmental estrogens are present simul taneously. Thus, a 1000 times increase in response has been demonstrated by combining two weak estrogens Arnold, S.F. et al. (1996).

Several studies have investigated the possible leaching and transformation of EDCs following application of sludge to soil. One way of introducing the compounds to the soil and possibly the groundwater is the use of sludge as a fertiliser on agricultural land. Several Danish and international studies have investigated the aspect of EDCs in sludge treatments plants and use of sludge on agricultural areas Fauser, P. et al. (2001), Christiansen, L.B. et al. (2004b), Davis, G.A. et al. (1992), Vikelsoe, J. et al. (2002).

Fate and transport studies of of testosterone and beta-estradiol has been published Casey, F.X.M. et al. (2003), Casey, F.X.M. et al. (2004). Also, an EU-Project has been established on the subject "Assessment of Technologies for the Removal of Pharmaceuticals and Personal Care Products in Sewage and Drinking Water Facilities to Improve the Indirect Potable Water Reuse – Poseidon (www.eu-poseidon.com). Within this forum a number of fate and leaching studies has been presented, but the actual data available from the studies are not included in the publications – or presented with only limited details on experimental conditions.

The relevance of the compounds within this group of contaminants is highly dependent on use and source aspects. For example, some compounds in sewage may not be considered as a possible contaminant as the content is removed by degradation in sewage treatment plants. However, if such compounds were introduced into the environment by some other means – such as widespread use of soakaways (soil infiltration) – they may cause concern.

The emission of natural estrogens from farm animals (cattle, pigs, chicken, etc.) is potentially a major source of estrogen pollution in the environment. The major components are E1, E2, 17β-estradiol (E2-17β) and their conjugates. After storage in the manure-tank, estrogens excreted from stabled animals may be released to the soil environment when manure is used for fertilisation of soil.

Most fate–studies have dealt with unconjugated estrogens of high biological activity and low aqueous solubility. However, swine excrete 17-β-estradiol and estrone mostly as sulfate- or glucuronide conjugates of low biological activity and high solubility (Hanselman et. al. Environ. Sci. Tech.; 37:5471-5478; 2003). Transport of conjugates and their environmental transformation into biologically active compounds have been virtually non-investigated.

Recently a Danish study (Personal communication Mette Lægdsmand) applied pig-slurry with a natural content of estrogens to intact soil monoliths (60 cm diameter and 100 cm long) by direct injection. Concentrations of estrogens in the effluent leached from the monoliths were up to 10 times the effect-concentrations of aquatic wildlife. Most of the leached estrogens were present as estrone. Leaching of estrogens continued when outflow resumed after a dry summer period with no outflow. These results indicate (i) that estrogens can be transported to one meter depth under certain conditions and (ii) that degrada tion of estrogens in soils when applied with slurry by direct injection was retarded compared to aerobic degradation of estrogens under laboratory conditions.

Overall, the data available for risk evaluation is focused on sludge treatment plants and fate studies in topsoil and surface water biotopes. Thus, in relation to groundwater risk assessment very few data are available considering sorption, degradation and transformation. The lack of scientific knowledge is thus related to the processes and fate of these compounds in deeper soil layers. Only a few studies have focused on compounds with hormone effects in groundwater, such as Rie, M.T. et al. (2000). A prerequisite for the research is methods that can identify and quantify the compounds at concentrations that can be expected in groundwater. Also, the analytical method must be sensitive enough to reach the levels relevant for the toxicology effect levels of the ECDs. A overview of toxicity identification and evaluation procedures used for the effect-based analysis of endocrine disrupting compounds has been published recently Petrovic, M. et al. (2004). To provide an indication of relevant concentrations to be measured the effect level in fish can be considered. Thus, it has been demonstrated that low nanograms per litter levels of estrogens cause estrogenic responses (vitellogenin production in male fish, Panter, G.H. et al. (2000)). Such analytical methods are only just starting to be published Ternes, T.A. et al. (1999 & 2002), Fine, D.D. et al. (2003), Richardson, S.D. (2004), Petrovic, M. et al. (2002). Consequently case studies and monitoring results on groundwater are very limited.

