The flow of chemicals within the sewage systems - possibilities and limitations for risk assessment of chemicals

**Lidia Strandberg, Magnus Johansson, Helena Palmquist
and Mats Tysklind**

August, 2001

The flow of chemicals within the sewage systems - possibilities and limitations for risk assessment of chemicals

Lidia Strandberg[1], Magnus Johansson[1], Helena Palmquist[2] and Mats Tysklind[1]

[1]Environmental Chemistry, Department of Chemistry, Umeå University,
 SE-901 87 Umeå, Sweden
[2] Division of Sanitary Engineering, Department of Environmental Engineering,
 Luleå University of Technology, SE-971 87 Luleå, Sweden

Preface

Sustainable Urban Water Management is one of the 23 currently ongoing programs within the Swedish Foundation for Strategic Environmental Research (MISTRA). The program aims at evaluating how well different systems may meet the proposed goals for sustainable urban water and wastewater system related to economy, social factors, preservation and recovery of resources, technical aspects, hygiene, and environmental impact such as chemical risks. Chemical risks within different sewage systems have been identified as an area where knowledge is rather limited and needs to be further evaluated and investigated.

This project was focused on evaluation of the current knowledge in the field of chemical risk assessment. The main goal of this project was to find existing methods, which can be useful for evaluation of risks associated with the flow of potentially hazardous chemicals within defined sewage systems. In case of lack of such methods this project should propose new methods or at least present the new trends and developments in this area.

This report was performed based on a three month literature study. We emphasize that the present report is only a preliminary work, which should help to identify substantial gaps in knowledge and prepare for future research projects within the next years.

This report was performed by Environmental Chemistry, Umeå University in collaboration with the Division of Sanitary Engineering from Luleå University of Technology.

This project was financial supported by The Urban Water Program and Umeå University.

The authors

Contents:

1.   General Introduction

During the last three decades, the impact of chemical pollution has focused almost exclusively on conventional "priority pollutants" which are persistent organic pollutants (POPs) such as polychlorinated biphenyls (PCBs), polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs), polycyclic aromatic hydrocarbons (PAHs) and organochlorine pesticides, and different heavy metals. As the use and emissions of for example PCBs and PCDD/Fs have been restricted or banned over the last 20 to 30 years, new groups of substances have been in focus. These chemicals are however not "new" in terms of production and use, they are new because they have not yet received the same attention as the other more traditional chemicals in regard to their potential health and environmental effects [Alcock & Jones, 1999]. As an example, the pharmaceutical compounds have received comparatively little attention despite the fact that they are used in large amounts throughout the world. Most of these products are disposed or discharged into the environment on a continual basis via domestic and industrial sewage systems [Daughton & Ternes, 1999].

The sewage system and the wastewater treatment plants constitute a connection between the technosphere (industry and households, etc.) and the environment. Today, more than 75.000 chemical compounds are present in the technosphere and 30.000 of these are regarded as "every day" chemicals or regularly used in households. The sewage treatment plants can be seen as a funnel for waste and therefore chemicals transported from the technosphere to the environment.

Sludge from wastewater treatment is the predominant by-product from today's wastewater handling strategies. Sludge is contaminated by organic and inorganic pollutants to varying degrees, as a result of domestic and industrial wastewater discharges to municipal wastewater treatment plants. Research has shown that sewage sludge is a very efficient sorbent for all lipophilic contaminants that might be transported into the sewage system. It has been estimated that during the next years a significant number of new wastewater treatment plants in countries within the European Union will be build and consequently more sludge will be produced [Augulyte, 2001]. Thus, the growing volume of sewage sludge that needs to be taken care of in an environmentally acceptable way will increase.

Development of more sustainable wastewater systems includes the utilization of nutrients from human urine and faeces as fertilizers in agriculture. One potential approach for reducing pollutants in wastewater nutrients is to apply alternative wastewater handling strategies where *e.g.* separation of the wastewater fractions at the source could be one solution. Human urine contributes with approximately 80% of the nitrogen and 55% of the phosphorous in household wastewater, but only 1% of the total flow. This fact makes urine interesting to separate at the source [Jönsson *et. al.,* 2000]. The main argument supporting the diverting wastewater systems is to avoid mixing of polluted wastewater streams (industrial discharge, stormwater and grey wastewater from households) with less polluted wastewater fractions such as urine and faeces.

The Swedish Government decided in 1999 that the environment should be free from man-made substances and metals that represent a threat to the human health and the biological diversity. This means that the levels of substances that occur naturally in the environment must be close to background levels, while the levels of man-made substances must "be close to zero" [SOU 2000:53].

To accomplish the objective "a non-toxic environment" among other initiatives, new guidelines on chemicals policy has been adopted and the Swedish Government intends to implement the new guidelines within the next 10-15 years [SOU 2000:53]. One interesting part of these guidelines is the definition of substances, which can be considered as a risk for human health and the environment. In these guidelines, a general criteria model based on the two corner-stones persistence and bioaccumulative potential was suggested and this will be briefly presented herein. Hence, knowledge of toxicity is not necessarily needed for phasing out a chemical, which shows high persistence and bioaccumulation. This criteria model might be implemented in the assessment of potential risks associated with chemical substances in any water and wastewater system. These new guidelines do however not cover the assessment of mixtures of chemicals, which are one crucial point in all risk assessment attempts in an environmentally relevant situation, such as the case of *e.g.* wastewater and sewage sludge [SOU 2000:53].

2. Objectives

The aim of this project was to provide a basis for evaluation of the risks associated with the flow of potentially hazardous chemicals within two different sewage systems. The first was a conventional system and the second was an alternative, urine diverting wastewater system.

This report is a general overlook and review of the current situation in the field of risk assessment for existing and new chemicals within these sewage systems. It has to be emphasized that this report is a preliminary work, which should help not only to recognize the current situation and to identify areas where substantial gaps in knowledge exist, but also to plan a new strategy in order to build environmentally friendly sewage systems in our society.

This report was based on scientific, public and governmental papers and reports as well as on personal communications.

3. The flow of chemicals within the sewage system

One important aspect of risk assessment is the feedback to contaminant sources, which is essential for the possibilities to take action in order to improve any future design of sewage systems. To achieve this goal, a good characterization of all parts from the sources, the wastewater fractions to the waste products is required.

The schematic picture of the flow of chemicals within the sewage system is presented in Figure 1. The wastewater coming from different sources into the wastewater treatment plant (WWTP) is described as separated flows of five fractions (urine, black and grey wastewater, stormwater and industrial wastewater), while the outlet is represented by three fractions: sewage sludge and treated wastewater coming out from the WWTP, and wastewater nutrients originated from human urine and faeces.

Sources   *Flow fractions*
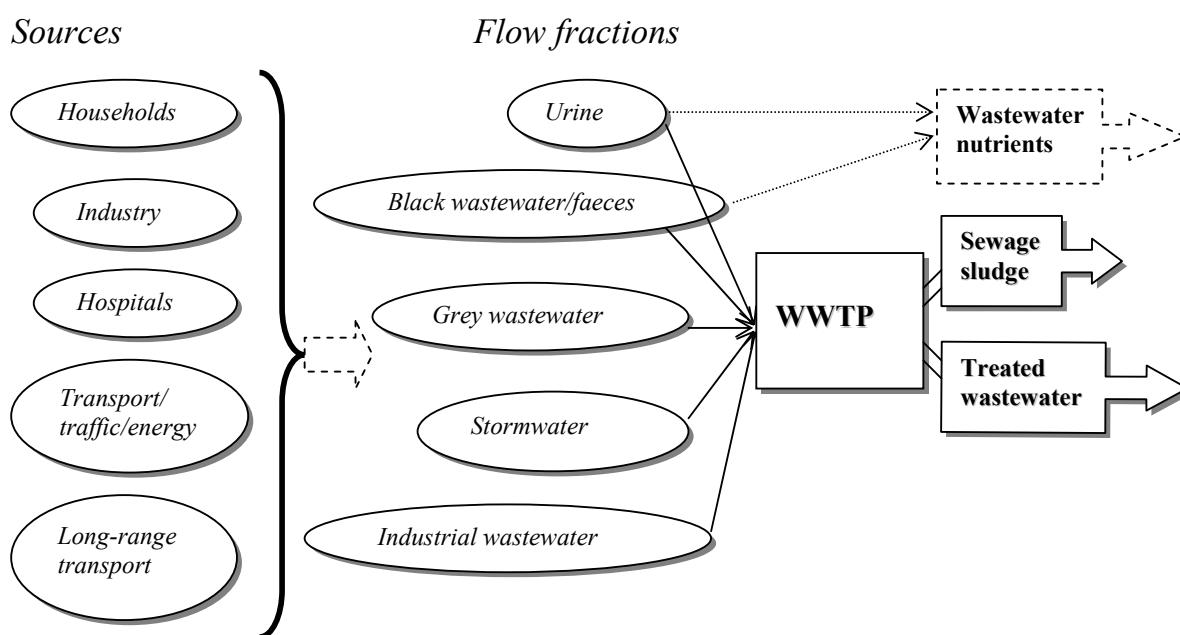
Figure 1. A schematic picture of flow of chemicals within the sewage system (WWTP: wastewater treatment plant).

3.1. Characteristic of sources

The composition of wastewater is a complex mixture of various pollutants from different sources (see Figure 1). The amount and content of wastewater depends on the number of inhabitants, hospitals, industries, etc. the sewage system is serving. The estimated contribution from different sources, here exampled by the Göteborg Regional Sewage Work (serves a population of about 550.000 people) showed that about 33% (of approximately 120 Mm^3 of wastewater treated annually) are coming from households, 5% from the public sector including hospitals and schools and about 10% from larger and smaller industries [Paxeus *et al.,* 1992]. The remaining 50% was coming as stormwater, infiltration and inflow of surface and ground waters; see Figure

2 [Paxeus *et al.,* 1992]. Worth mention is that industry includes a very wide range of different branches such as chemical industry and production industry. As a consequence, the composition of chemicals entering the sewage system originating from industrial activities cannot easily be described and must therefore be individually evaluated in each specific case. Further, the influence of stormwater address an important issue to what extent long-range transport and local sources contribute to the total burden of pollutants in wastewater.
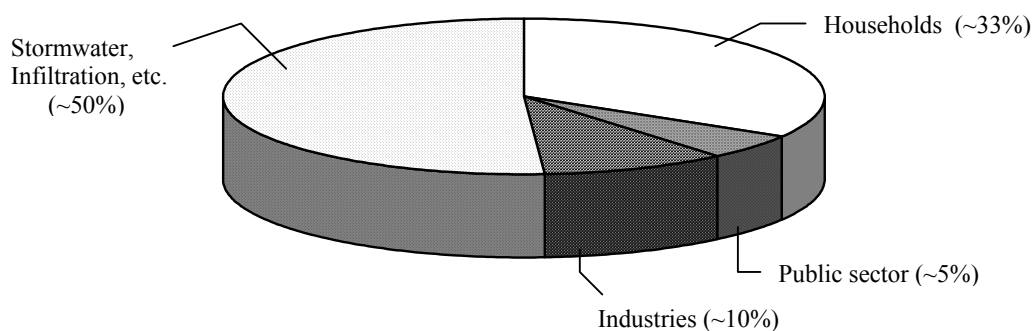

Figure 2. Estimated contribution from different sources at the Göteborg Regional Sewage Work [Paxeus *et al.,* 1992].

3.2. Characteristic of flow fractions

Wastewater coming into the WWTP is a mixture of toilet water, grey water, industrial wastewater, drainage and stormwater. The major part of nutrients originates from urine. Grey water originates from dishing, washing and bathing/shower and contains nutrients in small amounts except for phosphorus. The phosphorus content of grey water depends on the use of phosphate detergents.

Pollutants in stormwater originate from surfaces such as streets and roofs that are washed with rainwater and melt water from snow. The degree of pollution varies and depends on type of surface that the run off comes from. Stormwater has generally a higher content of metals and a lower content of oxygen consuming substances than domestic wastewater.

The chemical composition of industrial wastewater can vary a lot and depends on type of industrial process used. In Sweden every municipality may state restrictions on what substances that may be supplied to the sewer net. The municipalities may for example state limiting values or prohibition of certain substances. These restrictions are valid both for connected industries and households. Since 1988, special attention has been given to the organic priority pollutants. Previous to that the efforts were focused on traditional parameters like BOD (Biochemical Oxygen Demand), nutrients, oil content and content of a few heavy metals such as copper, cadmium and lead [Lundin, 1999].

