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Analysis of poly- and perfluorinated compounds (PFCs) in landfill effluent using HPLC-MS/MS

(Von der Fakultät III Umwelt und Technik der Leuphana Universität Lüneburg als Diplomarbeit angenommen)

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Jan Busch

85 pages with 12 figures and 25 tables

Abstract

Polyfluoroalkyl compounds (PFCs), such as perfluorooctane sulfonate (PFOS) or perfluorooctanoic acid (PFOA), are widely used in industry and consumer products. During the production processes or use of the products, PFCs can be released into the environment, but little is known about their fate in municipal and industrial landfills. Used consumer products are deposited in landfills. It is possible that landfills act as sources for PFCs in the environment. In this study several landfill leachates are investigated at different sites in Northern Germany. This is the first study which shows the widespread occurrence of PFCs in treated and untreated leachates of 22 landfill sites. In total 38 PFCs are detected with a concentration range between a few ng/L to 8,060 ng/L in treated leachate and 30.5 ng/L to 13,000 ng/L in untreated leachate. Dominating compounds are the shorter-chained PFCs, Perfluorobutane sulfonate (PFBS) and Perfluorohexane sulfonate (PFHxS), which show higher concentrations than longer-chained PFCs like PFOS and PFOA, in treated as well as untreated leachate. Discharges of landfills are estimated to be between <1 g/year and 350 g/year, depending on the treatment system. The large variability of the discharges indicates that some landfill sites could be a point source for PFCs. However, wastewater treatment plant (WWTP) discharges are approximately 50 times higher in comparison to landfill effluents. Nevertheless age of the landfill body is a determining factor for concentrations in untreated leachate, whereas in treated leachate the treatment system is the dominating factor of the PFC contamination. Wet air oxidation and biological treatment seem to be not effective for removal of PFCs from the leachate (mean concentration = 3300 ng/L and 6000 ng/L Σ PFCs), while reverse osmosis and activated carbon have a significant effect on reduction of the PFC contamination in the effluent (mean = 42 ng/L and 723 ng/L Σ PFCs).

Analyse von poly- und perfluorierten Verbindungen (PFCs) in Deponiesickerwasser mittels HPLC-MS/MS

Zusammenfassung

Polyfluoralkylverbindungen (PFCs) wie Perfluoroktansulfonansulfonat (PFOS) oder Perfluoroktansäure (PFOA), werden in vielen Industrie- und Konsumprodukten eingesetzt. Während des Produktionsprozesses oder in der Nutzungsphase der Produkte können PFCs freigesetzt werden.

Genutzte Produkte werden in der Regel Verwertet oder auf Abfalldeponien entsorgt. Das Wissen über PFCs in Abfalldeponien ist sehr begrenzt und möglicherweise sind Deponien eine Quelle für PFC Belastungen in der Umwelt. In der vorliegenden Arbeit wird untersucht, wie sich der PFC-Austrag von Deponien in Sickerwasser verhält. Hier wird Sickerwasser von 22 verschiedenen Deponien in Norddeutschland untersucht.

Insgesamt werden 38 PFCs in Konzentrationen zwischen wenigen ng/L und 8.060 ng/L in behandeltem und 30,5 ng/L bis 13.000 ng/L in unbehandeltem Sickerwasser gefunden. Kurzkettige PFCs wie Perfluorbutansulfonat (PFBS) und Perfluorhexansulfonat (PFHxS) können in höheren Konzentrationen gefunden werden als längerkettige Verbindungen wie PFOS und PFOA. Die geschätzten Jahresfrachten von 0,03 g/Jahr bis maximal 350 g/Jahr zeigen, dass Deponien im Vergleich zu Kläranlagen als Quelle nur eine untergeordnete Rolle spielen. Bei Frachten von PFOS und PFOA können einzelne industrielle Kläranlagen signifikant mehr emittieren als alle deutschen Deponien gemeinsam.

In unbehandeltem Sickerwasser ist ein Zusammenhang zwischen Alter der Deponie und Konzentration in Sickerwasser fest zu stellen, während Emissionen in behandeltem Sickerwasser überwiegend durch das Reinigungsverfahren bestimmt werden. Während nach Umkehrosmoseanlagen durchgehend sehr geringe Konzentrationen im Sickerwasser verbleiben (Mittelwert: 42 ng/L Σ PFCs), haben Nassoxidation (3300 ng/L) und biologische Verfahren (6000 ng/L) nahezu keinen Einfluss auf die Konzentration. Aktivkohle (723 ng/L) kann PFCs effizient zurückhalten; dies scheint aber vom Grad der Beladung abhängig zu sein.

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List of abbreviations

10:2 FTUCA	10:2 fluorotelomer carboxylic acid
^{13}C-PFBA	Perfluoro-n-[1,2,3,4-$^{13}C_4$]butanoic acid
^{13}C-PFDA	Perfluoro-n-[1,2-$^{13}C_2$]decanoic acid
^{13}C-PFDoA	Perfluoro-n-[1,2-$^{13}C_2$]dodecanoic acid
^{13}C-PFHxA	Perfluoro-n-[1,2-$^{13}C_2$]hexanoic acid
^{13}C-PFNA	Perfluoro-n-[1,2,3,4,5-$^{13}C_5$]nonanoic acid
^{13}C-PFOA	Perfluoro-n-[1,2,3,4-$^{13}C_4$]octanoic acid
^{13}C-PFOS	Perfluoro-1-[1,2,3,4-$^{13}C_4$]octanesulfonate
^{13}C-PFOSi	Perfluoro-1-[1,2,3,4-$^{13}C_4$]perfluorooctanesulfinate
^{18}O2-PFHxS	Perfluoro-1-hexane[$^{18}O_2$]sulfonate
^{13}C-PFUDA	Perfluoro-n-[1,2-$^{13}C_2$]undecanoic acid
6:2 FTCA	2-perfluorohexylethanoic acid
6:2 FTUCA	2H-perfluoro-2-octenoic acid
6:2 FTS	6:2 fluorotemomer sulfonate
8:2 FTCA	2-perfluorohexylethanoic acid
8:2 FTUCA	2H-perfluoro-2-decenoic acid
AbfAblV	Abfallablagerungsverordnung
AbwV	Abwasserverordnung
BAF	Bioaccumulation factor
BCF	Bioconcentration factor
BOD_5	Biological oxygen demand
COD	Chemical oxygen demand
D_3-MeFOSA	N-methyl-d_3-perfluoro-1-octanesulfonamide
D_5-EtFOSA	N-ethyl-d_5-perfluoro-1-octanesulfonamide
D_7-MeFOSE	2-(n-deuteriomethylperfluoro-1-octanesulfonamido)-1,1,2,2-tetradeuterioethanol
D_9-EtFOSE	2-(n-deuterioethylperfluoro-1-octanesulfonamido)-1,1,2,2-tetradeuterioethanol

DepV	Deponieverordnung
ECF	Electrochemical fluorination
FASAs	Perfluoroalkyl sulfonamides
FASEs	Perfluoroalkyl sulfonamidoethanols
FTCAs	Fluorotelomercarboxylic acids
FTOHs	Fluorotelomer alcohols
FTUCAs	Unsaturated fluorotelomer carboxylic acids
GFF	Glass fiber filter
HPLC	High performance liquid chromatography
HPLC-MS/MS	High performance liquid chromatography double coupled mass spectrometry
KrW/AbfG	Kreislaufwirtschafts-/Abfallgesetz
LC_{50}	Lethal concentration, 50 %
LD_{50}	Lethal dose, 50 %
LOEC	Lowest observed effect concentration
LOEL	Lowest observed effect level
Me_2PFOA	Perfluoro-3,7-bis(trifluoromethyl)-octanoic acid
MeFBSA	N-methylperfluorobutane sulfonamide
MeFBSE	N-methylperfluorobutane-sulfonamidoethanol
MRM	Multi response monitoring
NEtFOSA	N-methylperfluorooctane sulfonamide
NEtFOSE	N-methylperfluorooctane-sulfonamidoethanol
NMeFOSA	N-methylperfluorooctane-sulfonamide
NMeFOSE	N-methylperfluorooctane-sulfonamidoethanol
NOAL	No observed adverse effect level
NOEC	No observed effect concentration
NOEL	No observed effect level
PBT	persistent, bioaccumulative, toxic
PFAS	Perfluoroalkylated substances

PFBA	Perfluorobutanoic acid
PFBS	Perfluorobutanoic sulfonate
PFCs	Poly- and perfluorinated alkyl compounds
PFCA	Perfluorocarboxylic acids
PFDA	Perfluorodecanoic acid
PFDoDA	Perfluorododecanoic acid
PFDPA	perfluorodecylphosphonic acid
PFDS	Perfluorodecane sulfonate
PFDSi	Perfluorodecane sulfinate
PFHpA	Perfluoroheptanoic acid
PFHpDA	Perfluoroheptadecanoic acid
PFHpS	Perfluoroheptane sulfonate
PFHxA	Perfluorohexanoic acid
PFHxDA	Perfluorohexadecanoic acid
PFHxPA	Perfluorohexaphosphonic acid
PFHxS	Perfluorohexane sulfonate
PFHxSi	Perfluorohexane sulfinate
PFNA	Perfluorononane acid
PFNS	Perfluorononane sulfonate
PFOA	Perfluorooctanoic acid
PFOcDA	Perfluorooctadecanoic acid
PFOPA	Perfluorooctylphosphoric acid
PFOS	Perfluorooctanoic sulfonate
PFOSA	Perfluorooctane sulfonamide
PFOSi	Perfluorooctane sulfinate
PFPA	Perfluoropentanoic acid
PFPeDA	Perfluoropentadecanoic acid
PFPS	Perfluoropentane sulfonate
PFSAs	Perfluoroalkyl sulfonates

PFSiAs	Perfluoroalkyl sulfinates
PFTeDA	Perfluorotetradecanoic acid
PFTriDA	Perfluorotridecanoic acid
PFUnDA	Perfluoroundecanoic acid
POP	persistent organic pollutant
POSF	Perfluorooctanesulfonyl fluoride
PTFE	Polytetrafluorethylen
SPE	Solid phase extraction
TA Abfall	Technische Anleitung Abfall
TASi	Technische Anleitung Siedlungsabfall
Ww	wet weight
WWTP	Wastewater treatment plant

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1 Introduction

The group 'emerging contaminants' consists of pollutants which are subject to growing scientific interest within the last two decades (e.g. persistent organic pollutants or pharmaceuticals). The occurrence and fate of emerging contaminants in the environment is under investigation and leads frequently to results which show a widespread distribution of these compounds and potential ecotoxicological effects. One group of these substances are poly- and perfluoroalkyl compounds (PFCs) which are under examination in this thesis. PFCs, such as perfluorooctane sulfonate (PFOS) or perfluorooctanoic acid (PFOA), are widely used in industry and consumer products, due to their unique chemical properties for instance as surfactants and coatings [1]. During the production processes and use of the products, PFCs can be released into the environment. PFCs can be found ubiquitous in the environment, in industrial as well as in remote locations without direct anthropogenic influence [2]. PFCs are persistent, soluble and can be transported in water. Volatile precursor compounds can be degraded to PFCs and can be transported via atmospheric transport to remote places [3]. Subsequently PFOS belongs to the group of PBTs (persistent, bioaccumulative and toxic) [4]. They fulfill the criteria of POPs (persistent organic pollutants) [5]. Even though PFOS and derivates are banned by the European Union [6], environmental concentrations do not decrease of all PFCs. Perfluorobutan sulfonate (PFBS) concentrations were observed to be rising [7], since they act as substitute for other PFCs.

This study focuses on landfills which are possibly a source of PFCs [8]. Production waste as well as consumer products used end up in landfills, where they are subject to different chemical reactions and degradation processes. It is possible that PFCs can be set free and attain in leachates, which rinse out of landfills for a long period of time.

To investigate on PFCs in landfills samples of leachate from 22 landfill sites in Germany were taken. Samples of 20 treated leachates and samples of untreated leachate from 6 sites were examined. Additionally, on six sites samples were taken three or four times in a period of three to four months. On two sites leachates could be taken within three carbon containers of an activated carbon treatment.

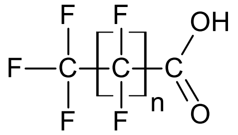
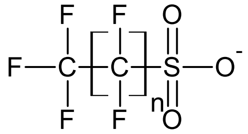
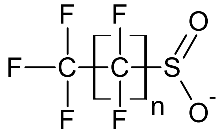
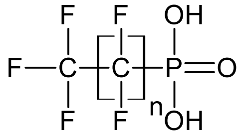
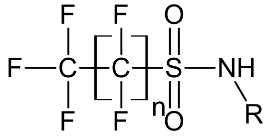
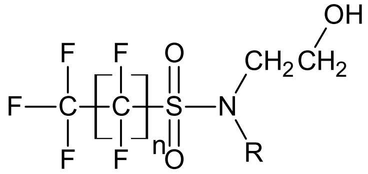
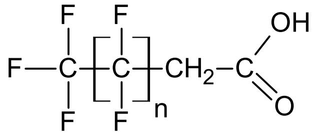
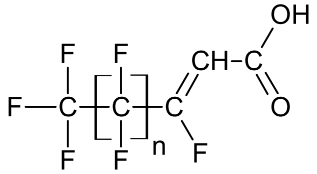
At first patterns of PFCs in leachate are investigated in order to determine which compounds are compounds of concern. Afterwards influences of time are investigated in treated and untreated leachate. The impact of age on the leachate is examined, and then short term changes in concentrations in treated leachates are investigated. Further, the effectiveness of treatment systems is discussed. Five types of treatment systems are compared with regard out flowing concentrations. Treated and untreated leachate of four sites is compared and treatment steps of two sites are examined. Adsorption behavior of PFCs on activated carbon is analysed. Since the chain length plays a major role in accumulation in biota and sediments, behavior in other matrices, it might be the same in activated carbon treatment. Afterwards concentrations will be compared to other aqueous environmental media and mass flows for landfills will be estimated as well. It is investigated if concentrations of PFCs in treated leachates can lead to ecotoxicological effects. A comparison to concentrations in other aqueous media will show if landfills are a source of PFCs into the environment. At last, a comparison with published literature data from Scandinavia and USA, as well as unpublished data from Germany is drawn.