6.2 Compounds of primary interest

In a recent report Christiansen, L.B. et al. (2004a) the research on numerous compounds with endocrine effect is reviewed. It is concluded that in relation to surface waters and feminisation of fish the most important compounds seems to be are 17ß-estradiol and estron as well as the synthetic estrofem ethinylestradiol. Considering possible endocrine effect the synthetic compounds such as alkylphenol and bisphenol seems less likely candidates. In relation to natural hormones and EDCs the sources of the contaminants are wastewater discharges as well as sewage manure. Thus, EDC contamination of surface water likely relates to manure used on farming areas, sewage and sewage plants whereas sources to groundwater contamination may be manure usede on farming areas, sewage used as fertiliser or pollution originating from leaking sewage systems. Consequently, the conclusion is likely to be relevant for groundwater as well. Also, as discussed elsewhere in the present report, several industrial products may be relevant as emerging groundwater contaminants for other reasons than EDC effects. Considering endocrine-disrupting effects in relation to groundwater contamination a basic understanding on sorption, transport and degradation needs to be established. In particular, this is relevant for the prime candidate compounds 17ß-estradiol, estrofem ethinylestradiol.

7. Natural organic matter and toxins

Toxins are produced naturally by many plants, fungi and soil bacteria and if they are mobile and toxic to human health they may potentially be a treat to the groundwater resource. The number of toxins produced in nature is extremely high, but in general the compounds are degradable and only produced in small amounts and therefore not a threat to the groundwater resource. Examples are toxins produced by poisonous fungi and many soil bacteria e.g. *Clostridium tetani* the bacterium causing tetanus. Only in very specific cases with a dense population of toxin producing organisms toxic compounds may leach to the groundwater. Resent research in Denmark has focused on ptaquilosides which are found in brackens and is shown to be toxic to humans (Rasmussen, 2003). Ptaquilosides has been measured in concentrations from 4 to 6 µg/l in samples from two shallow Danish aquifers situated below bracken stands. In Sweden concentrations up to 45 µg/l has been measured also in shallow groundwater (Rasmussen, 2003).

Most agricultural crops do not produce toxic compounds but there are exceptions. Potato plants produce e.g. solanin, which is toxic and potentially may leach to the groundwater. Recently a joint project involving The Royal Veterinary and Agricultural University and GEUS has been initiated focusing on the fate of solanin in soil and groundwater.
Within the last decade, new crops genetically modified to produce toxic compounds with e.g. herbicidal or insecticidal effects have been invented. Such genetically modified organisms may limit the use of pesticides, but the compounds released by these plants may leach to the groundwater and therefore pose a threat to the drinking water and human health. Knowledge about compounds released from GMO, including their fate and human toxicity are meagre at present, but needed to make more complex risk assessments of modern agricultural practise.

8. Pharmaceuticals and antibiotics

8.1 Introduction

This group of compounds contains very differentiated compounds. A number of sources to these compounds has been described Kummerer, K. (2001), Halling-Sorensen, B. et al. (1998). In relation to groundwater the sources to these contaminants are livestock manure and sludge that is spread on arable land. Also, the compounds may be introduced from leaking sewage systems etc. Many of the compounds are water soluble, only slightly absorbing to top soil, and may be rather stable in the soil and groundwater environment (Heberer, T. (2002c), Heberer, T. (2002b), Stuer-Lauridsen, F. et al. (2000) and references herein). Thus, it is very likely that some emerging groundwater contaminants may be concealed within this class of compounds. The problem is the lack of monitoring results describing occurrences and time trends of contamination in relation to soil and groundwater. At present, the Danish national groundwater monitoring program does not include pharmaceuticals or antibiotics. Further, ecotoxicological data are available for less than 1% of pharmaceuticals in the open peer-reviewed literature and ecotoxicological databases ECETOX (EU) and ECOTOX (US) Sanderson,H. et al. (2004), and much of the basis used for toxicological evaluation is based on modelling by tools such as QSAR programs. Many of the QSAR models is targeted on describing compound effects on biota, particularly aquatic biota, and very few tools can describe the transport, sorption and degradation in related to groundwater contamination as the basic data for the models has not been established.

In general, the literature available on fate of these compounds is related to processes in sludge and sewage treatment plants. A number of German publications describe the presence of pharmaceuticals in groundwater, and the source to these findings are suspected to be impact of municipal or industrial waste water Sacher, F. et al. (2001). However, in general, knowledge on more widespread contamination is limited. Within recent years an effort has been made by USGS to address the problem of possible emerging contaminants within this group. From the USGS National Reconnaissance Studies it is found that some compounds are frequently detected in the aquatic environment. Among these are steroids, drugs, disinfectants, antibiotics and fragrances. One of the prerequisites for this study has been the development of analytical procedures that allows for detection and quantification of the compounds of interest. Thus, a large effort has been made by the USGS in recent year, and the outcome has been methods for a large number of possible emerging contaminants. However, it should be emphasised that not all compounds used in US are relevant to Danish conditions due to differences in use and treatment approaches.