3.3.   Combined sewage system (with urine) *versus* alternative system

The development of a sustainable sewage system includes the utilization of nutrients from human urine and faeces in agriculture as fertilizers. One important reason for this strategy is the fact that urine is the source of around 55-70% of phosphorus and around 80-90% of nitrogen in toilet water. When the combined system is applied, a mixing of human organic waste occurs with other forms of pollution, leading to contamination of wastewater nutrients by hazardous compounds such as heavy metals or organic pollutants.

The separation of different fractions of wastewater for example urine and faeces (see Figure 1) will obviously increase the control of the flow of hazardous chemical compounds. Furthermore, those fractions could potentially give waste products with low contents of toxic chemicals but high contents of nutrients. It is important to mention that the urine fraction besides beneficial nutrients also may contain some unwanted compounds, for example excreted pharmaceuticals.

The experience from systems with urine separation is quite limited and most systems in use in Sweden are small-scale systems serving less than 100 users. One study from northern Sweden [Hanaeus *et al.,* 1997] showed that when the sewage system was equipped with urine separation, less than half of the nitrogen and phosphorus from human urine disposed through the toilets of the village where the system was applied was successfully collected. In another study Jönsson *et al.* [2000] recommended some technical improvements for such separating systems and they also discussed some aspects concerning hygiene, reliability, resource usage and environmental effects. Moreover, based on Life Cycle Assessments (LCA) the authors concluded that urine separating toilet systems were of advantage for the environmental effects when comparing to the conventional wastewater system. The human urine fraction mainly contained substances that originate from intake of food and pharmaceuticals. However, the detailed information about those substances as well as about their potentially effects after spreading to arable land were not investigated in this study.

In another study the use of human urine was reported to be problematic with regard to management, storage and transportation [Lind *et al*., 2001].

Summary

- *Wastewater coming into the wastewater treatment plant (WWTP) is a complex mixture of various pollutants from such sources as household activities, the public sector, industries and long-range transport.*

- *Human urine and faeces are a dominating source of phosphorus and nitrogen in wastewater.*

- *When the combined system (without separation of urine and faeces) is applied there is a mixing of human organic waste with other forms of pollution such as heavy metals or organic pollutants.*

- *The separation of human urine and faeces from the other fractions of wastewater may increase the control of the flow of hazardous chemicals within the systems.*

- *Up to date, the experience from systems with urine separation is limited.*

4.   Sewage sludge as a "useful" product from WWTP

Sewage sludge is the predominant by-product from today's wastewater handling strategies. Sewage sludge production in Sweden was estimated to be approximately 240.000-ton dry weight per year in 1996 [SNV, 1996a].

4.1.   Chemical characteristic of sewage sludge

Typical sewage sludge contains organic matter, nutrients such as nitrogen (N), phosphorus (P), and potassium (K), pathogens such as bacteria, viruses and parasites, and metals and various organic compounds [US-EPA, 1995]. The composition of sewage sludge is variable, because of different wastewater influents received by the WWTPs. The most important fluctuations in the concentration of various contaminants are dependent on locality and season. The different technologies used in the treatment plants also play a very important role [Schnaak *et al*., 1997].

Examples of metals that are commonly present in sewage sludge are given in Table 1, while some toxic organic compounds are listed in Table 2.

Table 1. Examples of heavy metals commonly present in sewage sludge. Concentrations are given as mg/kg dry weight (mg/kg dry wt.).

Metals	Northern Sweden 1993-1995[1]	Umeå 2000[2]	Southern Sweden 1981-1997[3]	Swedish muni-cipal sludge 1997[4]	Swedish legislation[5]
Lead (Pb)	4-59.5	14-33	59-180	27	100
Cadmium (Cd)	0.2-2.7	0.31-1.1	1.3-3.5	1.1	2.0
Copper (Cu)	16-425	15-110	651-2000	270	600
Chromium (Cr)	11-58.5	11-23	28-406	23	100
Mercury (Hg)	0.3-2.2	0.36-0.88	2.0-6.9	0.8	2.5
Nickel (Ni)	3.8-37	6.7-19	13-111	12	50
Zinc (Zn)	150-860	340-440	595-1100	450	800

[1] Sludge from northern Sweden (Västerbottens län) collected between 1993-1995 [Olofsson & Eriksson, 1996]
[2] Sludge from Umeå collected in 2000 [Augulyte, 2001]
[3] Sludge from southern Sweden (Lund and Malmö) collected between 1981-1997 [Andersson & Nilsson, 1999]
[4] Municipal sludges in Sweden 1997 (median value given here) [Levlin *et al.,* 2001]
[5] The maximum concentration for the heavy metal content in sewage sludge for utilization in agriculture according to Swedish legislation [Levlin *et al.,* 2001]

Metal concentration in sludge depends on the type and amount of industrial wastewater discharged into the municipal sewage system. As metals generally are insoluble, they usually are present at higher levels in sewage sludge than in wastewater. Among different metals, cadmium frequently is found to exceed the maximum allowed concentration in sewage sludge as can be seen in Table 1.

In a resent study Eriksson [2001] investigated sewage sludge from 48 treatments plants from all over Sweden. The results showed that concentrations of metals in most cases were below the maximum concentration in sewage sludge allowed for utilization in agriculture. However, nine

of these plants had one or more metals (*e.g.* Cu, Cd, Zn, Hg, Ni, Pb) that were above the allowed maximum concentration in sewage sludge.

Many synthetic organic chemicals from industrial waste, household products, and pesticides are potentially hazardous. They are here referred to as toxic organic chemicals (TOs) (see Table 2). Based on a literature survey, sludges from European countries and North America from recent years typically contained about 1 to 100 mg/kg (dry wt.) TOs. Of this, more than 90% were at concentrations less than 10 mg/kg (dry wt.) [O'Connor, 1996].

Table 2. Examples of toxic organic compounds commonly identified in sewage sludge. Concentrations are given as mg/kg dry wt.

Compound	International Survey[1]	Umeå 1993-2000[2]	Southern Sweden 1981-1997[3]	Swedish legislation[4]
Phthalate esters: Di(2-ethylhexyl)phthalate	≥ 100		70-313	
Polycyclic aromatic hydrocarbons: Benzo [*a*] pyrene Fluoranthene ∑PAH	1-10 1-10	0.41-2.5	1.0-4.3	3.0
Polychlorinated biphenyls: ∑PCBs	0.5-1[*]	0.015-0.079[**]	0.2-0.9	0.4
Chlorinated pesticides: ∑ DDT	< 1	0.0025-0.16		
Volatile aromatics: Benzene Toluene	1-10	0.042-8.7	3.0-7.0 1.5-4.5	5.0
Nonylphenol		1.7-42	17-1285	50

[1] [O'Connor, 1996]
[2] Sludge from Umeå collected between 1993-2000 [Augulyte, 2001]
[3] Sludge from southern Sweden (Lund and Malmö) collected between 1981-1997 [Andersson & Nilsson, 1999]
[4] The permissible concentrations for the indicator compounds content in sewage sludge for utilization in agriculture according to Swedish legislation (∑PCBs is sum of seven selected congeners, while ∑PAHs is sum of six compounds) [SNV, 1995]
*Aroclor 1248, 1254
**Data from 1993-1999

Table 2 includes only a few examples of organic compounds present in sewage sludge. The data are collected from various sources and the number of compounds analysed for each chemical class (*e.g.* ∑PCBs, ∑PAHs, ∑DDT) varied. The aim was to get a general idea of what concentration that can be found in sewage sludge.

There are a few broad surveys undertaken about chemicals potentially present in sewage sludge. A British survey presents an extensive list of about 300 organic compounds, which have been individually identified in sludge worldwide [Wilson *et al.,* 1996]. The list includes such compounds as monocyclic aromatics (e.*g.* chloroanilines, chlorobenzenes, phthalates and phthalate acid esters), organotin compounds, PAHs, PCDD/Fs, organochlorine pesticides,

surfactants and their metabolites, etc. Two other studies [Alcock *et al.,* 1999; Klöpffer, 1996] suggest that it is important to give priority also to new groups of compounds such as brominated aromatic compounds, chlorinated paraffins, polychlorinated naphthalenes, quintozene, polydimethylsiloxanes, nitro musks, biologically active compounds and pharmaceutical compounds.

4.2. Disposal routes and benefits associated with application of sewage sludge on arable lands

There are many routes for disposal of sewage sludge. In Europe, a major route is land applications, which may include both usages on agricultural lands as well as on forestlands. Alternative ways of disposing sludge, besides spreading it on arable land, include landscaping (final covering of landfills, road shoulders, etc), deposition on landfills and incineration. No full-scale incineration of sewage sludge occurred in Sweden in 1996, while about 15% of the total mass of sludge treated in Europe at present is incinerated [SNV, 1996; Augulyte, 2001].

The application of sewage sludge on arable land might affect the soil on both a short- and long-term basis. It is well known that amendment with organic residues can give beneficial effects such as provision of plant nutrients, increasing humus content and thereby increased water holding capacity, improved structure and an increase of the cation exchange capacity [Johansson *et al.,* 1999]. Further, a Swedish study "Sludge application on agricultural land" [Andersson & Nilsson, 1999] covering a period of 16 years (1981 – 1997) showed that spreading of sludge has positive effects on the ecosystem. The nutrient status of soil improved after sludge application and the impact on crops was clearly positive. Application of sludge also had a positive effect on the earthworms, which were stimulated in growth and fertility.

4.3. Potential risks associated with using sewage sludge on arable lands

The use of sewage sludge is not only beneficial but can also have negative effects. As described earlier (paragraph 4.1) sludge contains besides plant nutrients and organic matter also residues from all effluent sources in the community connected to the sewage plants. These residues might be harmful and the three most important groups of concern are heavy metals, persistent organic compounds and pathogens. It is notable that the concentration of heavy metals in the sludge from Swedish wastewater treatments plants is clearly decreasing over time [Eriksson, 2001]. Also, the level of many organic compounds such as PCBs (see Figure 3), nonylphenol and dioxins are decreasing. It is important to mention though that due to lack of data for many specific organic compounds, it is difficult to present their time trend in Swedish sludge.
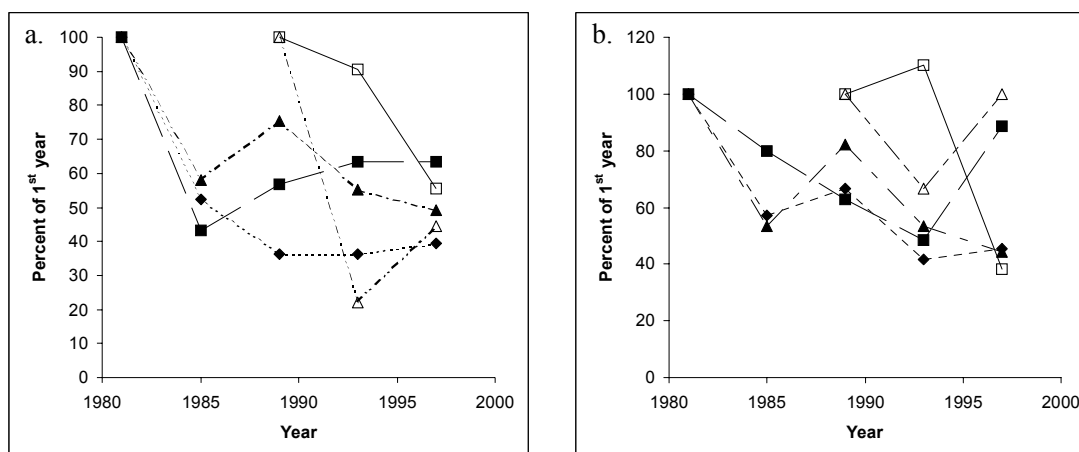
Figure 3. Time trends of the concentration of lead (♦), cadmium (■), mercury (▲), PCB (△) and EOCl (□) in sewage sludge from WWTPs: in Igelösa, Lund (a) and Petersborg, Malmö (b) both situated in southern Sweden (EOCL: Extractable Organic Chlorinated Compounds) [Andersson and Nilsson, 1999]. The time trends are presented as a percentage related to the year 1980 (100%).