2 Basic information on PFCs

2.1 Analysed compounds

The PFCs that are surveyed in this study are a wide group of different substances which are all based on a fluorinated alkyl carbon chain with different functional groups and different environmental behavior. The analysed compounds are perfluoroalkyl carboxylic acids (PFCAs), perfluoroalkyl sulfonates (PFSAs), perfluoroalkyl sulfinates (PFSiAs), perfluoroalkyl phosphonic acids (PFPAs), perfluoroalkyl sulfonamides (FASAs), perfluoroalkyl sulfonamidoethanols (FASEs), fluorotelomer carboxylic acids (FTCAs), fluorotelomer unsaturated carboxylic acids (FTUCAs) and 6:2 fluorotelomer sulfonate (6:2 FTS). All substances except the FTCAs, FTUCAs and 6:2 FTS consist of a fully fluorinated carbon chain with the corresponding functional group. The structures of the compounds are shown in table 1. A complete list of analytes, acronym, formula and corresponding internal standards is given in appendix 1.

Table 1: Structures of the analyzed compounds.

Structure	Compound
	Perfluoroalkyl carboxylic acids (PFCAs) n = 1-12, 14, 16 (additional Me2-PFOA)
	Perfluorinated sulfonates (PFSAs) n = 3-9 (additional 6:2 FTS)
	Perfluoroalkyl sulfinates (PFSiA) n = 5, 7, 9
	Perfluoroalkyl phosphonic acids (PFPAs) n =6, 8, 10
	Perfluoroalkyl sulphonamides (FASAs) n = 3, R = CH3 n = 7, R = H, CH3, C2C5
	Perfluoroalkyl suphonamidoethanols (FASEs) n = 3, R = CH3 n = 7, R = CH3, C2H5
	Fluorotelomer carboxylic acids (FTCA) n = 5, 7, 9
	Fluorotelomer unsaturated carboxylic acids (FTUCA) n = 4, 6, 8

2.2 Chemical properties

PFCs are chemicals with anthropogenic origin. Substances with more than one fluor atom, except trifluoroacetic acid, cannot be produced by natural sources [9]. The fluor-carbon bond is the most important characteristic to explain the chemical properties of PFCs. Fluor possesses the highest electronegativity with 4.0 of all atoms, which leads to a strong covalent bond with carbons. The energy of this bond is 460 KJ/mol or 110 kcal/mol, which is one of the strongest covalent bonds known [1] and leads to the persistence in the environment. Except volatile precursor compounds, like FTOHs, which can be degraded to PFCAs [10], PFCs are persistent in the environment and resist to hydrolysis, photolysis, biodegradation, and metabolism [1]. They are resistant to thermal degradation [11]. Fluorotelomer-based polymer products can be destroyed by incineration at temperatures higher than 1000 °C. [12].

Most of the objected PFCs, except the FASAs and FASEs, dissociate in water to an anion with a hydrophilic head and a hydrophobic and lipophphilic carbon chain with a high ionization potential, which leads to marginal intermolecular actions and a repellence of oil and water [1].

The potassium salt of PFOS is a white powder with a boiling point higher than 400 °C and a density of approximately 0.6 g/cm^3. The other salts of PFOS, lithium-, ammonium- and diethanolamidesalt have densities of approximately 1.1 g/cm^3. The pK$_a$ value is -3.27 [13]. The vapour pressure is stated to be between 1.9x10^{-9} and 3.3x10^{-9} PA and the water solubility is in average 600 mg/L. The shorter chained PFBS has higher water solubility of 51 g/L [13]. An indirectly estimated n-octanol-water coefficient by 3M lies at -1.08 log Kow, an other measurement states a value 4.13 log Kow for the potassium salt of PFOS and 6.28 log Kow for the acid. The Henry's Law constant is less than 2.0x10^{-5} and therefore PFOS is not volatile. The melting point of PFOA is determined to be at 45–50 °C, the pKa value is 2.5, and the vapour pressure is 13.3 PA. The water solubility is 3.4 g/L [4, 14].

FTOHs are volatile precursor compounds for PFCs, which have a higher vapor pressure than the investigated PFCs [15]. The atmospheric half-life is 20 to 164 days [11, 16–18]. These compounds are transportable to remote places via atmosphere. Neutral precursor compounds were observed to biodegrade in biota [18], sludge [19, 20], and in the atmosphere [21, 22].

2.3 Production and legislation

The industrial production of perfluorochemicals started in 1947 by the 3M Company (Minnesota Mining and Manufacturing Company, St. Paul, Minnesota, USA) [23]. There are two major ways in producing perfluorochemicals: The electrochemical fluorination (ECF) and the telomerisation.

The ECF was invented by Simons in the 1940's. An organic compound is dissolved or dispended in anhydrous hydrogen fluoride. An electric current, usually between five and seven Volt (V) is set between two nickel-electrodes. The hydrogen from the carbon chain gets replaced by the fluorine, while the functional group of the educts remains. This reaction leads to 30 % impurities due to fragmentation of the alkyl chain and appearance of non-linear isomers [1, 24, 25].

The other possible production process is the telomerisation, which was invented in 1949 by Haszeldine and adapted by the Du Pont Company. Here tetrafluorethene reacts with iodpentafluoroethane to perfluorooctyl iodide and ethylene. The iodide group can be changed to a functional group of choice in another production step. This reaction yields important precursors like FTOHs, that have linear chains, but are not fully fluorinated. This process leads to a higher purity of the compound but is more expensive than the ECF [1, 25].

The total production of perfluorooctane sulfonyl fluoride (POSF), which is the industrial feedstock for the production of PFCs, is estimated to be 96,000 t for industrial processes and 122,500 t including unusable production waste. The annual production of POSF is estimated to have grown to 4650 t/year in the year 2000 whereof 3665 t were produced by 3M [8]. The production of PFOS and PFOA in the USA was voluntarily phased-out by 3M in 2000 and 2002, respectively, [26] in order to avoid legal activities by the United States Environmental Protection Agency (USEPA) that classified PFOS as a PBT-chemical [5, 25]. After this agreement the annual production of PFCs decreased to 74–175 t in 2005 [27].

In the European Union the production of PFOS was decided to be stopped by the end of 2007 [6]. Therefore the production of other PFCs will increase, due to the lack of unfluorinated chemicals that can replace PFCs [28]. This compound will especially be PFBS, which might be less harmful to the environment [29]. In May 2009 PFOS was voted to be a POP under annex B of the Stockholm Convention [30]. The Stockholm Convention is an internationally binding agreement based on the United Nations Environmental Programme (UNEP) that forces the member states of the agreement to take legal action on the application and production of these compounds.

2.4 Usage

PFCs offer special chemical properties, which cannot be offered by other chemicals; for this reason PFCs are ingredients in a variety of applications. Due to their property to repel oil and water they are used for coatings of carpets, clothes, paper and packaging, as performance chemical in hydraulic fluids and aqueous fire fighting foams, polishes and shampoos [8]. Polytetrafluorthylene (PFTE)-based membranes are used widely because of their ability to 'breathe'; to let steam out, but no water in [31]. The allocation of PFCs from American production to the different usages is estimated to be 41 % as coatings on paper and packaging, 37 % for impregnation in fabric, leather and carpet goods, 10 % as ingredient in industrial surfactants, additives and coatings and 3 % was used in aqueous fire fighting foams [32].

2.5 Environmental sources

Masses up to 7,300 t have been estimated to be discharged to the environment by direct and indirect sources. Direct sources are the production sites, fluorotelomer manufacturing and processing, fluortelomer dispersions, aqueous fire fighting foams and consumer and industrial products. Indirect sources are POSF-based products, fluorotelomer-based products, which can degrade to PFCAs [23]. The production took place only in a few large sites, but the use of the products was widespread, therefore the potential for dispersal is given. It is assumed that a POSF adjusted treatment of production waste was not given; therefore the disposal is probably in normal waste streams into WWTPs [8]. Industrial point sources are described to be metal working industry, especially galvanizing industry, and paper working industry with high concentrations in WWTPs [33]. Indirect sources are assumed to show other patterns of emission. The releases are depending on the lifespan, use and disposal of the products. While secondary sources like carpets have a long lifespan in apartments, others, like paper and packaging, have a short lifespan and are carried out to waste disposal [8]. The disposal of treated products may lead to new point sources in form of landfill sites [25, 32, 34], even though used precursor substances might have to be degraded in situ before they attain in leachate [35].

2.6 Environmental occurrence

Not only in industrialized areas, even at remote places, PFCs can be found in wildlife [2], and water [36]. Tissue samples from animals [2], and water samples from Oceans [37] in remote areas are less polluted than in highly industrialized zones. This indicates a specific global distribution of PFCs. The scientific discussion examines ways of transport in remote areas: The first theory says that volatile precursors like FTOHs are supposed to be the main source for long chained PFAS in the arctic. The second transport way is aquatic transport via currents. The third and fourth possibility is the transport bound to particulate matter on are marine aerosols, like sea spray, respectively [23]. Since most PFCs are not biodegradable or get degraded to a stable PFC, the final sinks of PFC are assumed to be deep ocean water and sediment burial [23].

Temporal trends in animal tissue show rising concentrations in general [38, 39], but changing patterns: After 2002 the concentration of PFOS in harbour seals (*phoca vitulina*) from the German Bight has declined, which might be result of the ban of PFOS, but perfluorodecane sulfonate (PFDS) is still rising [40]. Studies from other authors show similar results in other animal tissues [41–43].

In marine mammals the mean Σ PFC concentrations were 1988 ng/g wet weight (ww) and 907 ng/g ww, respectively, in younger and older than seven months harbour seals' liver tissue from Germany [44]. Liver samples from the Canadian Arctic show concentrations of 325 ng/g Σ PFC and 3112 ng/g PFOS-equivalents in polar bears (*ursus maritimus*), 53 ng/ng and 269 ng/g in samples from arctic foxes (*alopex lagopus*), 18 ng/g and 42 ng/g in brook trout (*salvelinus fontinalis*) and 19 ng/g and 38 ng/g in lake trout (*salvelinus namaycush*) [45]. PFCs can as well be found in humans. Concentrations of PFOS and PFOA range from ~5 ng/mL of both compounds in Colombia to >50 ng/mL and >20 ng/mL, respectively, in Poland [46].

Air samples show maximum concentrations of 40 pg/m^3 for several volatile precursor compounds in outdoor air in Canada [47]. In USA and Germany mean concentrations of several compounds are up to 400 pg/m^3 and 359 pg/m^3, respectively [48, 49].

Rivers in industrialized areas show high concentrations of PFCs up to 1371 ng/L PFOS in the river Krka in Slovenia. The river Scheldt shows concentrations up to 153 ng/L, the Seine 97 ng/l and the Rhine 32 ng/l. High concentrations of PFOA were measured in Danube 25 ng/l, Scheldt 88 ng/l, and Rhone 116 ng/L [50]. In Japan PFOA was found in River water at 54–192 ng/L. Usually Σ PFC concentrations range between <10 ng/L and <300 ng/L [51]. Concentrations in coastal waters from the Pacific and Atlantic Ocean are in a range of 0.23–57.5 ng/L PFOS and 0.24–192 ng/L PFOA. In the open Ocean concentrations are between the limits of detection and 0.1 ng/l for PFOS and 0.15–0.5 ng/L for PFOA [36]. Concentrations in the dissolved phase are the river Elbe between 16 ng/L Σ PFC in the estuary and North Sea and 38 ng/l Σ PFC in Hamburg. The fluxes were estimated to be 802 kg/year Σ PFC in the dissolved phase and 152 kg/year Σ PFC in the particulate phase [52]. Wastewater treatment plants (WWTPs) seem to be one important source of PFCs into the aquatic environment. PFOS is found at concentrations of 2.4–195 ng/L, PFOA at concentrations of 5.7–250 ng/L in four tested WWTPs. Mass flows were estimated to be 0.03 g/d to 8.0 g/d for PFOA and 0.02 g/d to 3 g/d for PFOS [53]. Other studies [54–56] show similar results. Lakes contain concentrations at 21–70 ng/L for PFOS and at 27–50 ng/L for PFOA [34]. Concentrations in landfill leachate are shown later.