Considering toxicology a model study has demonstrated a negligible human risk connected to the environmental exposure for the substances 17α-ethinylestradiol, phenoxymethylpenicillin and cyclophosphamide Christensen,F.M. (1998). In this context it should be mentioned that in relation to other (non-mammalian) eco-organisms the pharmacodynamic effects might potentially play a major role Seiler,J.P. (2002). Thus, the ongoing debate on how to establish ecotoxicology assays is highly relevant for the compounds of this class.

Reviews on the occurrences and fate of pharmaceutical substances in the environment has been published Sanderson,H. et al. (2004), Halling-Sorensen, B. et al. (1998), Daughton, C.G. and Ternes, T.A. (1999), Kolpin, D.W. et al. (2002), Heberer, T. (2002a), Richardson, M.L. and Bowron, J.M. (1985), Zuccato, E. et al. (2000), Jorgensen, S.E. and Halling-Sorensen, B. (2000). An environmental risk assessment has been made for the 25 most used pharmaceuticals in the primary health sector in Denmark Stuer-Lauridsen,F. et al. (2000). The PEC/PNEC ratio exceeded one for ibuprofen, acetylsalicylic acid, and paracetamol. A similar evaluation of the 25 most used pharmaceuticals in UK has been published recently Jones, O.A.H. et al. (2002). Based on exceedings of aquatic PEC/PNEC ratios the drugs Paracetamol, Amoxycillin, Oxytetracycline and Mefenamic acid were identified as priority compounds. A recent Danish report has investigated the content of environmental contaminants in liquid manure, including veterinary drugs. From this study a number of eight possible antibiotic contaminants can be identified: sulfadiazine, sulfadimidine, sulfatroxazole, sulfadoxine, sulfamethoxazole, tiamulin, trimethoprime and tylosin, and the compounds in Schwærter,R.C. and Grant,R. (2003). In addition to searching the existing literature an examination of the use of drugs in Denmark may help identifying possible emerging contaminants. Considering the Danish use of human antibiotics the following candidates can be identified based on a calculation of use:

Group	**doses**
Antibakteria drugs for systemic use	5,19E+08
Penicillins	3,24E+08
Beta-lactamase sensitive penicillins	1,97E+08
Phenoxymethylpenicillin	1,97E+08
Penicillines, broad spectrum	9,79E+07
Makrolides, lincosamides, streptogramines	8,44E+07
Makrolides	8,40E+07
Tetracyklines	8,17E+07
Amoxicillin	4,45E+07
Erythromycin	4,31E+07
Sulfonamide and trimethoprim	2,99E+07
Beta-lactamase resistant penicillines	2,79E+07
Dicloxacilline	2,75E+07
Pivmecillinam	2,67E+07
Pivampicilline	2,55E+07
Tetracykline	2,00E+07
Azithromycin	1,73E+07
Nitrofurane derivatives	1,59E+07
Nitrofurantoin	1,59E+07
Sulfamethizol	1,44E+07
Sulfonamider (short time effective)	1,44E+07
Trimethoprim	1,41E+07
Trimethoprim and derivatives	1,41E+07
Roxithromycine	1,39E+07
Methenamine	1,35E+07

A calculation has been published previously Halling-Sorensen,B. et al. (1998), and a summary of recent use can be calculated using the ongoing statistics published by the Danish Medicines Agency (number of doses used in 2000-2003, primary sector as published by the Danish Medicines Agency, www.dkma.dk).

Considering candidate compounds erythromycin, sulfamethoxazole, fluoxetine, carbamazepine, ibuprofen, diclofenac and triclosan is included in the US surface water screening program.

Considering veterinary drugs a few publications on Danish and international research are available Nielsen, S.N. et al. (2004), Boxall, A.B.A. et al. (2003a), Boxall, A.B.A. et al. (2003b), Tolls, J. (2001), Gavalchin, J. and Katz, S.E. (2004), az-Cruz, M.S. et al. (2003), Hirsch, R. et al. (1999), Jjemba, P.K. (2002).