Several investigations have been performed regarding the effects of sewage sludge on soil microorganisms [Johansson *et al.,* 1998]. Silver, for example in concentration known to occur in sewage sludge amended soil may seriously affect the microbial biomass [Johansson *et al.,* 1998]. Another study [Dahlin *et al.,* 1997] have shown that sewage sludge applications between 1966 and 1989 in studied field experiment in Sweden increased soil concentration of such metals as Cd, Cr, Cu, Pb and Zn. Additionally, most of the measured microbial properties (*e.g.* acetylene reduction activity) were affected by the sludge addition, although effects were generally moderate [Dahlin *et al.,* 1997].

Chemicals introduced to agricultural soils by sludge application may persist in the soil for different periods of time. Their persistency in soil depends mainly on their physico-chemical properties and their form in the soil. Other factors of importance for the fate of chemicals in soil are the strength by which they can bind to soil particles, their vapour-particle relationship, which determines their evaporation to the atmosphere from the soil surface. Moreover, they can leach down to the groundwater or be taken up by plants. The degradation processes in the soil are hydrolysis, photolysis and biodegradation by microorganisms [SNV, 1996].

It was suggested that due to strong sorption of metals to organic matter in soil, it would be expected that metals generally should stay in the soil and only to small amount leach down to the groundwater [CES, 2000]. However, an investigation performed 15 years after a single application of municipal sewage sludge onto soil showed that a large fraction of certain metals actually redistributed and moved out of the soil surface and that there is a risk for surface and ground water contamination [McBride *et al.,* 1997]. A similar observation has been reported by Richards *et al.* [1998]. In that study, some metals were found after nearly 20 years in the sludge plot leachate, at significantly higher concentration than in a control plot. The concentration of Cd, Ni and Zn exceeded concentrations recommended by American drinking water standards. Elevated levels of Cd, Cu and Ni were also found in grass growing on the sludge plot.

How long time a compound will persist in soil can be evaluated based on the pollutant half-life ($T_{1/2}$). $T_{1/2}$ is the time it takes for the concentration of a pollutant in a certain compartment to fall by 50 %. Gillett [1983] distinguished priority pollutants on the basis of their soil half-life as follows:

Class A: half-life <10 days – chemicals would most likely be lost from the soil-plant system before they could be taken up

Class B: half-life between 10-50 days

Class C: half-life >50 days – might be expected to be even more recalcitrant when sludge-borne or sorbed

According to Gillett [1983], a compound with a half-life exceeding 14 days is considered as sufficiently persistent to be of concern in the environment and might be taken up by plants.
The $T_{1/2}$ of compounds are estimations based on laboratory studies. For instance, half-lives in soil of nonylphenol (NP) and di(2-ethylhexyl)phthalate (DEHP), which are compounds very often present in sewage sludge, have been reported to be one to two weeks and almost three months, respectively [SNV, 1996]. For PCDD/Fs, the half-lives in soil has been estimated to be over 10 years, while for some PCBs it is between 2 and 6 years [SNV, 1996]. Thus, these recalcitrant will persist in the soil for years to come and likely become part of the soil humus [Gillett, 1983].

The half-life of compound has been reported to be a very useful property of compound in order to make criteria to decide if a certain organic chemical should be phase out or not [SOU 2000:53]. It was suggested that using the so-called "P/B matrix" (P=persistence and B=bioaccumulation) as a possible and conceptual tool, such classification could be possible [SOU 2000:53]. The "P/B matrix" is a classification limit based on opened, bold-lined square (see Figure 4). This categorisation is made based on half-lives of compounds as well as on the bioconcentration factors (BCF). The bioconcentration factor is determined as the ratio between the concentration of substance in the organism and in the surrounding medium at equilibrium. The bioconcentration factor reflects the bioaccumulation potential, which is the tendency for the substance to be enriched in organisms by uptake from the surrounding medium and from the food [SOU 2000:53].

	P0 $T_{1/2}$<2 weeks	P1 $T_{1/2}$>2 weeks	P2 $T_{1/2}$>4 weeks	P3 $T_{1/2}$>8 weeks	P4 $T_{1/2}$>26 weeks
B0 BCF<100					
B1 BCF>500					
B2 BCF>1.000					
B3 BCF>2.000					
B4 BCF>5.000					

Figure 4. The P/B-matrix, (P)-persistence is expressed as half-lives ($T_{1/2}$) and bioaccumulation (B) is expressed as bioconcentration factors (BCF).

According to the "P/B matrix" in Figure 4, the black field represents persistence and bioaccumulation properties of a chemical (chemicals that have "P4/B4" value) that could be considered for priority regulatory actions. Chemicals with lower P and B value (shadowed fields) have properties that could be considered for future regulatory actions, even in the absence of toxicity information. It should be stressed that even chemicals with values of P3/B3 or even P2/B2 should also be considered for eventual restrictions. Using this classification, the knowledge only on persistence and bioaccumulation of compounds is required, although the toxicity of the compound is not necessarily needed for phasing out the chemical [SOU 2000:53].

It should be emphasized that substances do not always behave in the way as one might expect on the basis of their physico-chemical characteristics. Experimentally determinated half-lives can be expected to vary considerably depending on under which conditions they are measured. For example, half-lives of PAHs determined from archived sludge-amended field soil samples were found to be significantly higher than those determined in laboratory experiments [Wild *et al.,* 1991]. The understanding of ageing processes are here of great importance.

As it was mentioned above, plants can take up chemicals through their leaves and roots system. Uptake and distribution of organic contaminants in plants are however complicated processes, which may involve active and/or passive processes. Uptake and distribution of these compounds showed to be affected by physico-chemical properties of the compounds, environmental conditions such as temperature, air disturbances and the soil organic matter content. Also plant characteristics, such as the shape of leaves, type of root system and characteristic and content of lipid and cuticle are important [Duarte-Davidson & Jones, 1996].

It is known that among metals, Zn and Cd are readily taken up by plants and can enter the edible portions of plants. This is an important difference compared to Pb, which is not easily accumulated by plants [Harrison, 1992].

For organic compounds, several investigations have showed that compounds such as PAHs, PCBs, PCDD/Fs and DDTs are generally strongly bound to soil particles since they are highly lipophilic. Despite that, they may accumulate on root surfaces and remain in cell membrane lipids. As a consequence, transfer into plants following retention on root surfaces will be very slow. Due to their high persistence, once they enter the root surface they may effectively be bound there during the lifetime of the plant and only very slowly be transported to other parts of the plant. Most of the compounds, however, have a high potential for translocation from the roots to the foliage of the plants. These compounds are predicted to be able to leach into groundwater. Such contaminants include chloroanilines and mononitrophenols. Plant roots could take up these types of compounds shortly after sludge has been applied onto the land but they might also leach down to the groundwater [Duarte-Davidson & Jones, 1996].

4.4. Swedish debate about use of sewage sludge on agricultural lands

Applying sewage sludge to farmland is an issue of great concern in many countries including Sweden. Already in 1990, the Swedish Government pointed out the importance of recycling of nutrients from wastewater. A special agreement on guidelines for maximum allowable amounts of heavy metals, organic substances and pathogens, between the Swedish Environmental Protection Agency (SNV), the Federation of the Swedish Farmers (LRF) and the producers of sewage sludge, was signed in 1995 [Lundin, 1999]. In 1995 it was estimated that 85 to 90% of the sludge produced in Swedish sewage plants fulfilled all criteria according to the agreement, but only about 35% of the sludge was used for agricultural production until 1999 [Lundin, 1999].

Since October 1999 farmers were recommended to not use sewage sludge as fertilizer in agriculture due to increased content of brominated flame retardants in sludge [Eksvärd, 1999]. At present, however, the use of sludge as fertilizer in agriculture have significantly decreased, despite the fact that the concentration of *e.g.* heavy metals in Swedish sludge are low compared to many other countries, and mostly well below the standard guidelines by the SNV.

According to SNV and LRF the amount of sewage sludge that can be used on Swedish agricultural lands as fertilizer, should not be establish from risk assessment based on maximum concentration of heavy metals in sewage sludge. Instead, the potential increase of metal concentration in soil after applying sludge should be calculated [Hellstöm, 2000]. This means for instance, that if the concentration for a specific metal may increase in soil twice, the accepted time for it should be 10.000 years. Such an increasing pattern can be as follows: 1.0% increase every year over the first 10 years, followed by 0.3% over the next 90 years and finally 0.001% over the last 9.900 years [CES, 2000].

All metals will, however, probably not follow such a recommended pattern. In an unpublished Swedish study [Eriksson, 2001] it was calculated that if sewage sludge would be applied in a rate of 1-ton (dry wt) of sewage sludge/ha/year the theoretical increase in the concentration of gold (Au) and silver (Ag) in soil would be doubled in less than 10 years, while for wolfram (W), boron (B), antimony (Sb), molybdenum (Mo) this would occur first after between 10 and 100 years.

The content of phosphorus (P) should also be taken into account. Sewage sludge should be used in a way that the quality of soil, surface and groundwater is preserved. The maximum amount of total-P per hectare to be spread per year with sludge should be 22 kg (the III-V phosphorus class of the soil) and 35 kg (the I and II phosphorus class of the soil) [Lundin, 1999].

The most important question in this debate is to decide what rate of increase of the concentration of metal and organic chemicals in soil after sludge amendment is acceptable. To make such decision both advantages and disadvantages should be considered. It is very difficult to clearly say what level of a certain metal or organic compounds is hazardous. It should be, however, kept in mind that a slight increase of some potentially hazardous metals and organic compounds can be acceptable.

Summary

- *Land application is a major route for disposal of sewage sludge in many European countries.*

- *Heavy metals and persistent organic compounds present in sewage sludge as residues might be harmful and affect the environment (soil, plants and human) on both short- and long-term basis.*

- *Chemicals introduced to agricultural soils by sludge application may persist in the soil for different periods of time. For instance, PCDD/Fs ($T_{1/2}$>10 years) and PCBs ($T_{1/2}$<6 years) will persist in the soil for years to come and likely become part of the soil humus.*

- *Chemicals introduced to agricultural soils by sludge application can leach down to the groundwater or be taken up by plants mainly through their roots system.*

- *It is very difficult to clearly say what level of certain metals or organic compounds in sewage sludge applied on agricultural lands is hazardous for plants, various soil organisms, human health and the environment as a total.*

- *It is likely to believe that a slight increase of some potentially hazardous metals and organic compounds can be acceptable.*

5.   Is it possible to trace back target compounds from treated wastewater products towards its original sources?

One important step in tracing back hazardous compounds within the sewage system is to clearly define "the target compounds" we can find in different parts of the system. The three most important spots of concern are: (1) raw wastewater coming into the WWTP, (2) the processes inside the WWTP and (3) the treated wastewater products coming out from the plant (see Figure 1).

One alternative for the selection of target compounds can be to use so-called "priority pollutants" (PP) lists. There are several priority lists suggesting different compounds to be of concern due to their toxicity, resistance to degradation and bioaccumulation potential.

The American Environmental Protection Agency (US-EPA) has defined 129 toxic chemicals as priority pollutants. Here follows a summary of the list:
31 are purgeable organics (benzene, toluene, chloroform, etc.)
46 are base/neutral extractable organic compound (nitrobenzene, naphthalene, pyrene, etc.)
11 are acid extractable organic compounds (phenol, etc.)
26 are pesticides (aldrin, chlordane, etc.) and PCBs
13 are metals (antimony, arsenic, mercury, nickel, etc.)
The list also includes total cyanides, total phenols and asbestos [Lundin, 1999].

The Norwegian Environmental Protection Agency and Norwegian Center for Industry Research (SI-Senter) based on the US-EPA list compiled the list with priority pollutants to be measured in sewage sludge in the Scandinavian countries. The full list is presented in the Swedish Environmental Protection Agency's (SNV) Report #4085 [SNV, 1993] and consists of 70 substances.

However, SNV selected only four compounds (so-called indicator compounds) or group of compounds to be regularly monitored in sewage sludge in Sweden. They include toluene, PCBs, PAHs and nonylphenol. These compounds were selected because they were present in sludge, or because the authorities attempted to restrict their distribution in the environment. These compounds can serve as "indicators" of other organic pollutants that might be present in sludge. These indicator compounds are monitored in Sweden since 1990.