2.7 Toxicology and ecotoxicology

Fluorinated compounds have toxicological effects on animals and human beings. The toxicity of PFCA is amongst other things based on peroxisome proliferation [25, 57]. For other PFCs it is suspected to have similar toxicology effects [58]. Subchronic effects manifest in significant weight loss, hepatoxicology, reduction of cholesterol in serum and decrease of thyroid hormones [59], as well as gastrointestinal effects, haematological abnormalities and convulsions [25]. Maternal effects, like reduction of foetal weight, cleft palate, delayed ossification of bones, and cardiac abnormalities, could be observed trough a wide range of species [59]. Additionally higher tumour-rates were found [60].

The lethal dosis for 50 of the tested animals (LD_{50}) was investigated for rats and resulted in >250 mg/kg for PFOA and 251 mg/kg for PFOS. Chronic effects can occur in fatheaded minnow below concentrations of 1 mg/L [25]. 'No observed effect levels' (NOEL) and 'lowest observed effect levels' (LOEL) are for PFOS 0.1 mg/kg and 0.4 mg/kg, respectively [61]. A calculated 'no observed adverse effect level' (NOAL) for Rhesus monkeys (*macaca mulatta*) is 0.15 mg/kg/day. A toxicological test with 4.5 mg/kg/day ended lethal for the whole group [57]. In Fish the fatheaded minnow (*Pimephales promelas*) was the most sensitive species with a LC_{50} of 9.1 mg PFOS/L in 96 hours. The ranges in this study were from 7.2 mg/L in 28 days for fatheaded minnow to 22 mg/L in 96 hours for rainbow trout (*Oncorhynchus mykiss*). NOEC ranges between 0.29 mg/L for fatheaded minnow and 6.3 mg/l in rainbow trout. 'Lowest observed effect concentrations' (LOEC) were 0.58 mg/L and 13.0 mg/l, respectively [14]. In summary it is assumed that PFOS is moderately toxic to fish and slightly toxic to invertebrates, but non-toxic for algae [25]. PFBS, which is the designated substitute for PFOS, shows in general a LD50 >2000 mg/kg and a NOEL of >1000 mg/kg/day [29].

The bioaccumulation factor (BAF) of PFOS ranges between 6,300 and 125,000 in fish in field-based data; and 8 to 30,000 in lab-based data [62]. In rainbow trout the bioconcentration factors (BCFs) increases from 4.0 to 23,000 for PFOA to PFTDA. The BCF increased by the factor of eight for each carbon atom in the fluorinated chain between C = 8 and C = 12 chain length. PFCAs and PFSAs with carbon chains of seven and less are considered not to bioaccumulate [63]. PFSAs have greater BAFs, half-lives and uptake-rates than PFCAs [64]. The Biomagnification factor (BMF) was 18 for PFOS in Minks (*Neovison vison*) [65]. The half-lives are estimated to be 3.9–28 days in rainbow trout for several PFCs [63]; PFOS is estimated to have a half live in rats of >90 days and 100 to 200 days in cynomolgus monkeys (*Macaca fascicularis*). PFOA is estimated to have half-lives from 1.9 hours (females) to 9 days (males) in rats (*Rattus spec.*), with a large gender-based difference. For Beagle dogs (*Canis lupus familiaris*) half-lives were estimated to be 202 and 473 hours, respectively [59]. In humans the half-lives were estimated to be 8.7 years for PFOS and 1–3.5 years for PFOA [25].

3 Basic information on landfills

3.1 Aim and regulation of landfills

Landfills are man-made to construct "environmentally friendly" sinks for neither avoidable nor utilisable wastes. Therefore harmful substances have to be locked out of the cycle of materials [66]. Landfills are built to provide a civil work in which treated wastes can be deposited under conditions where remaining pollution are acceptable for environment and location over a long period of time [67]. To assure environmental safety, landfills have to satisfy legal rules.

The German legislation is based on the law for recycling and waste (Kreislaufwirtschafts-/Abfallgesetz) [68], the enhancement for waste depositioning (Abfallablagerungsverordnung) [69], the enhancement for landfills (Deponieverordnung) [70], as well as the technical instruction for waste (Technische Anleitung Abfall) [71], and the technical instruction for municipal waste (Technische Anleitung Siedlungsabfall) [72]. Another relevant rule is the Water Management Act (Wasserhaushaltsgesetz) [73] which sets rules, how clean wastewater must be to be in order allowed to freight in receiving waters.

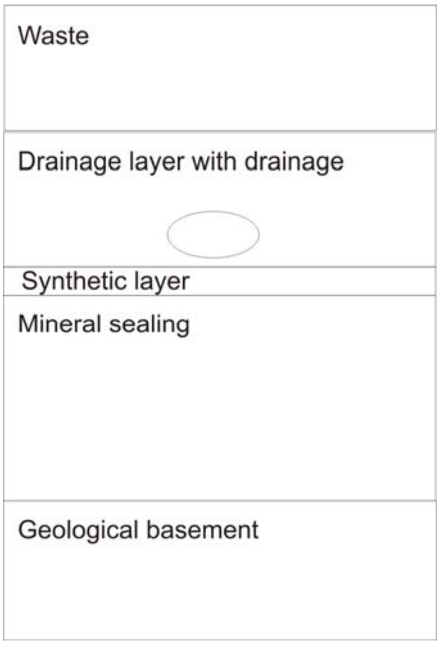
The most important rule is the technical instruction for municipal waste (Technische Anleitung Siedlungsabfall) [72], which describes the design of landfills. Furthermore it states that leachate has to be collected, monitored and treated wherever possible. The waste depositing enactment (Abfallablagerungsverordnung) [69] states additional rules, for example that wastes containing organic matter have to be pre-treated by incineration or biological treatment in order to reduce organic pollutants and chemical activity.

3.2 Design of landfills

To assure environmental safety of landfills, the planning, constructing and operating has to search for geological and hydrogeological adequate places, useful sealing, proper installations of fillings, and achieving of assignment criteria of the given laws, which construct different independent barriers for the disposal of pollutants [74]. The multibarrier-concept is based on six different points: geology, sealings, landfarming, operating, monitoring and aftercare [75].

There are five different classes of landfills in Germany: 'Class 0' is for excavated soil, like sand or flint, and underlies no further regulation and leachate treatment relevant here. 'Class I' to 'class III' are aboveground landfills, which are allowed for waste with different properties. 'Class I' is for construction waste and excavated soil, 'class II' is for municipal waste and 'class III' for waste with a higher amount of pollution and other characteristics than 'class II'. 'Class IV' landfills are underground depots for special wastes [76]. Additionally there are landfills installed before laws were established. They are referred here 'old type' landfills. 'Class I' landfills can have sections with a 'class II' allowance, depending on the concession.

Since municipal landfills are the mostly sampled subject in this study, a closer look at the construction of landfill 'class II' is taken: The TaSi gives specifications for a standard assembly, which contains a base seal and a surface sealing. The base seal (graph 1), has to be build on adequate ground with a mineral sealing of 75 cm thickness composed out of three layers, a synthetic layer of more than 2.3 mm thickness and a drainage layer which contains pipes for the collecting of leachate. Other classes of landfills have to fulfill analogous rules with layer formations [72]. The main function of base seals is to keep groundwater out of the landfill body, in order to keep the solid waste dry and to avoid the solution of contaminants in fluid. Leachate has to be kept inside the landfill, in order not to pollute the surrounding soil. The reasons for collecting leachate are minimizing the backwater at the base and to get water out of the landfill to treat it properly [77].



Graph 1: Standard assembly for base sealing from 'class II' landfills. (Own illustration based on [72])

Landfills have to have a surface sealing wherever possible. Active construction sections do not need a sealing until they are filled; chemically active sections get a provisory sealing due to settlings [71]. The surface sealing is constructed of an equalizing layer with a height of 50 cm, which can be pervaded by gas collecting pipes, and a mineral layer of 50 cm thickness. On top of that a drainage layer for rainwater discharge and a vegetation layer with plant cover are installed [72]. See graph 2 for a sketch.

Graph 2: Standard assembly for surface sealing of 'class II' landfills. (Own illustration based on [72])

3.3 Emissions from landfills

3.3.1 Gaseous emissions

Landfill gas is one kind of emissions from landfills. Biological degradable substances like carbohydrates, fat and proteins are decomposed to 30 to 60 % methane, 30 to 50 % carbon dioxide and around 2 % trace amounts of hydrogen sulphide, carbon monoxide, nitrogen, quicksilver, and trace gases like fluorochlorocarbons [75]. Due to a heating value of 10 kWh/m^3 landfill gas is burned to win energy [74]. One million tones waste can replace 1,000 m^3 fuel oil.

3.3.2 Leachate

The water which comes out of landfills is referred to as ‘leachate’. Leachate originates in humidity of waste, rain [78] or in infiltrating groundwater, if the landfill has no base sealing. The amount of leachate depends on rain, evaporation, run off [75], and adsorption in the landfill body [74]. The amount of leachate is quantified to be 4–10 m^3/ha/year in open areas, 1–4 m^3/ha/year in vegetated areas and less than 1 m^3/ha/year in sealed areas [78]. Leachate contains various organic and inorganic contaminants [79].

It is not permitted to discharge leachate uncleaned into downstream receiving waters if certain limit values are not reached. The limits are given in appendix 51 of the wastewater ordinance (Abwasserverordnung) [80]. Selected parameters from the ordinance are a chemical oxygen demand (COD) below 200 mg/L, biological oxygen demand in five days (BOD %) BSB_5 below 20 mg/L, Nitrogen below 70 ng/L, and hydrocarbons below 10 mg/l. Estimations state these values can be reached after 65–320 years for COD and after 120–450 years for Nitrogen without a cleaning treatment. A typical value for an active landfill is COD of 1,500–2,500, and NH_4-N of 600–1,000 mg/l [78], which causes adverse effects in aqueous environments; therefore leachates usually have to be treated.

3.4 Treatment of leachate

The treatment of wastewater has generally the aim to clean water from pollution, chemical stabilizing of remaining substances, and disinfection, if the water should be used for drinking water purposes [81]. There are different ways to treat leachate. The law does not specify one way to treat leachate, but advises to treat with 'state of technology' ('Stand der Technik') [71]; therefore a proper way of treatment for any leachate in particular has to be searched. An overview on the different treatment ways is given in table 2. The different treatments are usually combined in order to combine amenities regarding cleaning different groups of pollutants.

Table 2: Different treatment systems and their adequacy for different pollutants (Reduced from [78]). Abbreviations: + = applicable, - = inapplicable, o = applicable on limited extend.

	Nitrogen	BSB	CSB	AOX	hydrocarbons
Biological treatment	+	+	o	o	o
Reverse osmosis	o	o	o	+	+
Adsorption	-	o	o	+	+
Chemical oxidation	+	o	o	o	o

3.4.1 Mechanical pre-treatment

The first cleaning step for landfill effluent is a mechanical pre-treatment. Sand or pea gravel prevents solid matter from floating into the downstream treatment systems. This is not necessarily prerequisite for all biological treatments, but useful for most other treatments [82]. Single- or multilayer systems can be considered, depending on the composition of leachate [81]. The treatment system can be cleaned by refluxing into the landfill body.

3.4.2 Biological treatment

Almost every biological treatment with activated sludge and nitrification/denitrification is possible as treatment for leachate. Usually biological treatments are a first cleaning step with a downstream filtration step [82]. Biological treatments are technical implementations of natural purifications as it is happening in natural water bodies [83]. The most important aim of biological treatments is to take out Nitrogen, due to high oxygen demand in microbiological oxidation of nitrification, and toxicological effects of NH_4+ ions on fishes [83]. The denitrification step, which is not necessarily following the nitrification step, converts nitrogen in the gaseous form and sets it free into the atmosphere [83]. As residue of the cleaning treatment activated sludge is generated. This sludge was taken out on landfills, but has to be pre-treated since 2005 [69].

3.4.3 Chemical treatment – wet air oxidation

Wet air oxidation is a treatment system for organic substances. The main aim is to reduce AOX to water, carbon dioxide and inorganic chlorine [82]. Therefore Ozone is given in combination with different other treatments to the leachate. The most common combinations are O_3/H_2O_2, O_3/UV and H_2O_2/UV [84]. Ozone can directly react with a compound or produces hydroxyl radicals that react with the compound. The aim is to provide unselective and rapid OH-radical to oxidise pollutants, natural organic and inorganic compounds, disinfection, and the removal of color and taste [84]. Ozone mostly affects carbon double bindings [85]. Leachate is recommended to be piped into municipal WWTP [82].

3.4.4 Membrane treatment

Membrane treatment is an umbrella term for physical treatments that separate leachate into a cleaner permeate and a dirtier residue via a membrane. Therefore leachate is send trough a membrane using pressure. The used treatments are micro filtration, ultra filtration, nano filtration and reverse osmosis. The main difference is the range of sizes of pollution that is separated. Micro filtration works in a range of 10^{-4}–10^{-7} m size of pores, ultra filtration works in a range of 10^{-5}–10^{-8} m, nano filtration at 10^{-7}–10^{-9} m and reverse osmosis at 10^{-8}–10^{-9} m [82]. Reverse osmosis is operated at pressures up to 100 bars. Micro filtration and nano filtration are suitable as a first cleaning step or for the separation of activated sludge after a biological treatment, while reverse osmosis is more suitable as a secondary cleaning step. The resulting concentrate has to be treated adequately, due to high chemical charges [82]. The treatment is depending on filtration at the membrane and therefore the leachate of reverse osmosis has constant concentrations in permeate unlike activated carbon, where changing concentration in leachate can result in changing concentrations in effluent.