Household products often have content of antibiotics as for example trichlosan. The majority of data is related to sludge and wastewater treatment plants Bester,K. (2003), Singer, H. et al. (2004), Paxeus, N. (1996). So, in general for pharmaceuticals as well as antibiotics, only limited data are available considering sorption, degradation and transport in relation to groundwater reservoirs.

8.2 Possible emerging contaminants within pharmaceuticals and antibiotics

It must be emphasised that frequent use does not equal high groundwater contamination risk. Evidently, aspects of concentrations, degradation, effect levels, mixtures and leaching characteristics must be taken into consideration. However, as data for such assessment of groundwater contamination potential is not available it may be relevant to search for possible emerging candidates within the drugs that are frequently used, as exemplified above. Also, formation of metabolites is highly relevant for this group of compounds as many drugs are designed to be degraded before the pharmacodynamic effects are achieved. In relation to possible leaching such metabolites may differ significantly from the applied compounds. As very few groundwater related data exists the search for emerging contaminants within this group must be based upon use and source evaluation. Thus, from the literature survey and data on use a set of initial primary candidates can be identified:

aminoglycosides, ibuprofen, paracetamol, penicillines, sulfadiazine, sulfadimidine, sulfadoxine, sulfamethoxazole, sulfatroxazole, tetracyclines, tiamulin, trichlosan, trimethoprime, and tylosine

A literature search on "web of science" using the terms (water* or soil*) in combination with one or several of these compounds demonstrated that the majority of publications are addressing the analytical aspects such as LC-MS method development as exemplified by Hamscher,G. et al. (2002) and Lindsey,M.E. et al. (2001). A relatively large number of publications were related to tetracycline Jacobsen, A.M. et al. (2004), Lindsey, M.E. et al.

(2001), Hamscher, G. et al. (2002), Lindsey, M.E. et al. (2001), Hamscher,G. et al. (2001), Chee-Sanford, J.C. et al. (2001), Hamscher, G. et al. (2000), Rabolle, M. and Spliid, N.H. (2000) Also degradation and sorption studies has been made on these compounds, for example on tylosine Ingerslev and Halling-Sorensen (2001), Rabolle, M. and Spliid, N.H. (2000) Jacobsen, A.M. et al. (2004). A model for degradation of trichlosan has been made Zhang, H.C. and Huang, C.H. (2003). However, in general, the data in the existing literature are few and a probably insufficient for modelling studies and evaluation of fate and risk .

9. Microorganisms

Microbial contamination of waterbodies is a major concern for all waterworks and the use of chlorination is common practice in many countries. The use of chlorination is problematic due to taste and the fact that some microorganisms is resistant to the chlorination; thus many countries including Denmark resist to the use of chemical safeguiding the drinking water. Further the use of chlorination can at certain occations lead to the formation of chlorinated orgnic compounds with unknwn health effects.

Concerns for microbial contamination is in this review limited to the potential contamination of groundwater bodies with pathogenic microorganisms in the open land. Thus contamination of fresh water streams and lakes following surface runoff are not taken into account.

The major sources for microbial pathogens to enter the soil and subsequently the groundwater environment is in three areas: 1) the use of life stock manure as fertilizer in agriculture; 2) the use of wastewater sludge on farmland; 3) the septic sewage systems in the open land. The general problem reviewing these areas is the lack of systematic and representative methods that allows the measurement of pathogens in the groundwater. In the following three sections the current knowledge of microbial contamination of groundwater due to the above mentioned three sources will be addressed. The three major groups of microorganisms (bacteria, virus and protozoa) will be adressed and the section will be followed by an discussion of the available methodologies.

9.1 Bacterial contaminants.

In the city of Walkerton (Ontario, Canada) in May 2000, 2300 people where medical treated (7 died) due to contamination of the water system with two bacteria, *Eschericia coli* 0157:H7 and *Campylobacter jejuni*. The bacterial contamination originated from life stock manure. The bacteria were most likely transported to the aquifer by infiltration water although direct entry of surface runoff into the groundwater well could not be ruled out (Unc and Goss 2004). Bacterial contaminants entering a groundwater aquifer through infiltration after “current best manure management practices” has lead to an unexpected high risk in connections with the safe use of groundwater as drinking water source (Unc and Goss, 2004). In an older work (Goss et al., 1998) it was found that the proportion of groundwater wells with contamination of faecal bacteria were higher in areas where manure was spread compared to areas where only mineral fertilizers were used. In other cases drinking water associated outbreaks of *Eschericia coli* O157 has been reported and related to cattle faeces but not demonstrated if the contamination of the water body was done through badly maintained wells or through soils (Dev et al. 1991; Swerdlow et al. 1992).