A number of different approaches to select compounds which can be recognized as priority pollutants and make the "re-use" of wastewater nutrients on arable land inappropriate due to environmental risks, are presented in an unpublished paper "Selection of hazardous substances in the urban water system as indicators for pollution of wastewater flows and end products" [Palmquist, 2001]. Based on six different approaches it was concluded that the identification of hazardous substances or groups of substances was a very complicated process. Priority pollutants in different conventions had been selected based on different criteria. Thus, the priority pollutants were not identical according to different proposed lists. The author concluded that it is impractical to create a comprehensive list of indicator substances. There are too many substances, which there is too little knowledge about and it is not achievable to assess chemical risks on such weak basis. Moreover, it is unachievable to practically measure/monitor *all* hazardous substances that contribute to the chemical risks and in this way assuring safety for recycling of wastewater nutrients on arable land and discharge in receiving waters.

An alternative way to estimate which candidates that can be present in sewage sludge is to look for new compounds instead of following the known priority pollutants from the existing lists.

Since it is known that sewage sludge is a very efficient sorbent for all lipophilic contaminants transported into the sewage system, it is expected that a number of other relatively unknown lipophilic compounds could be found in the sewage sludge as well. Litz [2000] suggested evaluating the fate of organic pollutants in sewage sludge based on their chemical-physical behaviour in soil and also on their environmental properties such as toxicity to humans and soil. According to this concept, based on available data, selected compounds were classified as compounds of primary and secondary relevance, and also substances for which there is need for further information.

A similar concept, but based on physico-chemical properties of compounds such as melting and boiling points, octanol-water partition coefficient, vapour pressure, solubility in water, Henry's law constant, the fate of compounds that might end up in WWTPs were proposed by Alcock *et al.* [1999]. In this study, attention was paid particularly to compounds which were not always present in the PP-list such as chlorinated paraffins, organotin compounds, brominated aromatic compounds, polychlorinated naphthalenes, quintozene, polydimethylsiloxanes, nitro musks, biologically active compounds and pharmaceutical compounds.

After choosing the target compounds, the main question that still remains is if it is possible to trace back the selected target compound within the sewage system. Thus, if it would be possible to know exactly from where a target compound that was found in the sewage sludge originated and continuing this strategy, if it could be possible following the scheme stepwise backwards (see Figure 5) and measure the contribution from each fraction and finally from each source.
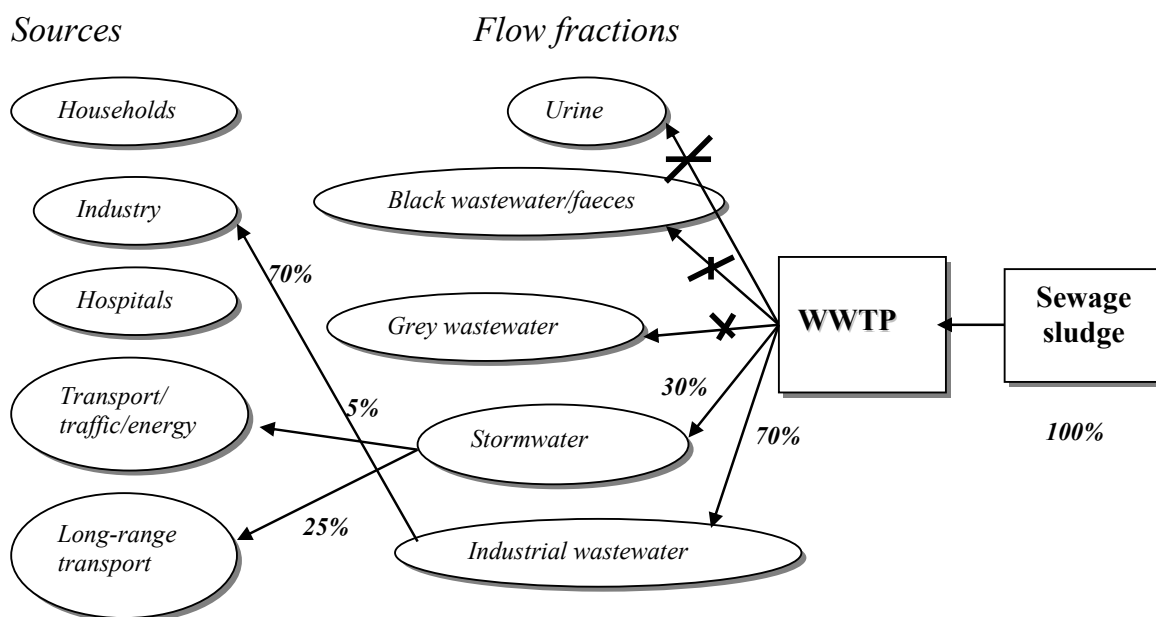

Figure 5.   A schematic picture how to possibly trace back chemicals found in sewage sludge to its originate source (WWTP: wastewater treatment plant).

To our knowledge there is no study following the flow of compounds from their particular source through WWTPs and finally ending up in wastewater products such as for example sewage sludge. There are, however, reports for a few compounds on the chemical fate, chemical degradation, etc in the WWTP, but since the amount and the variety of compounds coming into the WWTP is large, the interactions between compounds are still unknown.

For the prudent selection of target compounds it requires a thorough knowledge about potential wastewater constituents, *e.g.* about the sources, what kind of chemicals that might be discharged with the wastewater. What do we know about contaminants coming from household activities? About 30.000 chemical products are regarded as "every day" chemicals and these are in regular use. The effluent coming from household activities also varies a lot. What about the industry? In general, in Sweden every community may state restrictions on what substances that might be supplied to the sewer net. The community may for example state limiting values or prohibition of certain substances, but still the effluent may contain a very wide range of unknown substances. Of a special concern is stormwater, which might flush out substances from streets and roofs.

Since our knowledge about sources of chemicals coming into the WWTPs is quite limited, the task to trace back hazardous compounds from their final destination towards their sources is very difficult and complicated.

Summary

- *In order to be able to trace back hazardous compounds within the sewage system to their source or sources, it is necessary to clearly define what are "the target compounds".*

- *There are several priority lists suggesting different compounds as "hot candidates" to be expected to be present in such media as sewage sludge.*

- *It is a very difficult task to create a comprehensive list of indicator substances that possibly might be present in sewage sludge. The selection of target compounds requires thorough knowledge about potential wastewater constituents, e.g. about the sources of the chemicals discharged with the wastewater.*

- *Since our knowledge about sources of chemicals coming into the WWTPs is quite limited, the task to trace back hazardous compounds towards their sources is very difficult and complicated.*

6.   Current methods for identification and quantification of potential risk of chemicals

Risk assessment is usually based on the evaluation of the fate and toxic effects on single chemicals. However, many chemical products are not pure compounds but complex mixtures, of which the precise composition is often unknown [Verbruggen & Hermens, 2001]. Once emitted into the environment, all chemicals in effluents and surface waters are part of a complex mixture, of which the composition is largely unknown [Verbruggen & Hermens, 2001]. Thus, humans are typically exposed to low doses of combination of chemicals rather than to one or two chemicals at a time. In addition, most of the available toxicity data provide information on single chemicals or binary pairs, rather than on whole mixtures [Teuschler & Hertzberg, 1995].

6.1.   US-EPA approach – two examples: risk assessment for chemical mixture and for PCDD/Fs

In the early 1990s the US-EPA developed a "Guideline for risk assessment for chemical mixtures". According to this guideline a chemical mixture is defined as "any combination of two or more chemical substances regardless of source, or of spatial or temporal proximity that influence the resulting toxicity in the exposed population" [Teuschler & Hertzberg, 1995]. To perform a risk assessment a three-tiered approach is recommended (see Figure 6).

In *the first tier*, data on the mixture of concern are available, so the quantitative risk assessment can be conducted directly from these data. This situation is rare. When data are not available for the mixture of concern, then *the second tier* recommends using data on a "sufficiently similar" mixture. If no major differences are expected, then the quantitative risk assessment for the mixture of concern may be derived from the health effect data on the similar mixture. This situation is also not common.

Finally, when data on the mixture of concern, or on a similar mixture are not available, *the third tier* suggests evaluating the mixture through an analysis of its components. All three assessments should be done when possible.
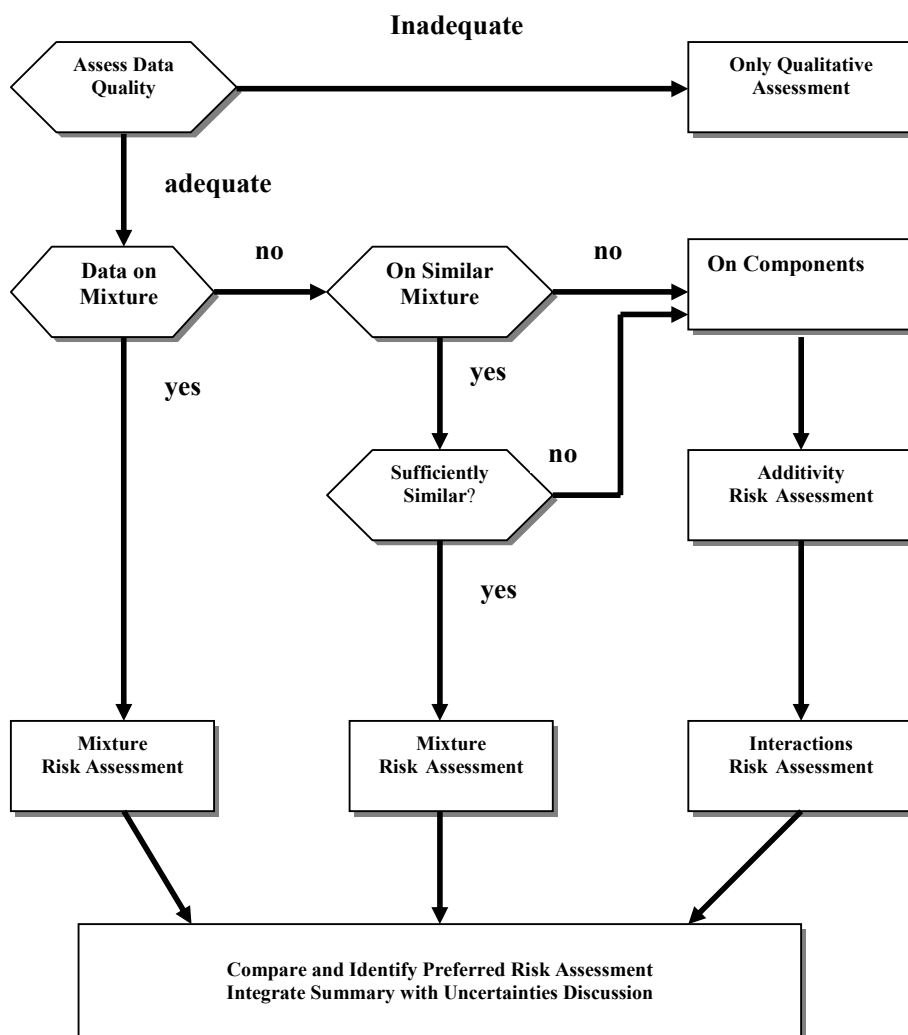
Figure 6. A schematic picture of an approach for risk assessment of chemical mixture according to the US-EPA [Teuschler & Hertzberg, 1995].