3.4.5 Adsorption

Organic contaminants can adsorb to surfaces of carrier material like activated carbon, resin or smectite. Therefore organically polluted leachates are often send trough an adsorption system as a last cleaning step [82]. Activated carbon is the most common adsorbent in the treatment of leachate; in deed, in this study no other adsorbent was used. Activated carbon, which can be used in different form as powder, granulate material, or for gaseous emissions pressed in forms, is the optimal treatment for unpolar and low polar organic compounds, whereas resin is suitable for more polar components [85]. Activated carbon for the use in cleaning treatments shows surface areas from 600–1,300 m^2/g and therefore provides a big surface to adsorb [85]. The adsorption is based on van-der-Waals-forces. After a certain time the activated carbon is charged by compounds. To avoid breakthroughs the carbon has to be changed or regenerated regularly [85].

3.5 Knowledge about PFCs in landfills

The recent knowledge about PFCs in landfills in peer-reviewed literature is quite small, even though local authorities are collecting data, which are either not sorted, like in Lower Saxonia, where a few districts (Regierungsbezirke) have data for single landfills, or like the federal state North Rhine Westphalia (Landesamt für Natur Umwelt und Verbraucherschutz, LANUV) that owns a pool of not evaluated and published data. Nevertheless some published data is available: A total of 15 landfill sites is covered by four surveys [56, 86–88], whereof one survey was conducted by a major fluorochemical producer [86]. Fifteen treated and one untreated leachates were tested. The ∑PFC concentration ranged between below the limits of quantification

(0.0025 µg/L) for three tested compounds in Columbus, Georgia, USA [86] to 5227 ng/L for twelve compounds in Högbytorp, Sweden [87]. The average of Σ PFC is 1456 ng/L for all observed landfill sites. The averages and standard deviations for the single compounds are listed in table 3. One tested untreated landfill leachate showed concentrations of several thousand ng/L for PFHxS (8,900 ng/L), PFOS (9,600 ng/L), and PFOA (4,200 ng/L), whereas nine other compounds were not quantifiable, due to limits of detection (LOD) at levels between 11 ng/L for PFDS and 1,300 ng/L for PFBA. High LODs might have been resulted from not specially optimised methods for leachate. No study was on the matter of landfill leachates, therefore methods were not adjusted, which might have led to high detection limits.

Table 3: Averages, median and standard deviations for PFCs in landfill leachate in ng/L, based on literature data ([56, 86–88]). NQ = not quantifiable

	[86](n =3)	[87](n =4)	[88](n =6)	[56](n =2)	Average concentrations from all sites
PFBS	-	<0.5-110 (37.25)	5.64-112 (51.5)	-	57±42
PFHxS	-	12-1800 (518)	12.4-143 (77.0)	<0.2-3.1 (0.8)	231±499
PFOS	<25-52.7 (17.7)	32-1500 (555)	32.8-187 (82.5)	<1.5-3.8 (1.1)	213±388
PFDS	-	<1-0.28 (0.07)	-	-	0.3
PFBA	-	<12-30 (7.5)	-	-	30
PFHxA	-	<7-310 (77.5)	26.4-697 (228)	-	238±215
PFHpA	-	<20-260 (197.5)	-	-	146±104
PFOA	NQ-48.1 (16.9)	38-1000 (537)	92.4-516 (293)	<2-5.8 (2.9)	331±301
PFNA	-	<18-100 (43.5)	4.7-61.5 (34.8)	<0.8	43±28
PFDA	-	<20-220 (82.5)	-	<1.6	165±55
PFUnA	-	<59	-	<2.2	NQ
PFOSA	-	<2-7 (2.75)	NQ-3.28 (1.17)	<0.3	1.20±1.06

However, besides the available data, different authors [8, 23, 25, 32, 34] suggest landfills as potential source of PFCs to the environment. Direct emissions of existing PFCs are as well suggested as decomposition of precursors like fluorotelomer acrylate polymers [35] and gaseous emissions of FTOHs [48].

4 Materials and Methods

4.1 Chemicals

In this study 43 poly- and perfluorinated compounds were analysed, including 16 PFCAs, 7 PFSAs, 3 PFSiAs, 3 PFPAs, 4 FASAs, 3 FASEs, 3 FTCAs, 3 FTUCAs and 6:2 FTS. All chemicals have purity equal or greater 95 % and were purchased by 3M, ABCR, Alpha Aesar, Fluka, Lancaster Sythesis and Wellington Laboratories. For a complete list of chemicals, formula, acronyms, corresponding Internal Standard, suppliers and mass transitions see table 1 in the appendix. Internal Standards have a purity of >98 % and purchased by Wellington Laboratories. For a complete list containing, formula, acronyms, and mass transitions see the appendix. Methanol (Suprasolv), acetonitrile (LiChrosolv), ammonium hydroxide (25 % p.a.) and ammonium acetate were purchased from Merck (Darmstadt, Germany). Pure water was produced by a MilliQ Plus 185 system by Millipore (Zug, Germany).

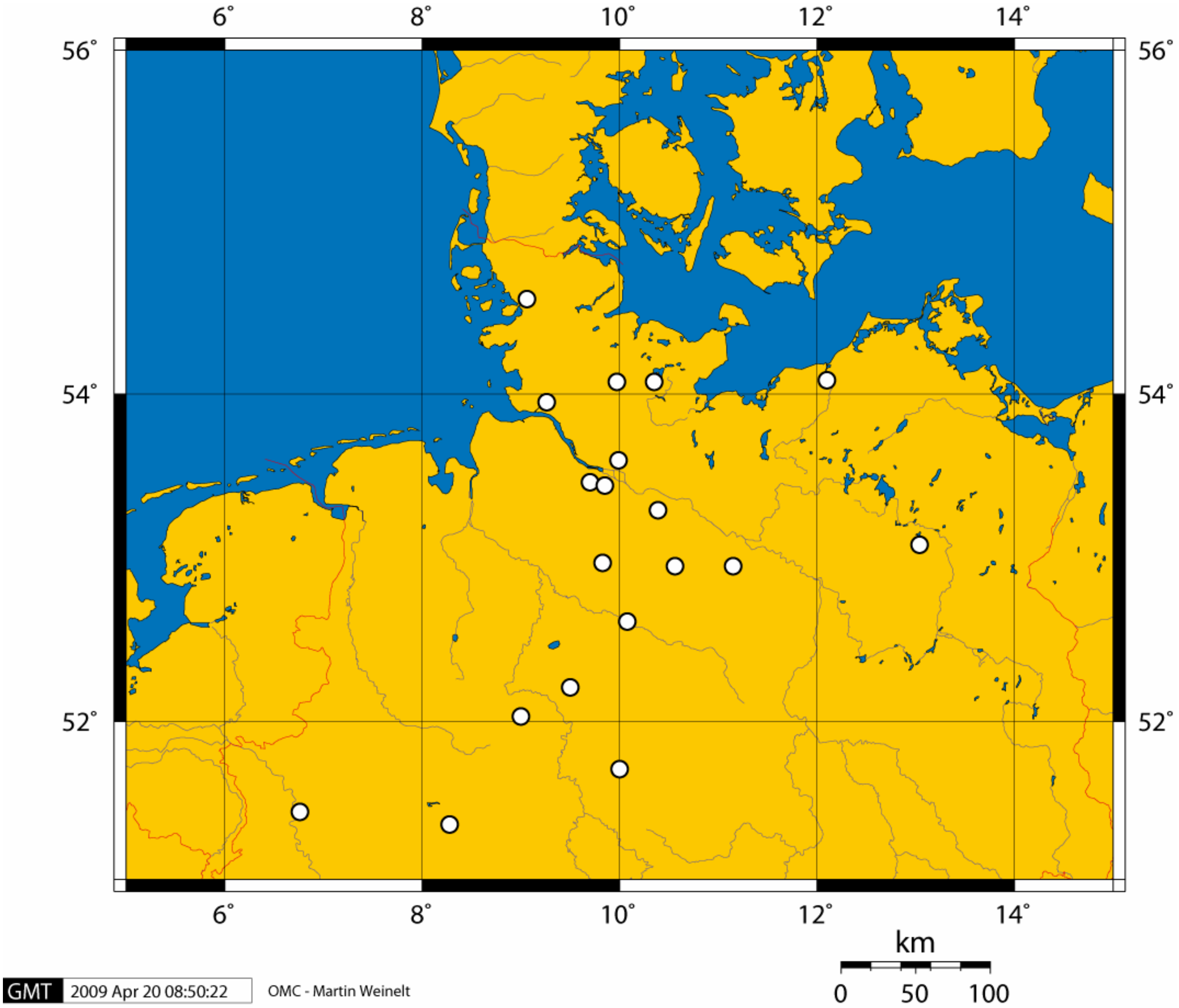
4.2 Sample collection and sampling sites

On 22 landfill sites samples were taken. An overview on the geographical position of the landfill sites can be obtained in figure 3. Twenty treated and six untreated leachates were taken. On four sites (sites 7, 8, 14 and 17) leachates before and after treatment were taken. Five sites were monitored for three and four months, respectively, with sampling rates between two and four weeks. On two sites samples were taken during different steps of the treatment process. Samples were taken at installed sampling points before, in between, and after the treatment process. Overall 58 samples were analyzed. Samples were taken in 250 ml polypropylene (PP)-bottles, cleaned in a dishwasher with clean water post-purge and dried at 60 °C in an oven. Samples were sonicated, due to bacterial growth in some samples in pre-tests, and stored at 4 °C until further preparation.

From the 21 sites, 20 sites had a treatment before discharging into wastewater or downstream rivers. On 11 sites only one treatment procedure was used, the other ten had a combination of two or more treatments (i.e., biological treatment and activated carbon). A complete list with landfill sites, cleaning treatments and annual amounts of effluent is given in table 4.

Table 4: Overview on tested landfills with estimated annual amount of leachate in m³/year, treatment process, status, landfill class, and sample.

Landfill	Amount of leachate (m^3/year)	Treatment process	Status	Landfill class	Sample of leachate
1	Unknown	external	Inactive closed 2005	I	Untreated
2	46,000	Biological	Active	II	Treated
3	26280	Biological, reverse osmosis	Active	II	Treated
4	7000	Biological, reverse osmosis	Inactive closed 1999	3 sites: 2xII and 1xIII	Treated
5	8000	Nitrification	Active	II	Treated
6	175200	Wet air oxidation	Active	I, partial II	Treated & untreated
7	28700	Activated carbon	Inactive closed 1979	Old Type partial unknown waste	treated
8	9000	Activated carbon	Inactive closed 1979	Old Type partial unknown waste	Treated & untreated
9	8000	Activated carbon	Inactive closed 2004	II	Treated & within treatment Steps
10	200	Nanofiltration	Inactive closed 1999	II	Treated
11	20000	external	Inactive closed 1986	II	Untreated
12	55000	Nanofiltration	Active	II	Treated
13	10000	Reverse osmosis	Active	II	Treated
14	20000	Flotation, biol, activated carbon	Active	II	Treated & untreated
15	8000	Reverse osmosis	Active	II	Treated
16	16500	Biological, activated carbon	Active	II	Treated
17	19500	Flotation, biological, activated carbon	Active	II	Treated & untreated
18	131400	Activated carbon	Active	II	Treated & within treatment steps
19	27500	Biological, reverse osmosis	Inactive closed 1999	II	Treated
20	26500	Flotation, biological, activated carbon	Active	II	Treated
21	29000	WWTP/external	Active	II, only filter-cake from a WWTP	Treated
22	41100	Reverse osmosis	Active	II	Treated



Graph 3: Geographical position of the tested landfill sites (Graph designed with [89]).

4.3 Sample preparation

The sample preparation followed a procedure described before by Ahrens [37] with small modifications. The samples were prepared within four weeks after sampling. They were filtered by glass fiber filters (GFF, GC/C, Whatman, Ø 47 mm, 1.2 µm), which were baked out at 450 °C prior to use. An aliquot of 50 mL of treated leachate and 5 mL of untreated leachate, respectively, was adjusted to a pH-value of 7–8 using ammonia. Most samples had a pH lower than 7, since acids are added in preparation for membrane treatments. At pH 7–8 the mean recoveries were best. Short chained compounds had higher recovery rates at low pH-values, but longer chained PFCs (C>6) had low recovery rates. This was already mentioned by Skutlarek [90]. The aliquots were spiked with 100 µL of a mass-labeled internal standard mix (IS) with a concentration of 100 ng/mL in order to correct matrix effects. See annex 2 for a complete list of IS. The extraction was conducted via solid-phase extraction (SPE) using OASIS WAX cartridges (Waters, 150 mg, 6 cc, 30 µm) in a Teflon free SPE manifold by Baker. Prior to use the cartridges were preconditioned by 5 mL 0.1 % ammonium hydroxide (NH4OH) in methanol, 5 mL methanol and equilibrated by 5 mL millipore water. Even though the manufacturer approves loading rates up to 3 drops per second, the recovery rates were best at loading rates of approx. 1 drop/sec. After loading the cartridges were washed with 5 mL 0.1 % NH_4OH in Millipore water and dried by centrifugation at 3000 rpm for 2 min. For good results the cartridges were not allowed to run dry after the first contact with conditioner until the end of washing.