A Danish study (Brüsch et al. 2004) found colifom bacteria and termotolerant coliform bacteria in respective 26% and 15% of 621 individual wells. The source of the contamination could not be disclosed since most of the investigated well (also the ones having no coliform bacterial contamination) is placed within the close distance to a septic sewage system. Further all wells were situated in agricultural areas and no registration have been done whether the area are impacted by manure or not.

The heterotrophic plate count (HPC) is the traditional method to enumerate the totale count of microorganisms in drinking water (Allen et al 2004). The HPC technique enumerates a culturable fraction of the bacterial community including potential pathogens but also unproblematic soil and groundwater associated bacteria would be enumerated using the technique. The HPC counts can therefore not be linked to any apparent health associated effect and no WHO or EPA guidelines exist for these counts (Allen et al 2004). However some countries, including Denmark, have established mandatory limits for HPC (Allen et al. 2004), and in the Danish survey mentioned above heterotrophic plate counts (Plate count agar at 37°C, limit 20 CFU per 100ml) was exceeded in 200 of the wells (32%). In a study of 10 small waterworks in Quebec in Canada the total coliforms was between 2 and 41 cfu per 100 ml with HPC counts of between 100 and 2200 cfu per ml. The proportion between total coliform bacteria and HPC was anything but constant varying between 0,005 % and 0,12 % (Coulibaly and Rodriguez, 2004).

The survival of bacterial pathogens (*Eschericia coli* O157, *Salmonella*, *Campylobacter* and *Listeria*) where investigated in dairy slurries and old fashion heating manure heaps (Nicholson et al 2005). In the heating heaps the strains died out in between 2 and 8 days while in the dairy slurry the pathogens survived up to six months (Nicholson et al 2005). The survival after application to soils was further studied after land mixing into arable land topsoil or surface applying on grassland. In both cases the bacterial numbers were found to decrease markedly within one month, but the fraction of leached pathogens were not determined (Nicholson et al. 2005). Transport of *Eschericia coli* O157 from cattle slurry applied through drained plots were found to highly depended on rainfall and between 0.2% and 10% of the applied *Eschericia coli* O157 were found to leach to the drains (Ogden et al 2001). In a later study Vinten et al. (2002) also found leaching of *Eschericia coli* O157 to drains after application in dairy slurry, the first drain flow event contained between $1x10^3$ and $1x10^4$ CFU ml^{-1} which is regarded a high concentartion. No studies have been dealing with the subsurface transport and survival of pathogens. However Artz and Kilham (2002) found that *Eschericia coli* O157 was heavily predated in most well waters.

The genus *Salmonella* is a well known bacterial pathogen that can create human infection has in a recent field trial been found to survive for only short time in soil (Gessel et al. 2004). However some discrepancy exist since *Salmonella* sp. has previous been reported to survive well in soil (for review see Mandsley et al. 1995). Like it has been recorded for many bacteria the method of detection might be a case when looking at *Salmonella* sp. in soil, since an active but non culturable state of *Salmonella* sp. has been described (Marsh et al. 1998).

9.2 Virus contamination

A recent review of human enteric viruses in the environment Rzezutka and Cook (2004) includes only studies of survival of enteric viruses seeded into groundwater samples. The survival of poliovirus and echovirus were high at 5°C since no decrease could be observed in the 8 weeks experiment. The related survival in soil has been addressed in several papers including a paper showing survival of coxsackievirus B3 added to municipal sludge and duck into Danish soils placed in lysimeters (Damgaard-Larsen et al. 1977). This paper showed some decline of the virus over the time of the experiment but it was not possible to detect any viruses in the leaching water.

Detection of human virus has hitherto been dependend on difficult and timeconsuming method, if reliable methods at all have been available. Due to the recent establishment of methods to RT-PCR amplify viral RNA directly from environmental samples the quantification of human virus in the soil and water environment is now within reach. However the methods still need validation.