In 1993 the US-EPA adopted biosolids (sludge) regulations in which the risk-based regulatory analysis concluded that land application of biosolids presents negligible cancer risk from the metal and organic compounds that were reviewed. However, many organic compounds for instance, polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) were not included in this report [UWC, 1999]. In 1999 the United States Conference of Mayors released the report "Biosolids in land application - the dioxin situation" [UWC, 1999]. In this study the potential risk assessment was made based on an approach (see Figure 7) that includes all possible pathways to move PCDD/Fs to humans from sludge via soil, plants, and animals [UWC, 1999].
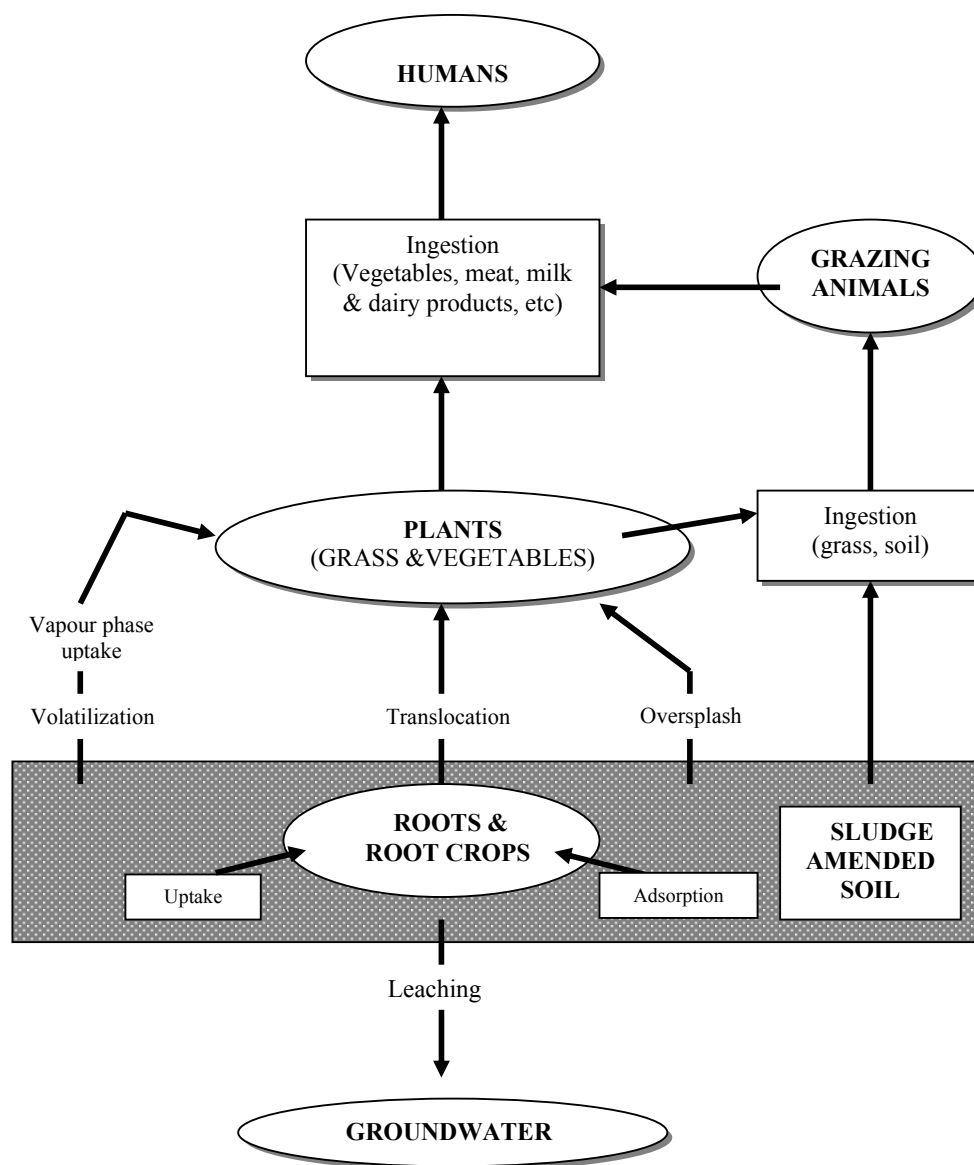
Figure 7. The overview of an approach for risk assessment of PCDD/Fs [UWC, 1999].

In practice, such an approach required a huge set of data on studied compounds such as physico–chemical properties of the compound, information about the exactly pathways and the fate of the compound from the time when it was applied. Information about other sources than sludge application such as long-range transport and information about degradation status of the compound was needed as well. Finally, this approach represents only one compound at a time. Noteworthy, using this approach nothing is told about effects of this compound in the long-term perspective.

Specific organic compounds have very different physico-chemical properties and therefore behave differently when applied to soil in sludge. As a result, specific human exposure routes may be relatively more important depending on the compounds behaviour.

6.2. European Union – Technical Guidance Document (TGD) for Environmental Risk Assessment for New and Existing Substances

The risk assessment described in Technical Guidance Document (TGD) [Tas *et al.,* 1997] consists of the following elements:

- Effect assessment, which leads to establishment of a Predicted No Effect Concentration (PNEC). PNEC is defined as the concentration below which unacceptable effects on organisms will most likely not occur, and is usually derived from laboratory toxicity data and recommended assessment factors.

- Exposure assessment, which is the determination of Predicted Environmental Concentration (PEC). The PEC can be derived using model calculations and/or representative monitoring data. PEC values are derived on a local (PEC_{local}) as well as on regional scale. Here, PEC_{local} is the predicted concentration resulting from release of a substance from a point source into a generic local environment.

- Risk characterisation is the estimation of the incidence and the severity of adverse effects likely to occur in a human population or the environment due to actual or predicted exposure to a substance by comparing the PEC to the PNEC. If monitoring data are available in *e.g.* water, sediment and soil, similar ratios are obtained with measured concentration instead of the predicted ones.

An assessment should lead to one (or more) of four conclusions [Leeuwen & Hermens, 1995]:
a) that a substance is of no immediate concern and need not be considered again until further information becomes available
b) that a substance is of concern and the competent authority shall decide what further information is required for revision of the assessment but shall defer a request for that information until the quantity placed on the market reaches the next tonnage threshold
c) that a substance is of concern and further information shall be requested immediately
d) that a substance is of concern and the competent authority shall make immediate recommendations with regard to risk reduction.

In practice it means that if:

$$\frac{PEC}{PNEC} < 1 -$$ it may be concluded that at present there is no need for the further testing or risk reduction measures

$$\frac{PEC}{PNEC} \geq 1 -$$ it should first be decided whether a stepwise refinement using new data could revise the PEC/PNEC ratio

6.3. Application of PEC/PNEC method according to the TGD – two examples

The first example discusses the risk assessment for musk ketone and musk xylene in the Netherlands [Tas *et al.*, 1997].

Musk ketone and musk xylene are used in fragrances for cosmetics (perfumes, personal care products), detergents, household cleaning products, air fresheners, etc. No other significant use of this product is known. However, the volume of use in fragrances is significant, reflecting their importance to the industry. For the fragrance industry these are very important fragrance ingredients because of their excellent substantivity as well as for their unique smell. The available evidence indicates they are not readily biodegradable, thus, it is not surprising that their presence has been detected in surface water and in fish albeit at relatively low levels [Tas *et al.*, 1997].
For both substances, PEC/PNEC ratios were at or below 0.1 for organisms in the aquatic environment, including sediment organisms. For soil organisms the PEC/PNEC ratio was 0.5 for musk ketone and 1.3 for musk xylene. Although in the Netherlands sewage sludge presently finds no application as fertilizer on agricultural soil, the aim of environmental policy is to upgrade the sludge quality to enable future applications on agricultural land and grassland. The reliability of the predicted soil concentrations can be greatly improved by obtaining experimental data on fate and behaviour of musk ketone and musk xylene in digested sludge and soil [Tas *et al.*, 1997].

While the risk assessment presented here is for the Netherlands, the assessment for all Europe is expected to be identical since these materials are used in products consumed in similar quantities *per capita* throughout the EU [Tas *et al.*, 1997].

The second example includes the risk assessment for long-chain phthalate esters in Sweden. Risk assessment for di(2-ethylhexyl)phthalate (DEHP), diisononylphthalate (DINP), and diisodecylphthalate (DIDP) have been made regarding their risks to the aquatic (surface water and sediment), terrestrial and atmospheric environments [Andersson, 2001].

Phthalate esters are a group of compounds used since 1920s as plasticisers [SNV, 1996]. They are also used in paints, varnish, glue, and cosmetics [Itävaara *et al.*, 1998]. The most widely used phthalate ester is DEHP. Although phthalates can leak from plastics, release of phthalaters to the environment occurs above all during their production and through combustion of products that contain phthalates [SNV, 1996]. Phthalates are easily degraded under aerobic conditions [Itävaara *et al.*, 1998].

Based on risk characterisation by comparing PNEC with PEC in a compartment it was concluded that:
-   For DIDP in all compartments assessed at present it is no need for further information and/or testing or for risk reduction measures.
-   For DEHP and DINP in the environment there is need for further information and testing.

6.4. Comparison of current risk assessment methods

Three different approaches, two from the US-EPA and the other from the European Union (EU) were summarised earlier (see paragraph 6.1-6.3 for details) in this report. The first US-EPA approach represents only a schematic picture how to deal with risk assessment in general, and the second gives one concrete example discussing PCDD/Fs. Thus, only the second US-EPA and the EU approach will be discussed and compared in this section.

The approach used by EU is commonly performed in order to make chemical risk assessment for substances, which were and are in use in the European countries. The goal for this "PEC/PNEC approach" (see paragraph 6.2 and 6.3 for details) known also as "the risk quotients approach" is a quantitative comparison of the results of the hazard identification/dose-response assessment (PNEC) and the exposure assessment (PEC) for certain ecosystems and populations. This method is based on a distinction between exposure and effects, which are assessed separately, and combined to risk quotients for each target compartment. Such risk quotients should inform the likelihood that unacceptable (adverse) effects could occur. Whenever possible, this likelihood is further quantified by an uncertainty analysis.

The goal with the second US-EPA technique was to evaluate if it at present is any risk to use sewage sludge on arable lands in regard to the PCDD/Fs content.

Despite the fact that those two approaches had not quite the same goal, in order to perform them a huge dataset was needed in both cases. Both methods were possible to perform using reliable and representative environmental monitoring data such as for example the relative contribution of the loadings from known sources of an investigated chemical, the quantity produced, the use pattern and intrinsic physico-chemical and environmental fate properties (including degradation of that substance). On the contrary to perform the "PEC/PNEC approach" many toxicological and ecotoxicological data were required.

These two methodologies for chemical risk assessment had one common feature, which is that both are suitable to describe the risk of a single substance only. In reality, many chemical products are not pure compounds but complex mixtures, of which the precise composition is often unknown [Verbruggen & Hermens, 2001]. Once emitted into the environment, all chemicals in effluents and surface waters are part of a complex mixture, of which the composition is largely unknown. Additionally, many chemicals are not directly mineralised, but transformed to other substances, and these transformation and degradation products might have a similar or even higher toxicity. In this case, new aspects need to be considered in risk assessment. First, the toxicity of the resulting mixture of the simultaneously available parent compound and transformation products need to be assessed. Second, a kinetic model has to be set up which allows one to calculate steady-state concentrations for the transformation products as they are formed from the parent compound [Kooijman *et al.,* 2001]. Besides that, both methods describe the chemical risk at present, but not in a long-term perspective. Moreover, these methods are very time and cost consuming.

Today, the human community requires adequate information on the risks of substances to man and the environment as well as on the protection from possible adverse effects from these substances. In order to ensure a high level of protection, two important types of information are needed. First, the character and the magnitude of the risk posed by substances needs to be assessed. Secondly, the options available for reducing high risks need to be defined.

Thus, the risk evaluation should be performed on a regular basis. The experts should judge the risk assessment results and take into account all the relevant information. However, because the risk assessment is generally based on many assumptions, possible uncertainties should be taken into account as well. It is important to remember that there are many new chemicals introduced into the environment every year and essential data on these substances are often not available. Therefore, the actual risks are often unknown and risk estimation is therefore required. Although, the above presented methods are based on number of assumptions they can be used in order to give general information about potential risks associated with certain chemicals under certain circumstances.

Summary

- *In this chapter two different approaches, one from the US-EPA and the other from the European Union (EU) were summarised and compared.*

- *The approach used by EU is commonly performed in order to make chemical risk assessment for substances, which at present are in use or have been used in the past in the European countries. The US-EPA technique was performed in order to evaluate if it at present is any risk to use sewage sludge on arable lands in regard to the PCDD/Fs content.*

- *Both methods have a lot of similarities:*
    - *they are both possible to perform using reliable and representative environmental monitoring data, intrinsic physico-chemical properties of compound, etc.*

    - *they are suitable to describe the risk of a single substance only*

    - *they describe the chemical risk at present, but not in a long-term perspective*

    - *they are time and cost consuming*

- *These methods are due to some limitations not completely sufficient, and they can give a general information on potential risks associated with a certain chemical in a certain situation.*

7.   What information do we need and what information do we have today in order to make risk assessment – gaps in knowledge?