The sulfonamides were eluted by 14 ml of acetonitrile into a 25 ml round bottom flask and reduced to approx. 2 ml using a rotary evaporation system (pressure 240 mbar, Buechi, Essen, Germany). The acids were eluted with 5 ml 0.1 % NH_4OH in Methanol into a 5 ml vial. Both extracts were combined and reduced under a gentle nitrogen stream in a Barkey system (Optocontol, Barkey, Leopoldshöhe, Germany) to 150 µl. The samples were transferred into a 0.25 ml vial and spiked with 50 µl of an internal standard (d5-Et-FOSAA) of 0.4 µg/ml.

The used glass was dish-washed by a Miele laboratory dish-washer (Miele, Gütersloh, Germany) with a last rinsing of the items by Millipore water. Used vials and pipettes were cleaned by sonication with Millipore water once and with methanol twice. All glass items were baked out at 250 °C for ten hours. Parts containing Teflon were avoided due to possible blank contamination.

4.4 Instrumental analysis

The reduced extracts were analysed using high performance liquid chromatography and tandem mass spectroscopy (HPLC-MS/MS) in an electrospray negative ionisation mode, as described before [44]. A HP 1100 HPLC (Agilent Technologies) system was used. The HPLC was used with a Synergy Hydro RP 80A column (150 x

2 mm, 4 µm) at constant 30 °C in combination with a Synergy 2 µ Hydro RP Mercury column (20 x 2 mm, 2 µm) by Phenomenex. In order to avoid blank contamination from Teflon parts the degasser system was disconnected and as far as possible all Teflon tubes were exchanged with PP tubes. The degassing of the mobile phases was accomplished by sonication prior to use. The mobile phases were 10 mM ammoniumacetate as ionisation aid in Millipore water and methanol, respectively. The operating flow was 200 µL/min in gradient mode, starting with 70 % of ammoniumacetate in water as mobile phase, decreasing to 30 % within three minutes, decreasing to 0 % over 28 minutes and being kept constant for the next seven minutes. A pre-run for equilibration of the column before all injections lasted seven minutes with pure methanol. The injection was 10 µL and the needle was rinsed in pure methanol before each use.

The detection was done with a triple-quadrupol mass spectrometer (API 3000, Applied Biosystems/MDS Sciex) in a multiple reaction monitoring mode (MRM) with Analyst 1.5.1 (Applied Biosystem/MDS Sciex) as operating software. The source block was set to 300 °C and ionisation voltage was -4500 Volt. Nebuliser, curtain and collision gas was set to 14, 8 and 6 L/min, respectively.

4.5 Quantification

Quantification was made using a calibration from 0.1 ng/mL to 300 ng/mL of the compounds. The calibration points were 0.1, 0.5, 1.0, 2.5, 5.0, 10.0, 50.0, 100.0, 200.0 and 300.0 ng/mL. For quantification response factors (analyte peak area/IS peak area) were taken. See table 1 in the annex for analytes and corresponding internal standard. The calibration curves had usually correlation coefficients of >0.99. In some samples some compounds (i.e., PFBS) were out of the calibration range, therefore the compounds were analysed again with the same method but with an extraction volume of 5 mL. For some compounds, e.g. PFOS, more than one peak could be identified. These peaks occur due to the detection of isomers [58] and are not quantified due to the lack of standards. For four compounds, PFPS, PFNS, PFPeDA and PFHpA no standards were available. These compounds were quantified by parameters of the shorter and longer chained compounds and are therefore only estimations.

4.6 Quality control

The quality control and assurance was made by using internal standards and recovery rates, method blanks, mass detection limits, mass quantification limits, control standards, repeating tests and the calculation of the matrix effect.

Blanks were prepared of Millipore water at least every eight samples together with the samples. They were calculated as concentrations in corresponding volume and subtracted from the measured values. Blanks were found in the samples processed with 50 ml for nine substances (PFHxS, PFOS, PFOSi, PFBA, PFPA, PFOA, PFDA, PFUnDA and PFOSA) at pg/L levels. PFOA and PFOS reached a blank value of over 1 ng/L three times for PFOA and 1 time for PFOS, respectively. Samples processed with 5 ml had higher blanks, up to levels of 39 ng/L for PFOA and 36 ng/L for PFBS, due to the low sample volume. The other blanks for samples of untreated leachate were less than 10 ng/L for each substance. All samples were corrected by the blank concentration.

Recovery rates were calculated as percentage of 100 µl added mass labelled standard with a concentration of 100 ng/L. They were in average 59±16 %. The lowest recovery rate was 49±15 % for D5-EtFOSA, the highest 70±21 % for 13C-PFOSi. An overview is given in table 5; a complete list is shown in the annex. Samples with mean recovery rates lower than 50 % have not been taken into further consideration, but were prepared again with lower extraction volumes to reach recoveries over 50 %.

Table 5: Recovery rates and standard deviation of Internal Standards in leachate samples in percent.

Substance	Recovery rate
$^{18}O_2$-PFHXS	59±25
^{13}C-PFOS	60±22
^{13}C-PFOSI	70±21
^{13}C-PFBA	43±24
^{13}C-PFHXa	58±26
^{13}C-PFOA	59±23
^{13}C-PFNA	62±23
^{13}C-PFDA	64±18
^{13}C-PFUDA	68±15
^{13}C-PFDoA	64±12
D_3-MeFOSA	50±14
D_5-EtFOSA	49±15
D_7-MeFOSE	58±13
D_9-EtFOSE	57±15
^{13}C-6:2 FTCA	57±19
^{13}C-FOEA	60±25
^{13}C-FDEA	58±18
^{13}C-FHUEA	57±27
^{13}C-FOUEA	64±22
^{13}C-FDUEA	69±14
mean	59±16

The mass detection limits and mass quantification limits were calculated as signal to noise ratio of three and ten, respectively, in samples. The calculation was made as average of multiple calculations in samples with a signal to noise ratio close to ten, if possible. Table 6 shows the detection and quantification limits. The lowest level was 0.01 ng/L and 0.05 ng/L, respectively, for PFHxSi. The highest levels were 6.8 ng/L and 22.8 ng/L for PFDPA.

Table 6: Mass detection limits (MDL) and mass quantification limits (MQL) in ng/L for all compounds in leachate. n.d.= not detected

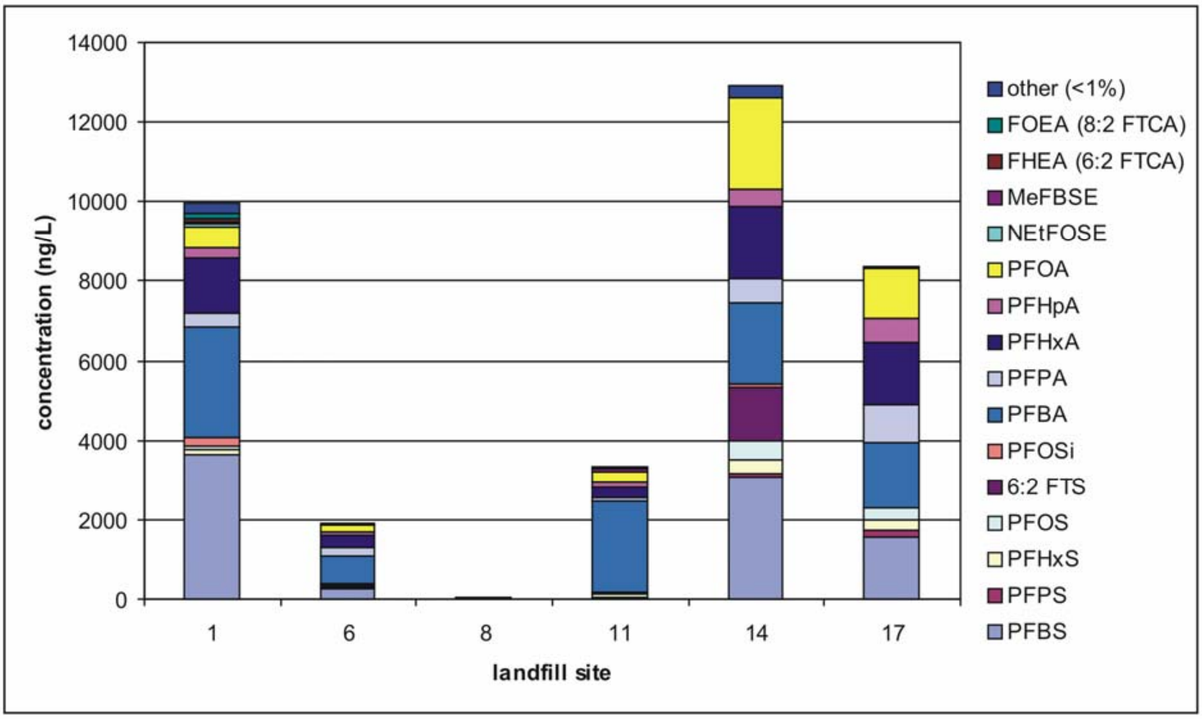
Substance	MDL	MQL
PFBA	0.12	0.39
PFPS	0.10	0.33
PFHxS	0.7	0.24
PFHpS	0.49	1.63
PFOS	0.03	0.11
PFNS	1.85	6.17
PFDS	n.d.	n.d.
6:2 FTS	1.93	6.44
PFHxSi	0.01	0.05
PFOSi	0.02	0.06
PFDSi	n.d.	n.d.
PFBA	3.36	11.20
PFPA	2.02	6.72
PFHxA	0.11	0.37
PFHpA	0.04	0.12
PFOA	0.12	0.40
PFNA	1.09	3.63
PFDA	0.06	0.21
PFUnDA	0.03	0.11
PFDoDA	0.04	0.14
PFTriDA	0.10	0.32
PFTeDA	0.06	0.21
PFPeDA	n.d.	n.d.
PFHxDA	0.39	1.30
PFHpDA	0.81	2.68
PFOcDA	0.50	1.65
ME$_2$PFOA	0.46	1.54
PFOSA	0.04	0.15
NMeFOSA	0.16	0.52
NEtFOSA	2.00	6.67
NMeFOSE	0.24	0.81
NEtFOSE	0.83	2.77
MeFBSA	2.40	7.99
MeFBSE	4.75	15.82
6:2 FTCA	1.58	5.27
8:2 FTCA	n.d.	n.d.
10:2 FTCA	n.d.	n.d.
6:2 FTUCA	0.32	1.07
8:2 FTUCA	0.05	0.17
10:2 FTUCA	0.09	0.29
PFHpPA	3.58	11.93
PFOPA	3.69	12.30
PFDPA	6.83	22.78

Reference standards of c = 50 ng/mL of each compound were measured regularly and showed the expected concentrations. Repeating tests of leachate from site 6 were measured and showed a deviation of <10 % in five samples. The matrix effect, an unspecific effect of the matrix that changes detection behavior, was calculated to be in average 0.89 for all compounds in leachate of site 9.

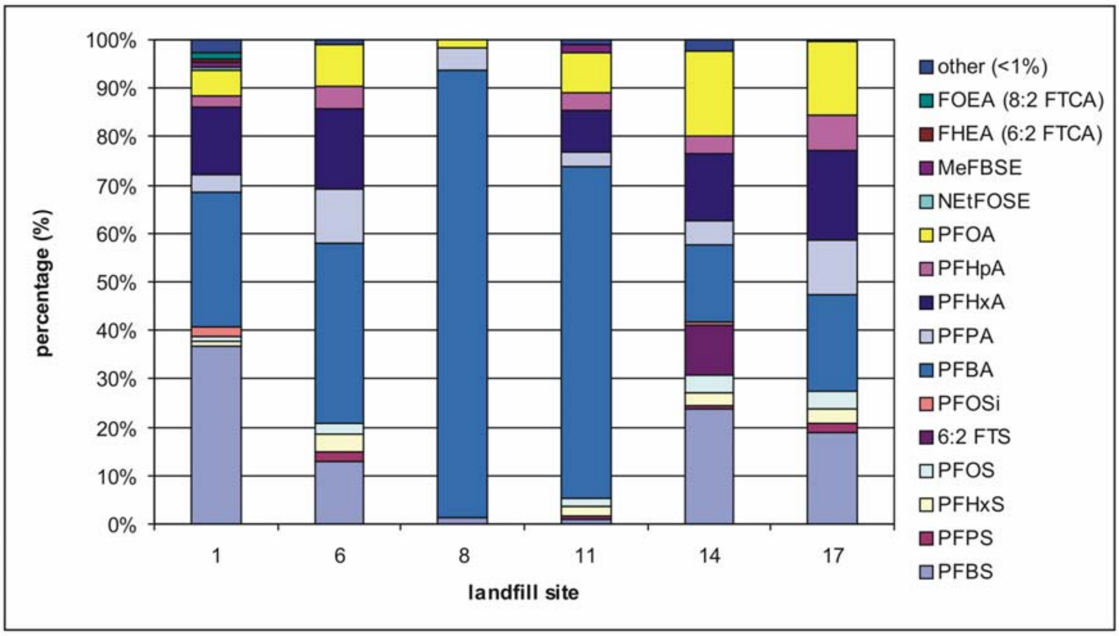
5 Results

5.1 PFCs in untreated leachates

In untreated leachates 25 of 43 compounds were detected. Sum PFC concentrations in untreated leachates ranged from 30.5 ng/L (landfill 9) to 12,922 ng/L (site 14). The mean concentration was 6086 ng/L with a standard deviation of 4638 ng/L. The median was 5847 ng/l. An overview on all tested sites is given in graph 4. The composition shows 9 substances with more than 1 % of the sum PFC concentration. These substances are PFBA with 27 %, PFBS with 24 %, PFHxA with 15 %, PFOA with 12 %, PFPA with 6.0 % PFHpA with 4.0 %, 6:2 FTS with 3.7 %, PFOS with 2.7 % and PFHxS with 2.3 %. An overview on the mass fraction is given in graph 5 and table 7. Concentrations of ΣPFOA+PFOS are in average 176±338 ng/L.