The use of bacteriophage is common in the investigation of survival and transport of viruses in the environment (Harvey and Ryan, 2004). From these studies it can be concluded that the bacteriophage PRD1 is transported through many soil matrices measured in meters per hour (McKay et al 1999, Paul et al. 2002). If these data for bacteriophage transport can be used directly as indicators for virus transport has not yet been proved.

9.3 Protozoan contamination

The protozoan parasite *Cryptosporidium* sp. is widely recognized as a pathogen of domesticated livestock and believed a wide spread threat to public health (Fayer, 2004). In a review by Carey at al (2004) mentioning a particular large outbreak of acute watery diarrhea in Milwaukee, USA that affected 400.000 residents, highlights the public health significance of *Cryptosporidium* sp. The review paper by Carey et al. (2004) quotes 263 references in various fields of biology, persistence and detection of *Cryptosporium* sp. The oocyst is very resistance to a long list of environmental stresses, and surface runoff is well understood (Davies et al. 2004). However, information on transport of *Cryptosporium* sp. through soil to groundwater after application to agricultural fields is non-existing.

In a technical report for American Water Works Association Hancock et al 1998 (cited in Fayer et al. 2004) claims that 9,5-22% of U.S. groundwater samples tested positive for *Cryptosporidium*. The UK drinking water inspectorate introduced *Cryptosporidium* legislation during 1999 not allowing more than one oocyst of *Cryptosporidium* sp. in 10 liters of water (Pearce et al. 2002).

Cryptosporidium sp. is the most well described protozoan water contaminant but also *Giardia lamblia* is important waterborne protozoan parasite (Thurston et al. 2001).

Giardia lamblia is 0,6-0,8 µm large and a quite hardly organisms that has been shown to survive for weeks in cold waters. We have not been able to retrieve peer reviewed information on transport of *Giardia lamblia* to groundwater but numerous US websites mention the possibility of groundwater contamination (for example http://www.des.state.nh.us/factsheets/ws/ws-4-4.htm).

9.4 The present technique and future developments.

Variants of the heterotrophic plate count / colony count in combination with enumeration of total coliforms and *Eschericia coil* is the traditional method to enumerate microorganisms in drinking water (Allen et al 2004). These techniques enumerate a culturable fraction of the bacterial community including both potential pathogens but also unproblematic soil and groundwater associated bacteria. The proportion between total coliform bacteria and HPC was anything but constant varying between 0,005 % and 0,12 % (Coulibaly and Rodriguez 2004). The total coliforms is maybe a better estimate but again an enumeration of coliforms is not a proof of problematic bacteria in the sample, neither is the lack of coliforms in the water sample proof of an unproblematic sample.

The nucleic acid based techniques are today developed for the detection of several major pathogens in water samples (Carey et al 2004; and Fey et al 2004), and the emerging technologies within automated gene analysis also indicates that prices per sample will decrease in the years to come.

10. Industrial and household wastewater products

A increasing number of compounds originating from industry and household have been detected in natural waters including ground and surface waters. Large scale reconnaissance study have for example been initiated by U.S. Geological Survey (USGS) to monitor pharmaceuticals, hormones, antibiotics, and personal care products in natural waters of the United States (e.g. http://toxics.usgs.gov/bib/bib-emerging.html). These actions have revealled a broad spectra of chemicals originating from wastewater (Kolpin et al. 2002). Similar detections have been reported in other national monitoring studies (e.g. Petrovic et al. 2004). A summary of the most detected compounds and groups included in the monitoring research in presented in table 3.

Group	**Compound**
Plasticizers	*bis*(2-Ethylhexyl)adipate
	Ethanol-2-butoxy-phosphate
	di(ethylhexyl)phthalate
	Diethylphthalate
	Triphenyl phosphate
Detergents and metabolites	*p*-Nonylphenol
	Nonylphenol monoethoxylate
	Nonylphenol diethoxylate
	Octylphenol monoethoxylate
	Octylphenol diethoxylate
Flame retardant	Bromated compounds
	Tri(2-chloroethyl)phosphate
	Tri(dichlorisopropyl)phosphate
Personal care products	Musk products
	Acetophenone (fragrance)
	Triclosan and methyl-triclosan (metabolite)
Others	Nicotine and cotonine (metabolite)
	Fluorinated organic compounds (FOCs)
	Caffeine