For the vast majority of substances in use or in possible use, there is insufficient information on their hazardous properties. Figure 8 illustrates that only for a few "existing chemicals" risk assessment, including hazard assessment, has been completed [Blok *et al.,* 2001].
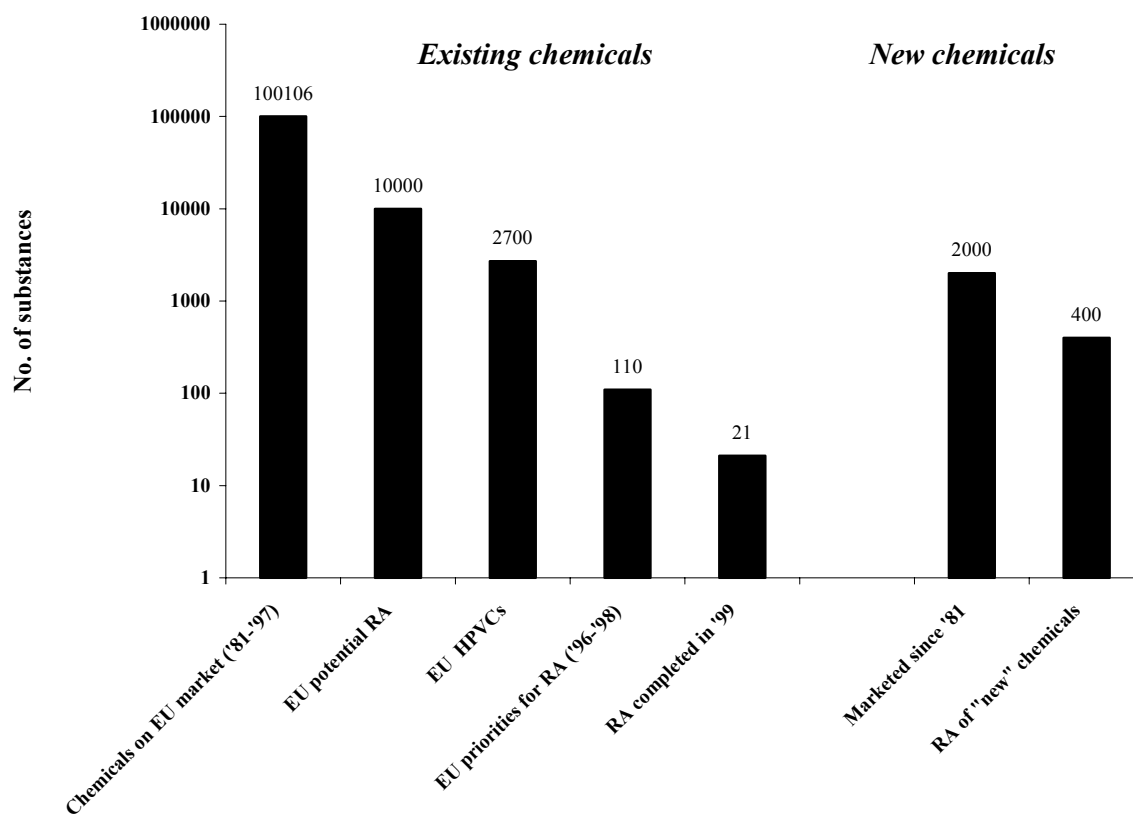

Figure 8.   Summary of number of substances on the European market before 1981 ("existing chemicals"); number of existing chemicals for which potentially a risk assessment (RA) needs to be performed; the number of High Production Volume Chemicals (HPVCs); the number of substances that are on the priority list, for which it is agreed that RA needs to be performed, and the number of substances for which RA has been completed in 1999. In addition, the number of chemicals that are notified since 1981, and the number of those "new chemicals" for which RA has been completed [Block *et al*., 2001].

"Existing chemicals" are those that were marketed on the European market before September 18, 1981. For the chemicals that are marketed after that date ("new chemicals", see Figure 8), there is currently more, but still insufficient information on hazard assessment.

To make risk assessments for chemical substances, knowledge of both their fate in various compartments or the studied media, and effects on humans and ecosystems are required. In 1989 it was estimated that research were focused only on 0.02% of all substances that were expected to eventually end up in the sewage sludge. It means, that totally 99.98% of the compounds were "unknown" [Lindgren, 1989]. Today, the number of man-made compounds is still growing.

In a SNV report #3514 [1988] it was presented that the concentration of organic pollutants expressed as Extractable Organic Chlorinated Compounds (EOCl) in the sewage sludge was about 100 mg/kg dry wt. In that study it was calculated that PCBs and PCDD/Fs were present in a total concentration of about 1 mg/kg, and the remaining 99% of the compounds were unknown. According to the above mentioned report it was also calculated that about 2-3% of PCBs and dioxin found in milk could originate from the application of sewage sludge on fields. The question of concern is - are those unknown chlorinated compounds (*ca* 99%, see above) also taken up at the same time? The presented risk assessment approaches (see paragraph 6) and the assessment performed by SNV in report #4674 [1996] are still treating the contributions from PCBs and dioxin separately. We do not know anything about the other compounds that might be taken up simultaneously and their eventual synergistic or antagonistic effects.

There are many ongoing studies focused on new compounds that can be expected to end up in WWTPs, sewage sludge or treated wastewater. All these approaches are based on physico-chemical data of compounds. It is worth to mention that substances do not always behave in the way as one might expect on the basis of their physico-chemical characteristics [SNV, 1996; Wild *et al.,* 1991].

Conventional approaches for analysis of chemical mixtures have large limitations when assessment of risk or effects should be undertaken. Target analysis suffers from the highly restricted number of substances that can be monitored. Furthermore, the selection of these target compounds in wastewater or sludge samples requires thorough knowledge about all potential constituents. Even if this knowledge is available, target analysis may completely fail to recognize the most harmful toxic wastewater or sludge constituents [Reemtsma, 2001]. Screening analysis is based on no pre-required information, but suffer from being a very laborious and time-consuming method. Initially a chromatogram is obtained containing a large number of peaks (substances). The tentative identification of one unknown peak often shows that this substance is of no relevance for the toxicity of the mixture or that no toxicological data were available to make an assessment. Thus, one must be very lucky to succeed in detecting and identifying toxic constituents by screening analysis.

For many compounds important information on toxicity is often lacking. Blok *et. al.* [2001] reported that with regard to the approximately 2.700 High Production Volume Chemicals in use in the European Union (before 1981), there is insufficient (eco)toxicity data for 70% of these chemicals. It is worth to mention that one of the largest aquatic toxicity databases (AQUIRE) developed at the US-EPA laboratory in Duluth (US), contains toxicological data for only 6.000 chemicals out of 100.000 compounds listed by the European Inventory of Existing Commercial Chemical Substances (EINES) [US-EPA Erl-Duluth, 1989-1994]. Of these 100.000 compounds are about 2.000 manufactured or imported to the European Union in quantities larger than 100.000 tonnes/year [US-EPA Erl-Duluth, 1989-1994]. However, when compare to terrestrial toxicity data there are relatively a lot of information available for the aquatic environment. For the moment, however, terrestrial toxicity data are seldom available, even for substances produced in high volumes. Nevertheless, the numerous heavily contaminated sites in the world and the effects observed there on organisms, population and entire ecosystems illustrate that these risks

cannot be ignored. Most of the toxicity test regarding soil is still in development. Even less developed is the understanding of the effects of substances to which species are exposed via the air. Therefore, data gaps will almost certainly exist for most substances.

The reason why so few toxicity data on chemicals exists is mainly attributed to high costs and time consuming tests. Additionally, the difficulties involved in elucidating the effects can be attributed to the very large number of new substances entering the market and to the many different ways in which they can affect organisms.

If there is insufficient laboratory (eco)toxicity data, the quantitative structure-relationships between the structure of chemicals (QSAR) may be used, especially for aquatic toxicity data. The role of QSAR in risk assessment of pollutants is two fold. QSAR models can be developed and used to predict the toxic effects of many other chemicals without testing them. Also, QSAR can help to understand the mechanisms of action involved in the toxicity of pollutants [Urrestarazu, 1998].

However, the current QSAR models are often not sophisticated enough to predict reliable estimates for many classes of substances. For example, in order to categorise and screen 23.000 substances listed on the Canadian Domestic Substances List (including such chemicals as pigments, organometallic compounds, surfactants, polymers, metal elements, metal salts and other inorganic substances, etc.), Canadian researches discovered that some of the challenges regarding modelling include the estimation of media specific half-lives, the estimation of the bioaccumulation potential for some classes of substances (*e.g.* pigments), and also the estimation of toxicity of many classes of substances *e.g.* organometallic substances and surfactants [Breton & Chenier, 2001].

Summary

- *Risk assessment has two components: an assessment of the potential environmental concentration of chemical, and an assessment of the environmental effects of the chemical.*

- *Up to date, the risk assessment has been completed only for a limited number of chemicals.*

- *Risk assessment is usually based on the evaluation of the fate and toxic effects on single target chemicals.*

- *Target analysis is often highly restricted to the certain number of substances that can be monitored. Thus, such target analysis may completely fail to recognize the most harmful toxic wastewater or sludge constituents.*

- *The number of chemicals potentially present in wastewater products such as sewage sludge or treated wastewater is almost unlimited. There are many ongoing studies focused on new compounds that can be expected to end up in WWTPs, sewage sludge or treated wastewater. All these approaches are based on physico-chemical data of compounds. However, substances do not always behave in the way as one might expect on the basis of their physico-chemical characteristics.*

- *For most chemicals in use, insufficient toxicity and ecotoxicity data is available.*

- *In case of missing information on effects from certain compounds the quantitative structure-relationships between the structure of chemicals (QSAR) and their toxic effects can be used.*

8.   New trends and developments in risk assessment approaches

In order to assess the "true" risk it is needed to summarise *all* information at the same time. Exposure, for example, should not be assessed separately without considering the effects. Such information as physico-chemical properties of compounds, degradation and metabolic products, toxicological effects on aquatic and terrestrial organisms are all depended on each other, and should be consider as a whole (see Figure 9). In other words, the chemical analysis should be integrated with a biological (toxicological) evaluation.
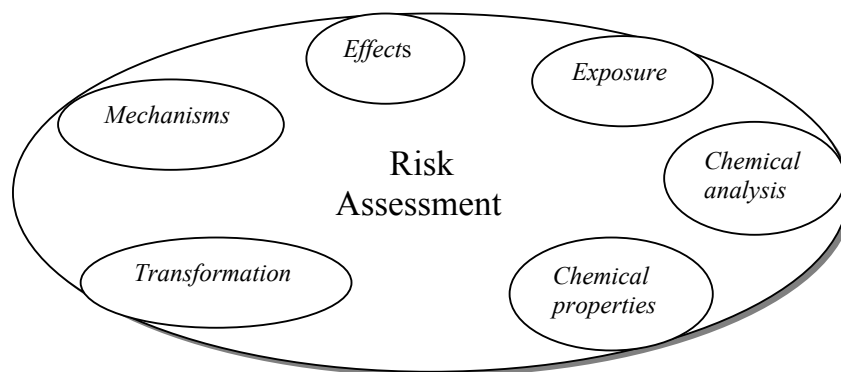

Figure 9.   A schematic picture of different environmental research areas that should be recognized together in a new risk assessment approach [TM, 1999].

As an example of an integrated approach we present here a toxicity-directed effluent analysis, a technique called "WET" (the whole effluent toxicity). This technique is commonly used by the US-EPA [Pardos & Blaise, 1999]. In this procedure, the organisms microinvertebrate (*Ceriodaphnia dubia)*, the fathead minnow (*Pimephales promelas)* or the green microalga (*Selenastrum capricornutum*) are used in compliance testing for exposure to all effluent constituents included in the sample. The combined effects of all effluent are quantified directly and the net effects of toxicant interactions or other variables are reflected in test organism responses. Thereafter the mixture is fractionated and any fraction, which causes toxicity, is subjected to a detailed investigation to determinate which hydrophobic organic compounds (POPs) that may be the major cause of the observed toxicity. This method has however major drawbacks and do not allow for a "true" assessment of the potential hazard of POPs on aquatic ecosystem [Pardos & Blaise, 1999]. One main drawback is that such contaminants like PCBs, PAHs and pesticides with K_{ow} above 10^4 will be more preferently bound to particles. Consequently, the filtration which is one important step in the whole procedure is likely to eliminate the major part of POPs with $K_{ow} > 10^4$ associated with the $>1\mu$m particle size from postfiltration bioassays [Pardos & Blaise, 1999].