Graph 4: PFC-Concentrations in untreated leachate.



Graph 5: Mass fractions of individual PFCs in untreated leachate.

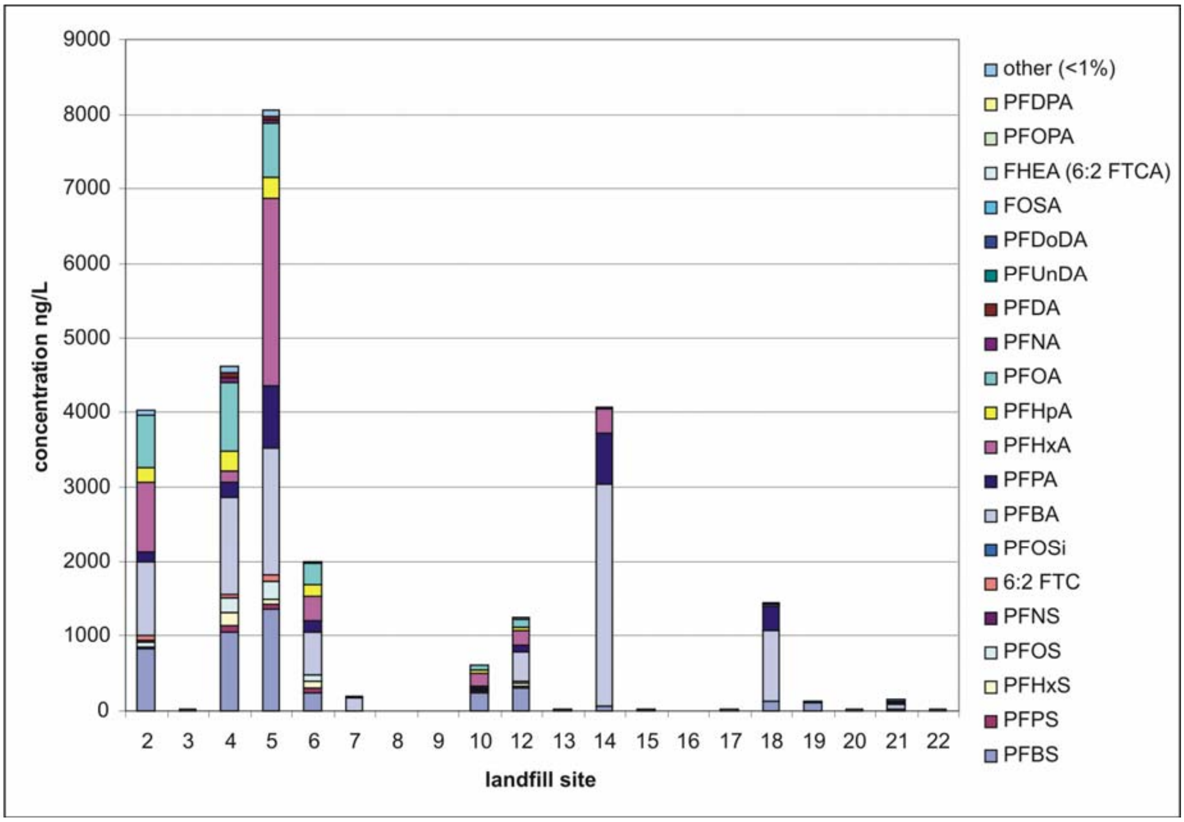
Table 7: Contribution of individual PFCs in untreated leachate in percent of Σ PFC. Only compounds with mass fraction of >1 % are shown.

Compound	Mass fraction
PFBA	26
PFBS	24
PFHxA	15
PFOA	12
PFPa	6.0
PFHpA	4.0
6:2 FTS	3.7
PFOS	2.7
PFHxS	2.3

5.2 PFCs in treated leachates

In the treated leachate 39 of 43 compounds are found in concentrations above the MQL. NEtFOSA, 8:2 FTCA and 10:2 FTCA could not be found at all. The sum concentrations of all compounds range between 3.97 ng/L in landfill 9 and 8060 ng/L in landfill 5. The mean ∑PFC concentration is 1336 ng/L with a standard deviation of 2139 ng/L; the median is 139 ng/L. A complete overview is given in graph 6. The mass fraction of compounds is shown in graph 7 and table 8. Nine compounds have a contribution of >1 % of the ∑PFCs (i.e., 34 % for PFBA, 18 % for PFHxA, 17 % for PFBS, 11 % for PFOA, 9.2 % for PFPA, 3.6 % for PFHpA, 2.3 % for PFOS and 1.7 % for PFHxS). This corresponds to 96 % of the ∑PFCs.

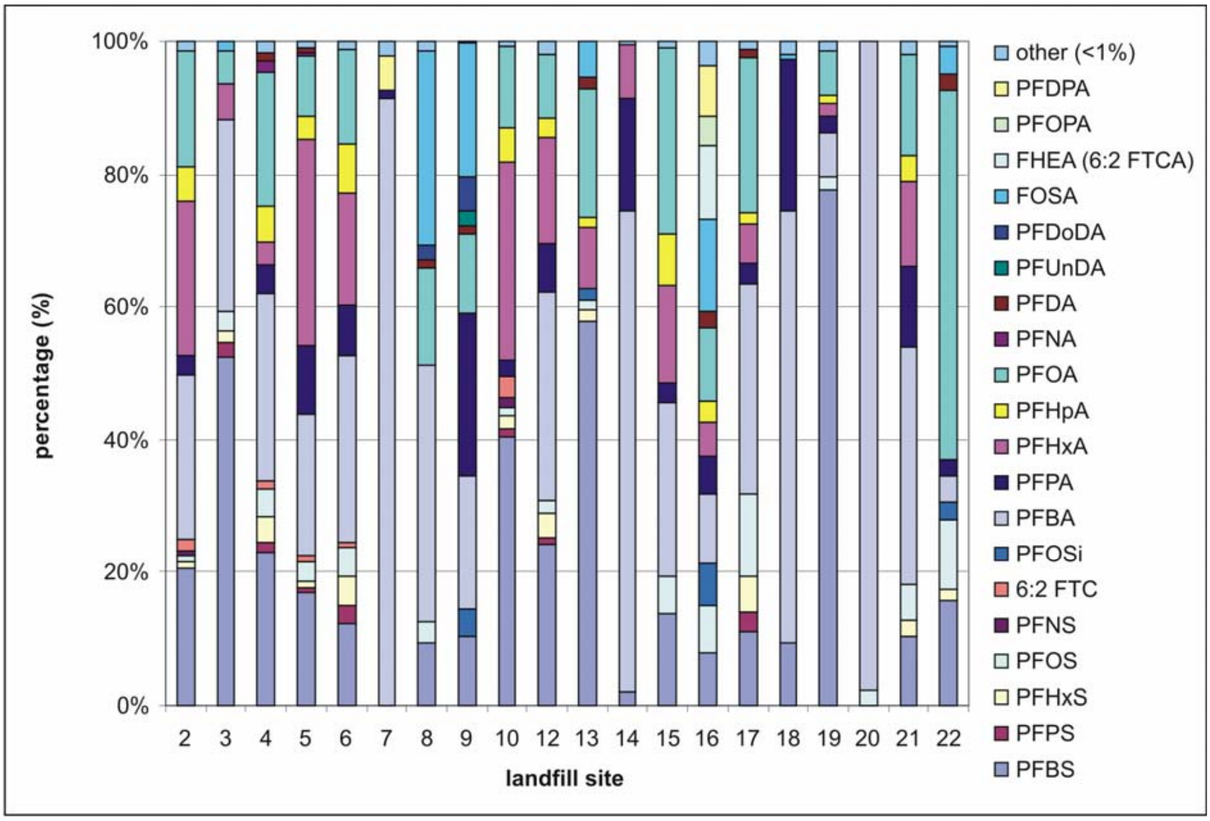
The mass flows are estimated to be between 0.03 g/year in landfill 9 and 349 g/year in landfill 6. The mean mass flow is 49.4±89.4 g/year and a median of 2.31 g/year. Mass flows are rough estimations, since temporal trends and short time changes in concentrations are unknown and only estimated by maximum four samples. The mass flows for each landfill is shown in graph 8.



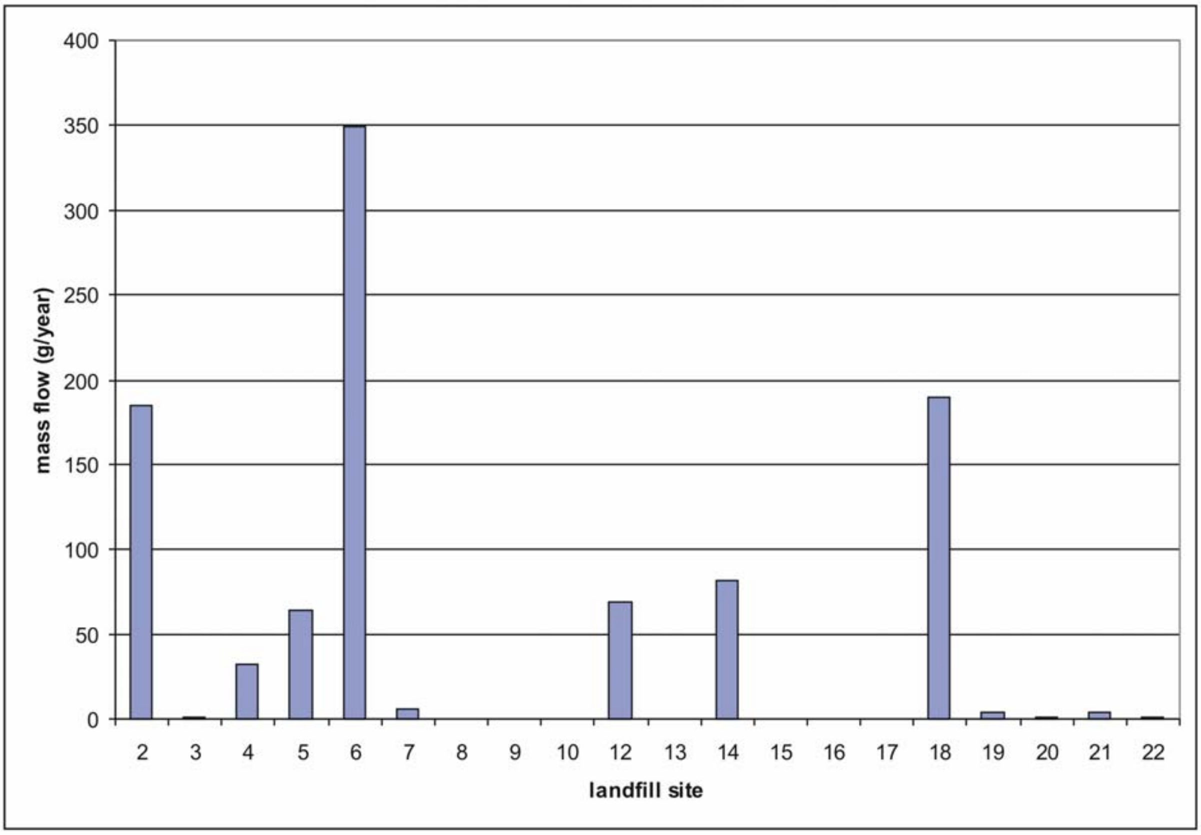
Graph 6: PFC-Concentration in treated leachate of all tested sites.

Table 8: Mass fractions of PFCs in treated leachate in percent for all compounds with >1 % mass fraction.

Compound	Mass fraction
PFBA	34
PFHxA	18
PFBS	17
PFOA	11
PFPA	9.2
PFHpA	3.6
PFOS	2.3
PFHxS	1.7
6:2 FTS	1.0



Graph 7: Mass fraction of compounds in treated leachate of all tested sites.



Graph 8: Mass flows of PFCs in treated leachate of all tested sites. Results are Σ PFCs in g/year.

5.3 PFC concentration after different treatment steps

On two landfills samples were taken within the Steps of the activated carbon treatment. Both sites had a treatment consisting of three containers that are consecutively arranged and filled with activated carbon. Landfill site 9 additionally has a lagoon after the cleaning treatment, which was sampled two times. The site was sampled altogether five times after each carbon container and two times after the lagoon; results are shown in table 9. The mean concentration is decreasing after every carbon container, but higher again in the outflow from the lagoon, due to PFOSA, which was not found before. See annex for the detailed results of container III and the lagoon.