Table 3. Industrial and household wastewater products detected In various monitoring programs involving surface and groundwater serving as drinking water (Barnes et al. 2004a, 2004b, Lee et al. 2004)
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Groundwater aquifers may be susceptible to industrial and household wastewater when for example being located down gradient of a landfill or following bank infiltrations from exposed surface waters receiving effluent from wastewater treatment plants. Recent research have shown that a broad range of compounds from wastewaters can be transported to groundwater ressources (e.g. Barnes et al. 2004b, Scheytt et al. 2004, Wick et al. 2004). USGS have studied the occurence of organic wastewater contaminants in 72 groundwater samples and detected compounds in 67 sites (93%) (Barnes et al. 2004b). Commonly mixtures of contaminants were detected and based on their primary groups of plasticizers, detergents and their metabolites, personal care products, flame retardants and various other compounds were detected.

10.1 Plasticizers

Several plasticizers have been detected in natural waters. In all reports di(ethylhexyl)phthalate is measured as the dominant phthalate ester. This is likely related to its high production (Petrovic et al. 2004). Plasticizers was among the most frequently detected group in US groundwater monitoring by USGS (Barnes et al. 2004b).

10.2 Detergents and their persistent metabolites

Programs addressing the occurence, distribution and impact of alkylphenol ethoxylates and their metabolites in natural systems have shown that the highest concentrations were found in industrial areas. This pattern was likely attributed to discharge of industrial wastewater (Petrovic et al. 2004). This group of compounds have however also been detected in agricultural areas where sewage sludge is used as fertilizer (Petrovic et al. 2002). Due to restrictions on industrial usage of detergents it appears that the concentraions have declined within recent years in Scandinavian countries, Netherland, Switzerland, Germany and the UK (Giger et al. 2002).

10.3 Flame retardants

Brominated flame retardants are chemical additives in plastics, electronic equitement, and in different consumer items that have been added to reduce potential risk of fire. Flame retardants, mainly the polybrominated diphenyl ethers, have been widely detected in the environment and they commonly occur in wastewater. This group includes a broad range of different compounds that may give rise to many different metabolites when introduced into various environments (Fisk et al. 2003). There is however no convincing evidence for the complete degradation of these compounds, and commonly the end-product is unknown (Fisk et al. 2003). Several different polybrominated diphenyl ethers have been detected in surface and groundwater near facilities for synthesis (Ronen and Abeliovich 2000). Other flame retardants detected includes tri(2-chloroethyl)phosphate and tri(dichlorisopropyl)phosphate (Table 3). However as for the rest of the industrial and household wastewater measured in groundwater the route and their further fate is unknown.

10.4 Personal care products

Compounds used in personal care products, such as cosmetics, food supplements, sunscreens, fragrances and the like, have been found in different natural waters (Daughton and Jones-Lepp. 2001). Synthetic musk products such as polycyclic musk, musk xylene and musk ketone amino metabolites have been measured in waters including groundwater. Highest concentrations was not supricingly measured near sewage treatment plants (Petrovic et al. 2004). The antibacterial compound triclosan, used in a variety of different consumer products, have along with its main metabolite triclosan-methyl been detected in several examination of surface waters. It howevere remains unknown if this compound is capable of reaching deeper groundwater ressources.

10.5 Fluorinated organic compounds (FOCs)

In recent years Fluorinated organic compounds (FOCs) has gained much attention as possible emerging contaminants Schultz,M.M. et al. (2003). Examples of these compounds are perfluorooctane sulfonate (PFOS), perfluoro-octannate (PFOA), and perfluorooctane sulfonylamide (PFOSA). They are widely used in the manufacture of plastic, electronics, textile, and construction material in the apparel, leather, and upholstery industries. FOCs have been found in blood and environmental samples throughout the world , and recent postnatal studies on developmental and reproductive indices have questioned the former findings of low toxicological risk Lau,C. et al. (2004),Lau,C. et al. (2003) and concern for endocrine disrupter effects has been published Austin,M.E. et al. (2003).
Studies of biochemical degradation of perfluorooctanesulfonate (PFOS) and perfluorooctanoic acid (PFOA) has been published, and Perfluorooctane sulfonate was found to be quite mobile Meesters,R.J.W. and Schroder,H.F. (2004). In the US perfluorooctanesulfonate and other perfluorinated surfactants has been found in groundwater samples. In conclusion, emerging contaminants may be found within this group of compounds

11. Discussion of emerging contaminants in Danish groundwater

In Denmark the protection of the groundwater resurce is of high priority, due to environmental as well as ressource considerations. Thus, in most other countries intensive use of surface water calls for concern over certain types of contaminants linked to the open freshwater environment. For instance compounds present in sun lotion is an increasing problem in warmer areas, where surface waters is used for leasure such as swimming, may be of lower priority in relation to Danish drinkingwater quality aspects. However, these aspects can not be totally ignored as surface waters is also used for drinking water in Denmark, although to a much smaler extent than groundwater, where more than 98% of the drinkingwater originate from groundwater reservoires. Such considerations are relevant to compounds as well as microorganisms escaping from municipal wastewater treatments facilities or substances that are subject to surface runoff.