The Toxicity Fraction Approach (TFA) is another example of a new advancement based on integration of toxicological and chemical data. The schematic outline of this approach is presented in Figure 10.
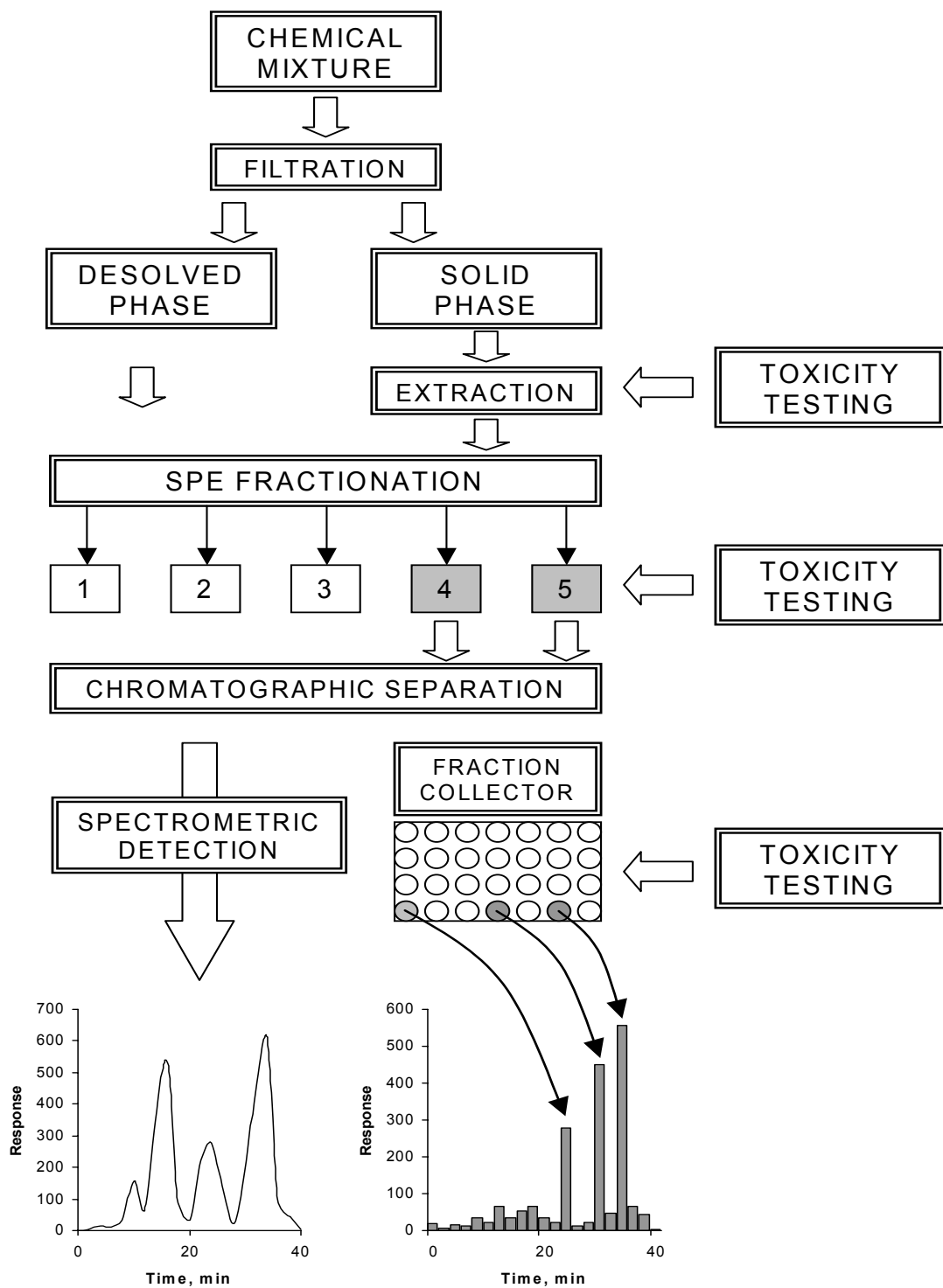
Figure 10. A schematic description of the Toxity Fraction Approach (SPE: Solid phase extraction).

The TFA concept aims at identifying unknown substances that are initially defined by their biological effects only. After filtration of the unknown mixture and extraction of the solid material, the dissolved phase and extracts are amended for toxicity testing. The toxic fractions are identified and amended for solid phase extraction (SPE). Here the fractionation is conducted with respect to polarity, planarity, acidity, etc. After biological testing of the fractions (for example microtox and mutatox tests, neutral red assay, etc.), those with high responses are further fractionated using modern chemical separation systems such as liquid chromatography (LC). General non-destructive chemical detection is here combined with collection of fractions for toxicity tests. Thereafter, the toxicological response can be directly related to the chemical response. For positive identification of the substance/substances causing the toxicological response a very well defined fraction is now available.

Certainly, a lot of very useful information is obtained during the course of this procedure. Already after the first fractionation and extraction of the solid material, the toxicity of the sample is measured. Samples giving low response are identified and no further analysis of the sample is needed. Furthermore, chemical-physical characteristics of the toxic compounds are obtained by the defined procedure of fractionation.

The TFA approach can be used for screening of treated wastewater products such as sewage sludge or wastewater. Chemical fractions of wastewater or extracts from the sewage sludge can be tested in order to identify biologically active mixtures of substances, which pose potential risk. The relative contribution of different groups of compounds to the risk will be established by using a number of assays comprising a variety of effect parameters. In Table 3, the results from multi assay toxicity tests (assay A-J), which are (in this case simulated) scored on a scale from 1-5, where 5 represent the highest response, are presented. In this way one number is obtained for each fraction of the sample as well as a total number for the overall toxicity of the sample. These numbers will be very useful on a relative scale and after calibration of the test method.

Table 3.   Example of a method evaluating the toxicity of fractions of unknown chemical mixture based on scores from different assays.

	Fraction, #				
Assay:	**I**	**II**	**III**	**IV**	**V**
A	2	1	3	3	4
B	1	3	2	3	5
C	2	2	3	5	5
D	3	1	1	4	5
E	2	1	2	4	4
F	2	3	3	3	3
G	1	1	3	2	5
H	2	2	2	5	1
I	1	2	3	3	4
J	3	2	2	3	3
$\sum_{fraction}$	19	18	24	35	39

$$\sum_{total} = 135$$

When using the method for screening of *e.g.* sewage sludge extracts, a "toxic sample" will be recognized. These studies can aid the newest fractionation and characterisation techniques, which are based on physico-chemical properties of the compounds, such as the TFA method.

The TFA method proposed here produce the information necessary for a risk assessment of the sample. A drawback is however the potentially overestimated exposure from the solid phase. The judgement was that *in vivo* testing would be too laborious and costly to motivate in comparison to the suggested *in vitro* test method. The cost and workload for development and evaluation of the TFA method will be large which is a drawback compared to *e.g.* target analysis.

The TFA method gives the possibility to identify the relation between the complex mixture of chemical substances and different biochemical and toxicological responses. The TFA approach is ultimately avoiding the major pitfalls associated with the more conventional methods. The analysis is avoiding the deceptive target analysis and the lack of decision criteria and guidance in screening procedures. The TFA approach will be as broad as the screening analysis but the biological response will provide guidance and define the target. It means, that after using the TFA approach, it should be possible to suggest a list of priority substances, from which certain indicator substances can be selected.

Summary

- *In order to assess the "true" risk it is needed to summarise all information at the same time. Such information as physico-chemical properties of compounds, degradation and metabolic products, toxicological effects on aquatic and terrestrial organisms are all depended on each other, and should be considered as a whole.*

- *The Toxicity Fraction Approach (TFA) is a new technique assessing the potential biological effects and environmental impact of chemical substances existing as complex mixture based on integrated toxicological and chemical evaluation.*

- *The TFA approach can be used for screening of treated wastewater products such as sewage sludge or wastewater. Using the TFA approach the identification of biologically active mixtures of substances, which pose potential risk can be primary made and then followed by the chemical evaluation.*

- *An approach such as TFA, in which the evaluation of a toxic fraction is based on the results from multi assay toxicity tests can also be used to access the risk of potentially toxic compounds in sewage sludge or treated wastewater.*

9. How can we use current knowledge to predict potential chemical risk when traditional or alternative wastewater systems are in use?

Given the knowledge available today, we can conclude that it is rather difficult to evaluate risk associated with one or the other sewage systems discussed in this report.

One thing we know today is that wastewater coming into the wastewater treatment plant is a very complicated mixture. Despite the fact that actually between 55 to 93% of the influent quantities are removed during the wastewater treatment, the number of new chemicals potentially present in sewage sludge or treated wastewater coming out from plants is still increasing. In studies earlier presented in this report [SNV, 1993; Andersson & Nilsson, 1999], a significant number of compounds were not found in for instance, sewage sludge, because of too high detection limits.

Substantial progress has been made in the synthesis and determination of organic compounds. Individual standards are now available enabling congener-specific, sensitive analytical methods. Growing evidence suggest that the new compounds such as, for instance, chlorinated paraffins, polybrominated diphenyl ethers and polychlorinated naphthalenes are widespread global environmental pollutants and that they are capable of bioaccumulatation in food chains.

Introduction of alternative sewage systems such as the separated urine fraction could potentially lead to a reduced mixing of pollutants with the nutrients in the wastewater. The total burden of pollutants would however overall be unchanged.

On the other hand there a are number of water soluble or metabolised chemical compounds in the urine fraction, which could eventually pose a risk. One example of such a group is pharmaceuticals. The knowledge about this rather large (in terms of number of compounds) group is very limited. Presently it is not possible to conduct a complete environmental risk assessment for any pharmaceutical compound [Jørgensen & Halling-Sørensen, 2000]. One important reason for this is the lack of fundamental data about the effects and distributions of pharmaceuticals in the environment [Stuer-Lauridsen *et al*., 2000].

Biologically active substances are often metabolised in the body prior to excretion. The information available on these more water-soluble metabolic products is also limited. Thus, no risk assessment can easily be conducted.

We can conclude however, that the urine fraction is largely free from the hydrophobic traditional pollutants. Therefore, from the knowledge today, the chemical risk associated with using human urine as fertilizer (as a consequence of application of separate wastewater system) is likely to be lower than for use of sewage sludge as fertilizer in agriculture.

10. Main conclusions

In order to assess the chemical risk within the defined sewage systems the knowledge about the potential effects of wastewater products are essential. The treated wastewater can have a direct effect on the aquatic environment in the proximity of the sewage treatment plants. Certainly, for relatively stable and water-soluble chemical substances effects can be expected on long distances from the sources as well. For sewage sludge the effects can be more complex. Human exposure of chemical substances originating from sewage sludge would most likely occur through uptake of xenobiotics by plants when the sewage sludge was used as fertilizer on arable land. However, the complexity connected with the risk assessment of chemicals involved in multiple phase transitions between source and effect would cause an immense workload just for risk assessment of one single substance. Therefore the system concerned in this study was limited to sewage sludge, treated wastewater and wastewater nutrients originated from human urine and faeces.

Due to the limited time frame of this project the work has been concentrated on reviewing and evaluating methods established by recognized organizations or researches in the area of risk assessment of chemicals. There are many ongoing research projects focusing on risk assessment of chemical substances however these needs time to be finalized.

In the course of this work, several areas where substantial gaps exist in knowledge have been identified.

Based on the literature study and on personal communications we conclude that up to date there are no universal methods for risk assessment of chemicals. In fact, existing methods are not sufficient due to some limitations. Identification and quantification of the chemical risk for such complex mixtures as sewage sludge and treated wastewater is an immense task using conventional methods like target analysis. The analysis should ideally work with no presumptions. The Toxicity Fraction Approach (TFA) described briefly in this report, could meet the requirements to be broad as screening, but guided by the toxicity response. This method could potentially provide results for a chemical risk assessment of sewage water and sludge.