Table 9: Monitoring the different treatment steps on landfill 9 over a period of three months with sampling rates of 2–4 weeks. Results are given in Σ PFCs. Concentrations in empty fields were measured, but are not taken into consideration due to low recovery rates.

Sampling period	Container 1	Container 2	Container 3	lagoon
1st time		0.93		
2nd time	10.77	2,77	1,68	
3rd time	17,3	10,9	10, 9	
4th time	6,92		8,95	11,0
5th time	14.0	16,4	1,95	7.28
Σ PFC mean	12.2±3.84	7.75±6.25	6.39±4.56	9.15±1.87

In the leachate from site 18 the concentration is 4384 ng/L after container I, 3908 after container II and 1442 ng/L after container III. Except the substances PFOSi and PFOSA, where concentrations increase during the treatment, concentrations of all substances are decreasing. See table 10 for results of individual compounds.

Table 10: Concentrations of indicidual PFCs in leachate from site 18 after each container of activated carbon (AC) treatment. All concentrations are in ng/L.

	Effluent of AC container 1	Effluent of AC container 2	Effluent of AC container 3
PFBS	2127	2108	136
PFPS	3.85	4.37	0.37
PFHxS	16.8	5.70	0.03
PFOS	9.70	2.75	1.60
PFHxSi	0.78	0.56	n.d.
PFOSi	n.d.	2.09	2.65
PFBA	830	819	945
PFPA	412	324	331
PFHxA	678	515	11.1
PFHpA	91.3	56.7	1.30
PFOA	210	62.3	2.99
PFNA	3.94	n.d.	n.d.
PFOSA	n.d.	7.03	9.87

5.4 Changes of concentrations in short times

Six landfill effluents were tested three and four times, respectively. The mean values are given above. Standard deviations within the time series are between 9.1 % and 88.4 % from the mean value. The results are shown in detail in table 11.

Table 11: Σ PFCs Samples of samples were taken three or four times with a sampling rate of 2–4 weeks from six landfills. All concentrations are given in ng/L.

Sampling site	Sampling period				Mean
	1	2	3	4	
7	166	206	198	-	190±17.3
8	1.8	12.2	7.8	-	9.3±2.1
9	1.3	6.8	5.9	1.8	4.0±2.4
12	1858	622	1298	-	1257±505
14	3635	4181	2246	5156	4079±690
16	0.9	4.3	12.5	25.7	10.8±9.6

6 Discussion

6.1 Patterns of PFCs

6.1.1 Patterns in treated and untreated leachate

The pattern of PFCs in untreated leachate shows a share of almost 50 % for the short chained compounds PFBA and PFBS. There are two other compounds with more than 10 % share of concentration; PFHxA and PFOA. In treated leachate the patterns show a share of 34 % for PFBA and between 10 % and 20 % for PFHxA, PFBS and PFOS, respectively. The three most present substances show shares in both leachates around 65 %. The composition in treated and untreated leachate is very similar. See table 19 for detailed information on shares in concentrations.

Table 12: Comparison of the patterns of PFCs in treated and in untreated leachate. Shown is every compound with an average mass fraction of more than 1 %.

Treated leachate		Untreated leachate	
PFBA	34,3	PFBA	26,1
PFHxA	17,5	PFHxA	14.8
PFBS	16,5	PFBS	23,5
PFOA	10,8	PFOA	12.3
PFPA	9,2	PFPA	6.0
PFHpA	3,6	PFHpA	4.0
PFOS	2,3	PFOS	2.7
		6:2 FTS	3.7
		PFHxS	2.3

6.1.2 Patterns in leachates after different treatment systems

Nevertheless the mass fractions in treated leachates show different patterns in leachates from different treatment systems. See table 20 for detailed information. Reverse osmosis lets predominantly pass short chained compounds. PFBA and PFBS share more than 70 % of the load. PFOA shows a high rate as well and PFOS is negligible. Activated carbon treatment lets out mostly carboxylic acids: More than 90 % of the load is determined by PFPA, PFHxA, and PFHpA, whereas sulfonic acids are almost not present. The other treatment processes, nano filtration, wet air oxidation and biological treatment let out more PFCAs than PFSAs. Except PFPS with shares between 18.3 % and 29.8 % PFSAs are almost inexistent. In sediments, PFCAs show lower accumulation rates than PFSAs [91], which is seen here, too.

PFPA and PFHpA are the major compounds with shares up to 30 %, each. Compared to untreated leachate PFBS is less present, while PFPS shares more. In other matrices, like biota [45], longer chained compounds show better adsorption capacity than shorter chained compounds. In leachate the share of compounds shorter than C = 8 chained compounds should rise. This is not observable since mainly shorter chained compounds are found in treated and untreated leachate and the three most abundant compounds share the same sum of percentages before and after the treatment.

Table 13: Comparison of the patterns of PFCs after different treatment processes. Shown are percentages of selected compounds.

	Reverse osmosis	Activated carbon	Nano filtration	Wet air oxidation	Biological treatment
PFBS	60	1.9	1.2	0.2	0.1
PFPS	0.2	3.7	30	20	18
PFBA	10	0.0	0.0	0.0	0.0
PFPA	2.0	70	21	29	23
PFHxA	3.8	18	5.8	5.5	8.0
PFHpa	1.6	5.6	21	7.5	29
PFOA	15	0.0	3.8	6.2	4.0
PFNA	0.0	0.1	11	19	12
Rest to 100 %	7.4	0.7	6.2	30.6	34.9

6.1.3 Comparison of treated and untreated leachate from four landfills

Leachate was taken before and after treatment on four sites. Changes in the pattern could be observed: In the samples from site 6 the share of PFBA decreased from 37 % to 28 %. Other compounds showed smaller differences in the comparison. In the activated carbon treatment bigger changes were observable. In site 8 PFBA decreased from 93 % to 40 %, while PFOA and PFOSA increased from 2 % and 0 % to 15 % and 30 %, respectively. In site 14 PFBA and PFPA increased from 16 % and 5 % to 73 % and 17 %, respectively. PFHxA and in particular PFOA decreased from 14 % and 18 % to 8 % and 0 %. In site 17 only smaller changes in the patterns were observable. In table 14 an overview is given. Overall every leachate shows a specific pattern before and after treatment. Coherences regarding the chain length are discussed later.

Table 14: Comparison of patterns of selected compounds before and after the treatment process in percentage.

Site	6		8		14		17	
Treatment	Wet air oxidation		Activated carbon		Flotation + biological activated carbon		Flotation + biological activated carbon	
	before treatment	after treatment	before treatment	after treatment	before treatment	after treatment	before treatment	after treatment
PFBS	13	12	1	10	24	2	19	11
6:2 FTS	0	1	0	0	10	0	0	0
PFBA	37	28	93	40	16	73	20	32
PFPA	11	8	4	0	5	17	11	3
PFHxA	16	17	0	0	14	8	19	6
PFOA	9	14	2	15	18	0	15	24
PFOSA	0	0	0	30	0	0	0	1

6.1.4 Concentrations compared to surface water and effluents of WWTPs

In aqueous environmental matrices a wide range of concentrations for PFCs can be found. In comparison the concentrations of landfill leachate are in a higher group. The smallest sum concentration found in this study is 4 ng/L, which is in the same field as the lowest concentrations in river water [92], sea water [40] or municipal WWTPs [54, 56]. The median concentration found in this study is 139 ng/L. This concentration is comparable to concentrations found in various WWTPs [54]. The mean concentration found in this study is 1336 ng/L. These concentrations can be found as well in few rivers in Europe [50] and industrial WWTPs [33, 56]. The highest amount found in this study is outbid by an industrial WWTP from a site used industrially, where metals are processed [33]. Actually the mean value of untreated leachate is smaller than the concentration from that particular WWTP. See table 13 for an overview. The concentrations of treated landfill leachate are, in the higher area of concentrations found. Nevertheless the mean concentrations are in the same range as industrial sources, and therefore not unusual to find.

Table 15: Concentrations of Σ PFCs in different aqueous environmental matrices in ng/L.

Aqueous sample type	Number of tested sites	Number of tested Substances	Min	Max	Mean or singular measurement	Source
Treated landfill leachate	20	43 ΣPFOS+PFOA	4 0.48	8,060 1117	1,335 176	This study
Treated landfill leachate	15	3-13	n.d.	5,227	1,456	[56, 86, 87]
Untreated landfill leachate	6	43	31	12,922	6,080	This study
Untreated landfill leachate	1	13			22,200	[87]
Rhine		43	4	268		[92, 93]
Rivers in Europe		PFOA PFOS		174 1371	12 39	[50]
WWTP NY-State	6	PFOA PFOS	58 3	1050 68		[54]
Industrial WWTP Municipal WWTP	4 6	7 6	12.7 n.d.	796.8 34.6	 24.0	[56]
north Sea		41	9.4	31.2		[40]
WWTP Printing industry	1	11			10.1	[33]
WWTP Textile industry	2	11	2.8	664		[33]
WWTP Laundry and cleaning	2	11	31.9	296.2		[33]
WWTP Paper industry	1	11			478	[33]
WWTP Electric industry	1	11			12.2	[33]
WWTP Metal industry	2	11	133.4	8472.0		[33]

6.2 Short time temporal variations

Six sites provided samples for three and four times with a sampling rate of 2–4 weeks. The results of the multi sampled sites should give an idea whether big variations are occurring over short time and to determine if a one time sampling can be enough to estimate mass flows or not. As seen before landfills discharge ten to one hundred times less PFCs than WWTPs it is enough to assure a certain quality of that estimation if concentrations do change less than one order of magnitude. See table 16 for complete data.

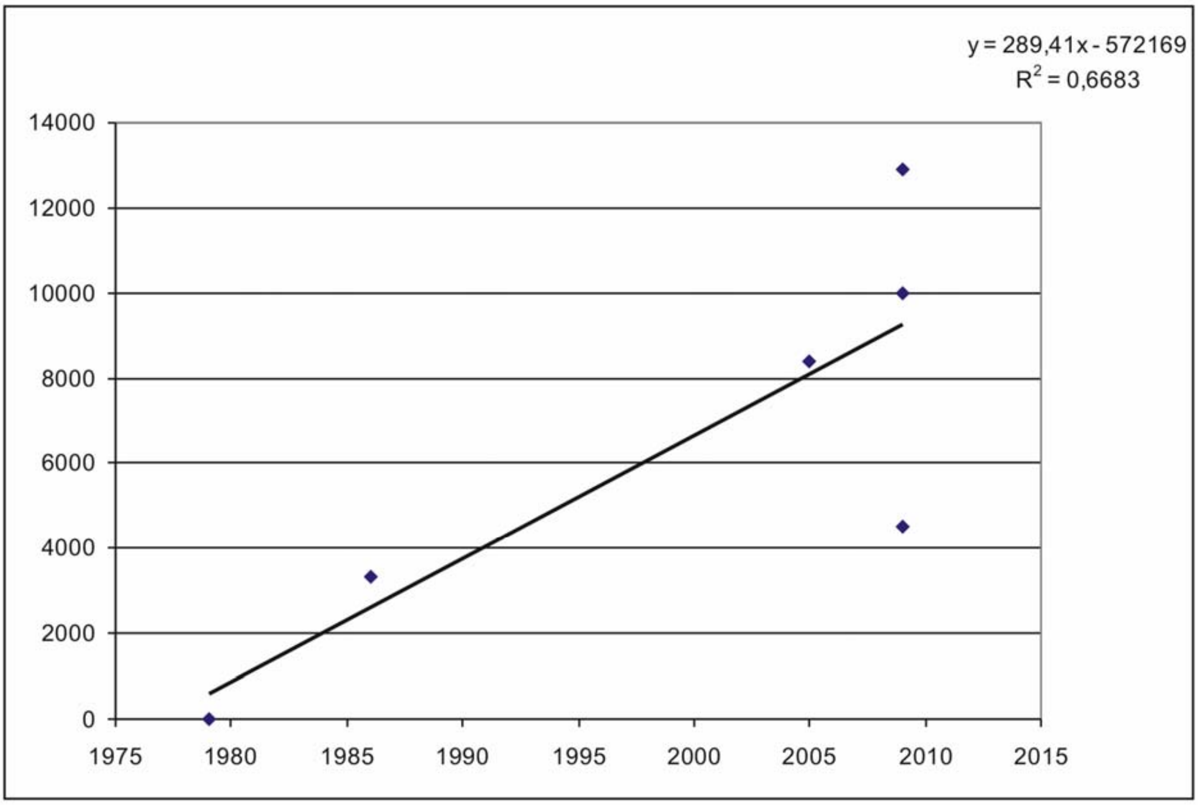
Table 16: Comparison of PFC concentrations in three and four time sampled sites. Shown are mean values in ng/L, deviation and a factor for the difference between the highest and the lowest observed concentration.

Site	Mean	Factor between highest and lowest concentration
7	190.1±17.3	1.2
8	9.3±2.1	1.6
9	6.39±4.6	6.5
12	1257.3±505	3.0
14	4070.2±690	1.5
16	10.8±9.6	28.6

Five of six tested sites show a variance of concentrations by a factor less than ten within three or four months. That means the criterion for acceptable quality is met. Only one site shows a factor of more than ten, but this is a site that shows very little concentrations. Higher polluted leachates show smaller variations. Therefore the variation in the concentrations and the estimation of mass flows is not compulsively correct or at least nearby correct in a few cases. Nevertheless, since three out of six sites show a factor of less than two for the range of concentrations found, it can be assumed that altogether no wrong conclusions are drawn from the concentrations found. The changes in concentrations are too small to change the order of magnitude of the annual mass flows.