In general, the most intensively monitored and analysed group of compounds is the pesticides. This is likely due to the simple but rigid detection threshold: 0.1ug per litre. Only few pesticides and metabolites found in ground water in Europe or in USA have not been included in the Danish monitoring system. However due to their persistence and mobility it is recomended that the following pesticides and degradation products are included in the national monitoring programme: Didealkyl-atrazine, deethyl-hydroxy-atrazin, deisopropyl-hydroxy-atrazin, didealkyl-hydroxy-atrazin, dieldrin and possible persistent transformation products from bromoxynil and ioxynil. For some of these compounds more knowledge on the fate in soil and groundwater is needed for designing a propper monitoring strategy.

Hormones relevant to the aquatic environment originating from wastewater treatment facilities have recently been concluded to be of minor importance. This may be related to the high activity within the estrogen degrading microbial communities. However, sources to groundwater contamination may be manure used on farming areas, sewage used as fertiliser or pollution originating from leaking sewage systems and perculation of domestic wastewater. It has recently been shown that estrogens leach through structured agricultural soils in concentrations 10 times higher than the known effect concentration on aquatic organisms. Considering endocrine-disrupting effects in relation to groundwater contamination a basic understanding on sorption, transport and degradation needs to be established. In particular, this is relevant for the prime candidate compounds 17ß-estradiol, estrofem ethinylestradiol.

Microorganisms being pathogenic to humans are a great concern in all drinking water production plants using surface water as source. However both a recent GEUS report and international literature point to the fact that groundwater exposure should be considered. Pathogenic bacteria have been quantified in high numbers in drains below agricultural soils treated with manure, and it is known that transport time of virus in soil is fast making carryover from sewage sludge and septic tanks a likely risk. However, for all classes of pathogens (virus, bacteria and protozoa) a need for accurate and meaningful detection and quantification methods is evident. This should likely be based on combinations of cultural organisms and DNA/RNA quantification using PCR based detection. Also here a basic understanding of sorption, transport and survival of microorganism in soils needs to be established to quantify and direct an optimal monitoring strategy.

Within pharmaceuticals several likely groundwater contaminants can be identified. An environmental risk assessment has been made for the 25 most used pharmaceuticals in the primary health sector in Denmark by Stuer-Lauridsen,F. et al. (2000). The PEC/PNEC ratio exceeded one for ibuprofen, acetylsalicylic acid, and paracetamol. A recent Danish report has investigated the content of environmental contaminants in liquid manure, including veterinary drugs. From this study a number of eight possible antibiotic contaminants can be identified: sulfadiazine, sulfadimidine, sulfatroxazole, sulfadoxine, sulfamethoxazole, tiamulin, trimethoprime and tylosin. Also, within the monitoring program a screening project is being been planed aiming at a clarification of the potential groundwater contamination risk related to several pharmaceutical compounds. Aiming for an overall screening of the invironment several other matrices such as wastewater, sediment and sludge is also intended for inclusion in the project being planned.

Synthetic musk products such as polycyclic musk, musk xylene and musk ketone amino metabolites have been measured in freshwaters systems including groundwater. Further the antibacterial compound triclosan, used in a variety of consumer products, have along with its main metabolite triclosan-methyl been detected in several examinations of surface waters. However, it remains unknown if this compound is capable of leaching to deeper groundwater resources.

The compounds and microorganisms highlighted in the present report are likely contaminants of large groundwater resources. Many other compounds has been considered including plant toxins, metals and several other classes of industrial chemicals – without finding them to be of particular concern. With the exception of the mentioned degradation products from pesticides it would be needed to establish recommended maximum concentrations. Also, in many instances analytical methods and monitoring startegies needs to be established for clarification of the potential risk to the groundwater ressource – and identification of the actual emerging contaminants.

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