It is difficult with present knowledge to assess the chemical risk associated with one or the other sewage systems discussed in this report. However, we can conclude that the urine fraction is largely free from the hydrophobic traditional pollutants. Therefore, the chemical risk associated with separated systems and the usage of urine in agriculture is likely to be lower than the use of sewage sludge as fertilizer.

Summary

- *Wastewater coming into WWTPs is a complex mixture of various pollutants from many sources.*

- *It is a very difficult task to create a comprehensive list of indicator substances that possibly might be present in sewage sludge. The selection of target compounds requires thorough knowledge about potential wastewater constituents, e.g. about the sources of the chemicals discharged with the wastewater.*

- *Heavy metals and persistent organic compounds present in sewage sludge as residues might be harmful and affect the environment (soil, plants and human) on both short- and long-term basis.*

- *It is however very difficult to clearly say what level of certain metals or organic compounds in sewage sludge applied on agricultural lands is hazardous to the environment.*

- *Existing methods for risk assessment of chemicals have following characteristics:*

  - *they are both possible to perform using reliable and representative environmental monitoring data, intrinsic physico-chemical properties of compound, etc.*

  - *they are suitable to describe the risk of a single substance only*

  - *they describe the chemical risk at present, but not in a long-term perspective*

  - *they are time and cost consuming*

- *Generally, risk assessment methods are due to some limitations (see above) not completely sufficient.*

- *Target analysis is often highly restricted to a certain number of substances that can be monitored. Thus, such target analysis may completely fail to recognise the most harmful toxic wastewater or sludge constituents.*

- *The Toxicity Fraction Approach (TFA) is a new technique assessing the potential biological effects and environmental impact of chemical substances existing as complex mixture based on integrated toxicological and chemical evaluation.*

- *An approach such as TFA, in which the evaluation of a toxic fraction is based on the results from multi assay toxicity tests, can also be used to access the risk of potentially toxic compounds in sewage sludge or treated wastewater.*

11. References

Alcock R.E., Jones K.C., "New Directions "New" organic compounds in the environment". Atmospheric Environment 33 (1999) 1645-1646

Alcock R.E., Sweetman A., Jones K.C., "Assessment of organic contaminant fate in waste water treatment plants I: selected compounds and physicochemical properties". Chemosphere 38: (10) (1999) 2247-2262

Andersson L., "Environmental effects and risk assessment of long-chain phthalate esters". Abstract 423 in: Abstract Book from Setac Europe 11th Annual Meeting (2001) Madrid, Spain

Andersson P.-G., Nilsson P., "Slamspridning på åkermark. Fältförsök med kommunalt avloppsslam från Malmö och Lund under åren 1981-1997". VA-FORSK Rapport 22 (1999) VAV AB, Sweden

Augulyte L., "Dewatering technologies, handling problems and effect to the environment from municipal sewage sludge". Project (10p.) (2001) Environmental Chemistry, Department of Chemistry, Umeå University, Umeå, Sweden

Blok H., Balk F., Okkerman P., Sijm D., "Selection and evaluation of persistent, bioaccumulative, and toxic criteria for hazard assessment". In: "Persistent, bioaccumulative, and toxic chemicals II. Assessment and new chemicals". American Chemical Society Symposium Series 773 (2001) Washington DC, USA

Breton R., Chenier R., " Environmental categorisation and screening of the Canadian domestic substances list". In: "Persistent, bioaccumulative, and toxic chemicals II. Assessment and new chemicals". American Chemical Society Symposium Series 773 (2001) Washington DC, USA

CES - "Opinion of the Economic and Social Committee on "The revision of Council Directive 86/278/EEC on the use of sewage sludge in agriculture". (2000) Brussels, Belgium

Dahlin S., Witter E., Martensson A., Turner A., Baath E., "Where's the limit? Changes in the microbiological properties of agricultural soils at low levels of metal contamination". Soil Biology and Chemistry 29: (9-10) (1997) 1405-1415

Daughton C.G., Ternes T.A., "Pharmaceuticals and personal care products in the environment: Agents of subtle change?" Environmental Health Perspectives 107: (Supplement 6) (1999) 907-938

Duarte-Davidson R., Jones K.C., "Screening the environmental fate of organic contaminants in sewage sludge applied to agricultural soils: II. The potential for transfer to plants and grazing animals". The Science of Total Environment 185 (1996) 59-70

Eksvärd J., Pressmedelande (1999-10-12) "Tillfälligt stopp för slam", (www.lrf.se)

Eriksson J., "Ovanliga element i avloppslam, stallgödsel, handelgödsel, nederbörd samt jord och gröda". Manuscript (2001), not published

Gillett J.W., "A comprehensive prebiological screen for ecotoxicologic effects". Environmental Toxicology and Chemistry 2 (1983) 463-476

Hanaeus J., Hellström D., Johansson E., "A study of a urine separation in an ecological village in northern Sweden". Water Science and Technology 35: (9) (1997) 153-160

Harrison R.M., In: "Understanding our environment: An introduction to Environmental Chemistry and Pollution". (1992) The Royal Society of Chemistry, Cambridge, UK

Hellström T., "Slamfrågan-problem och möjligheter". In: Meddelande VAV (M114) VAV-möte med föreningsstämma 2000". (2000) Strömstad, Sweden

Itävaara M., Venelampi O., Samsøe-Petersen L., Lystad H., Bjarnadottir H., Öberg L., "Assessment of compost maturity and ecotoxicity". Nordtest Technical Report 404 (1998) Espoo, Finland

Johansson M., Pell M., Stenström J., Kinetics of substrate-induced respiration (SIR) and denitrifications: Applications to a soil amended with silver". Ambio 27: (1) (1998) 40-44

Johansson M., Stenberg B., Torstensson L., "Microbiological and chemical changes in two arable soils after long-term sludge amendments". Biology and Fertility of Soils 30 (1999) 160-167

Jönsson H., Vinnerås B., Höglund C., Stenström T.A., Dalhammar G., Kirchmann H., "Källsorterad humanurin i kretslopp". VA-FORSK Rapport 1 (2000) VAV AB, Sweden

Jørgensen S.E., Halling-Sørensen B., "Drugs in the environment". Chemosphere 40: (7) (2000) 691-699

Klöpffer W., "Environmental hazard assessment of chemicals and products. Part V. Anthropogenic chemicals in sewage sludge". Chemosphere 33: (6) (1996) 1067-1081

Kooijman C., Fenner K., Scheringer M., Hungerbuehler K., "Risk assessment of mixtures of parent compounds and transformation products in a multimedia fate model". Abstract M/MF136 in: Abstract Book from Setac Europe 11th Annual Meeting (2001) Madrid, Spain

Leeuwen C.J., Hermens J.L.M., In: "Risk assessment of chemicals: an introduction". (1995) Kluwer Academic Publishers, Dordrecht, The Netherlands

Levlin E., Tideström H., Kapilashrami S., Stark K., Hultman B., "Slamkvalitet och trender för slamhantering". Manuscript in print, VA-FORSK (2001) VAV AB, Sweden

Lind B.B., Ban Z., Byden S., "Volume reduction and concentration of nutrients in human urine". Ecological Engineering 16: (4) (2001) 561-566

Lindgren G., "Miljöföroreningar i slammet hamnar i livsmedlen". Miljö och Framtid 8 (1989) 14-20

Litz N., "Assessment of organic constituents in sewage sludge". Water Science and Technology 42: (9) (2000) 187-193

Lundin L.-C., "Sustainable Water Management in the Baltic Sea Basin, book 2- Water Use and Management". Publication of Baltic University Programme (1999) Uppsala University, Uppsala, Sweden

McBride M.B., Richards B.K., Steenhuis T.S., Russo J.J., Sauve S., "Mobility and solubility in soil fifteen years after sludge application". Soil Science 162 (1997) 487-500

O'Connor G.A., "Organic compounds in sludge-amended soils and their potential for uptake by crop plants". The Science of Total Environment 185 (1996) 71-81

Olofsson C., Eriksson K., "Slamhantering i Västerbottens län". Länsstyrelsen Västerbottens län's Rapport, Meddelande 7 (1996), Umeå, Sweden

Palmquist H., " Selection of hazardous substances in the urban water system as indicators for pollution of wastewater flows and end products". Manuscript (2001), not published

Pardos M., Blaise C., "Assessment of toxicity and genotoxicity of hydrophobic organic compounds in wastewater". Environmental Toxicology 14: (2) (1999) 241-247

Paxeus N., Robinson P., Balmer P., "Study of organic pollutants in municipal wastewater in Göteborg, Sweden". Water Science and Technology 25: (11) (1992) 249-256

Reemtsma T., "Prospects of toxicity-directed wastewater analysis". Analytica Chimica Acta 426 (2001) 279-287

Richards B.K., Steenhuis T.S., Peverly J.H., McBride M.B., "Metal mobility at an old, heavily-loaded sludge application site". Environmental Pollution 99 (1998) 365-377

Schnaak W., Kuchler Th., Kujawa M., Henschel K.-P., Subenbach D., Donau R., "Organic contaminants in sewage sludge and their ecotoxicological significance in the agricultural utilization of sewage sludge". Chemosphere 35: (1/2) (1997) 5-11

SNV, Report #3514 (1988) "Organiska toxiska ämnen i slam från kommunala avloppsreningsverk"

SNV, Report #4085 (1993) "Slam. Innehåll av organiska miljöfarliga ämnen"

SNV, Report #4418 (1995) "Användning av avloppsslam i jordbruket"

SNV, Report #4665 (1996a) "Överenskommelsen om slamanvändningen i jordbruket mellan LRF, VAV och Naturvårdsverket: uppföljning av de första åren: 1994-1996"

SNV, Report #4674 (1996) "Organic Pollutants in Sewage Sludge. Contribution to Human Exposure to Certain Estrogen - Perturbing Compounds"

SOU 2000:53 - "Summary Report from Round-Table Discussion on Criteria for phasing out persistent and bioaccumulating organic chemicals". (1999) Steningevik, Sweden

Stuer-Lauridsen F., Birkved M., Hansen L.P., Holten Lützhøft H.C., Halling-Sørensen B., "Environmental risk assessment of human pharmaceuticals in Denmark after normal therapeutic use". Chemosphere 40: (7) (2000) 783-793

Tas J.W., Balk F., Ford R.A., van de Plassche E.J., "Environmental risk assessment of musk ketone and musk xylene in the Netherlands in accordance with the EU-TGD". Chemosphere 35: (12) (1997) 2973-3002

Teuschler L.K., Hertzberg R.C., "Current and future risk assessment guidelines, policy, and methods development for chemical mixtures". Toxicology 105 (1995) 137-144

TM – "Toxikologisk miljöforskning. Behovsanalys för den nya kemikaliepolitiken" (1999) (Bilaga 7). Forskningsrådsnämnden, Stockholm, Sweden

Urrestarazu E., "Aquatic toxicity of polar narcotic pollutants. Mechanism, modelling and environmental effect assessment. Ph.D. thesis (1998) Utrecht University, Utrecht, The Netherlands

US-EPA - "Process Design Manual-Land Application of Sewage Sludge and Domestic Septic". (EPA/625/R-95/001) (1995) Washington DC, USA

US-EPA ERL-DULUTH 1989-1994 - "Aquatic Toxicity Information Retrieval Database (AQUIRE)". US-EPA Environmental Research Laboratory – Duluth Scientific Outreach program, Duluth, MN, USA

UWC - The United States Conference of Mayors, Urban Water Council's Report "Biosolids in land application - the dioxin situation". (1999) Washington DC, USA

Verbruggen E.M.J., Hermens J.L.M., "Estimating accumulation and baseline toxicity of complex mixtures or organic chemicals to aquatic organisms. The use of hydrophobicity dependent analytical methods". In: "Persistent, bioaccumulative, and toxic chemicals II. Assessment and new chemicals". American Chemical Society Symposium Series 773 (2001) Washington DC, USA

Wild S.R., Berrow M.L., Jones K.C., "The persistence of polynuclear aromatic hydrocarbons (PAHs) in sewage sludge amended agricultural soils". Environmental Pollution 72 (1991) 141-157

Wilson S.C., Duarte-Davidson R., Jones K.C., "Screening the environmental fate of organic contaminants in sewage sludges applied to agricultural soils: 1. The potential for downward movement to groundwaters". The Science of Total Environment 185 (1996) 45-57