6.3 Influence of the age of leachate to concentrations

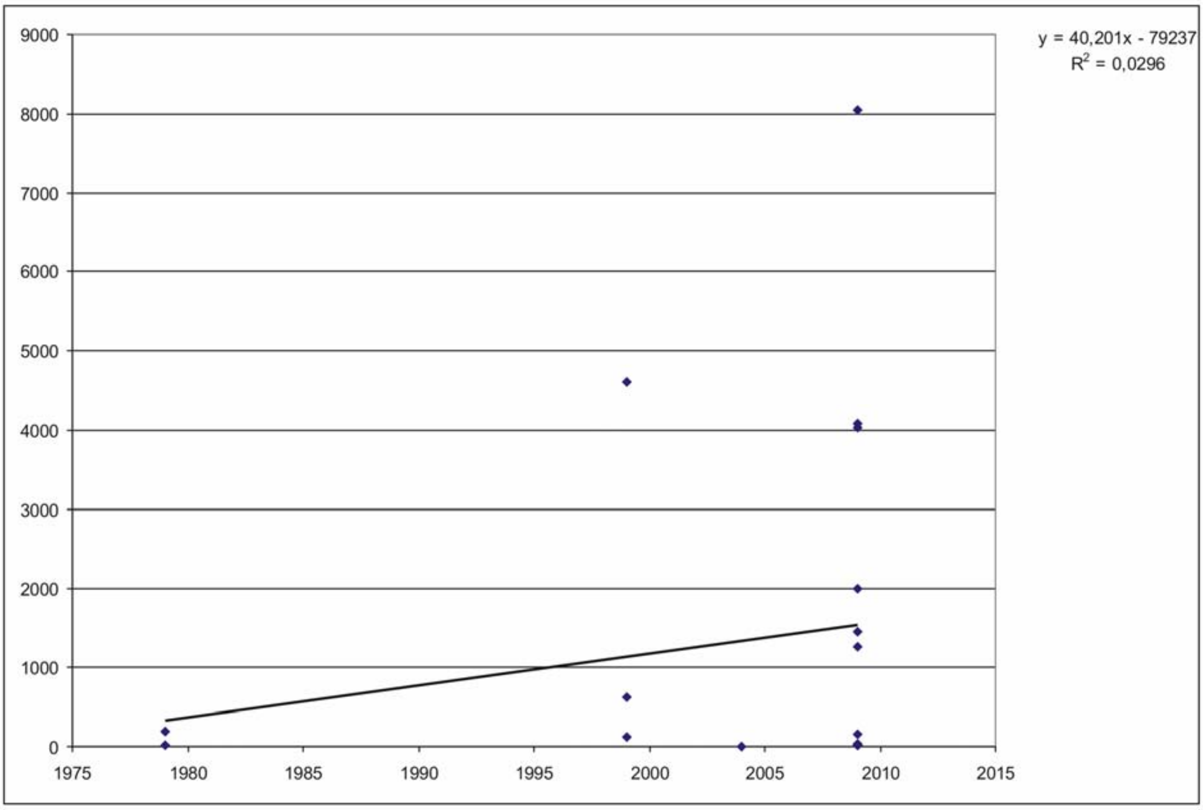
Correlations between the age of the landfill and the concentrations in leachate were calculated. The landfills where samples from untreated leachate were taken, were closed in 1979 (site 8), 1986 (site 11), 2005 (site 1) and three are still active (sites 6, 14 and 17). For mathematical reasons active sites were set as 2009 for closing year. If the year of closing of the landfill is mapped to the measured concentration in leachate a correlation can be found.



Graph 9: Correlation between the year of closing of landfills and Σ PFC concentrations in ng/L found in untreated leachate.

In treated leachate the line coefficient of $R^2 = 0.67$ shows that age is a factor for the concentrations of Σ PFCs that can be found in leachate, even though there are other factors that influence the composition of leachate. The correlation can get rise to $R^2 = 0.95$ if sites 1 and 6, which are 'class I' landfills are taken out of consideration. Admittedly, the database would be four sites and hence too small to conclude that correlation.

For treated leachate the mapping can be stated as well:



Graph 10: Correlation between the year of closing of landfills and Σ PFC concentrations in ng/L found in treated leachate.

Here R^2 is 0.03 and age of the landfill is not the main explanation factor for the concentrations of landfills. Anticipating the next chapter, correlations within the different cleaning treatments could be stated, due to the size of the database, only for activated carbon treatment at $R^2 = 0.21$. The correlation is almost ten times higher, but still too small for making age a relevant factor for PFC emissions. Since for all years of closing, the lowest concentrations are in a very low area, but the highest concentrations of Σ PFCs rise, the variance of concentrations is higher in treated leachates from active sites, than from closed sites.

If a simpler model of comparison is chosen, the differentiation between the status active and inactive and not the date of closing, a connection of the age is observable. This can be seen in table 15. The mean concentrations differ a factor of nine and the mean mass flows differ a factor of 29, although the median concentration is comparable. In this case age can show an observable difference in the amount of PFCs in leachate. The mean mass flows are about 29 times higher as in inactive sites.

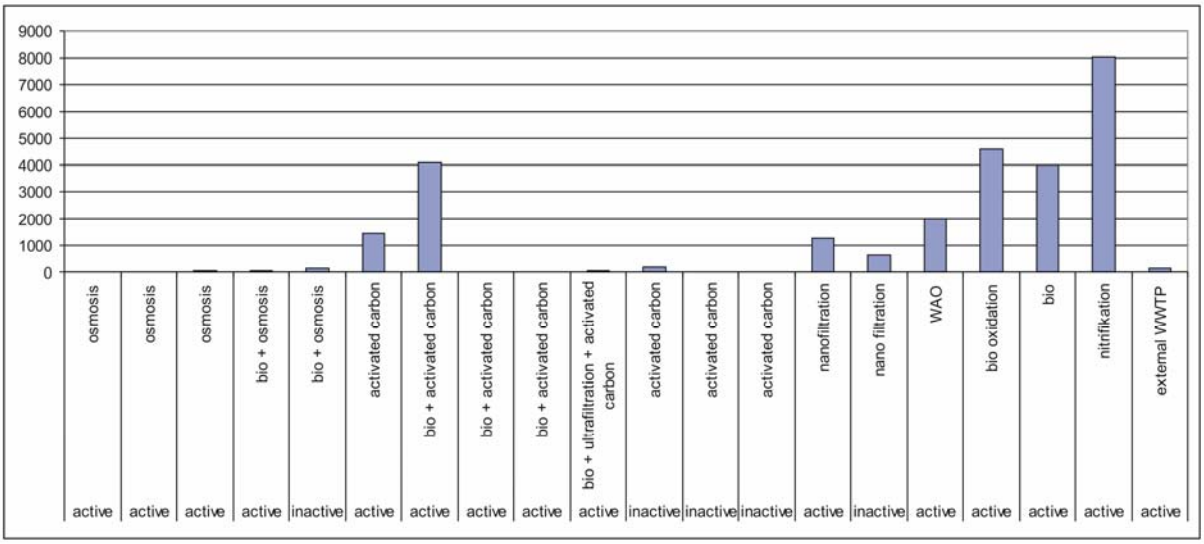
This effect is not only based on amounts of PFCs in leachate, but on a complete sealing in inactive landfill sites, that reduces the annual amount of leachate significantly.

Table 17: Comparison of Σ PFC concentrations and median concentrations in ng/L and the mean annual mass flow in g/year in active and inactive landfill effluent.

Status	Active	Inactive
Mean	1717 ±2303	191 ±227
Median	149	129
Mean Mass flow	53.4	1.85

6.4 The influence of the cleaning treatment on the concentrations in leachate

The question regarding the cleaning treatment is to test whether the cleaning treatment has an influence on the concentrations or not. The results are shown in graph 9 and table 17.



Graph 11: Concentrations of PFCs in leachate of all sites, sorted to treatment and status. (Abbreviations: bio = biological treatment, osmosis = reverse osmosis, WAO = Wet air oxidation)

Table 18: Mean concentrations, median concentrations and the highest concentration of sum Σ PFCs in ng/L after different cleaning treatment systems.

Treatment	Number (n)	Average	Median	Highest concentration
Reverse osmosis	5	42	24	129
Activated carbon	8	723	22	4079
Nano-filtration	2	940	940	1257
Wet air oxidation	2	3302	3302	4610
Biological treatment	2	6041	6041	8059

Reverse osmosis and especially activated carbon show big differences between average and median. One and two, respectively, outliers cause the differences, whereas the statistical database is too small to calculate sensuous data in mathematical outlier tests. Nevertheless based on this data it seems reasonable, that the cleaning treatments reverse osmosis and activated carbon can be the best for cleaning PFCs out of landfill leachate. Additionally, activated carbon might have a higher potential for the cleaning of PFCs than estimated here. The outlier concentrations of activated carbon treatment might be caused by fully loaded activated carbon in the samples with high concentrations. The next best treatment seems to be nano filtration, then wet air oxidation and at last only biological treatment. These results are reasonable: Nano-filtration cannot clean as well as reverse osmosis, since the membrane has not that small pores [82] and therefore molecules can pass more easily through the membrane. Wet air oxidation might not even have a chance to reduce the concentration of PFCs, since that treatment works on carbon double bounds [85], which are not existent in the tested compounds. Therefore, precursor compounds might be degraded during the wet air oxidation process. The same effect has to be taken into account for biological treatments, where precursor compounds might be degraded, too [54].

Based on the median values of 24 ng/L and 22 ng/L reverse osmosis and activated carbon treatment are the only processes which can reduce the concentrations in leachate to levels where drinking water quality as Σ PFCs ≤ 300 ng/L is reached. Based on the average and the highest concentration measured, only reverse osmosis can reach that level at all times. The other treatment processes leave higher concentrations in the leachate.

Due to the overwhelming effect of the cleaning treatment on the composition of leachate, correlations based on size of the landfill or the filling of special waste like sewage sludge could not be observed.

6.5 Cleaning efficiency

The comparison of treated and untreated leachate shows, cleaning treatments can eliminate PFCs. The mean concentrations are 6086 ± 4638 ng/L in untreated leachate and 1336 ± 2139 ng/L in treated leachate. Only 22 % of Σ PFCs remains in leachate during the cleaning treatment. For median values the same calculation leaves only 2.4 % of the PFCs in leachate.

Nevertheless a closer look has to be taken at these data: The smallest concentration in untreated leachate in an active landfill is 1889 ng/L for site 6, a 'class I' landfill. The lowest concentration of untreated leachate in an active 'class II' landfill is 8379 ng/L. Five landfill sites show – after cleaning treatment – higher concentrations than 1889 ng/L and one of these sites shows a concentration of 8060 ng/L. This is comparable to untreated 'class II' effluent. One site is cleaned with an activated carbon treatment; the other four sites are cleaned with biological treatments, wet air oxidation or a combination of both. The presumption wet air oxidation and biological treatment are not suitable for PFC cleaning is supported by this data. The presumption that highly polluted activated carbon is charged and cannot adsorb more PFCs, cannot be proven here.

Nevertheless a closer view can be taken on four sites, where treated and untreated leachate could be taken. See table 19 for results.

Table 19: Comparison of concentrations in treated and corresponding untreated leachate from four landfill sites in ng/L, including a calculation of concentration changes as remaining percentage after treatment and corresponding treatment.

Site	Untreated	treated	Concentration change	treatment	status
6	1889	1993	+5.5 %	Wet air oxidation	Active
8	31	9	-70.5 %	Activated carbon	Inactive
14	12819	4079	-68.2 %	Activated carbon	Active
17	8370	20	-99.8 %	Activated carbon	Active

On the one tested site with wet air oxidation treatment concentration of Σ PFCs increases during the treatment process by about 5.5 %, while the concentration decreases in activated carbon treatment on a level between 68 % and >99 %. As an average, activated carbon reduces 79.5 % of the sum PFC concentration. These case studies indicate the same results as before: Wet air oxidation might degrade precursor compounds during the treatment process and activated carbon can be a very good treatment, but leads to different results. Explained can the broad range of differences in the activated carbon treatment by the age of the carbon. Since carbon can be charged by contaminants, the adsorption capacity can be reduced or stopped at all and different results can be achieved. The production process is not standardized; therefore process-related differences between different activated carbons are possible.

6.6 Cleaning behavior of two three-step activated carbon cleaning treatments

On two sites, 9 and 18, samples could be taken after each of three activated carbon treatment containers. Site 9 was a site that was visited four times. See table 22 for results.

Table 20: Sum concentrations of PFCs in ng/L after every treatment step of two activated carbon treatment steps with three carbon containers. For site 9 mean values of four samples are shown.

Site	Step 1	Step 2	Step 3	Lagoon
9	12.2	7.75	6.39	9.15
18	4385	3909	1442	

In both sites the concentrations decrease during the cleaning treatment. On a low contamination level at site 9 the cleaning treatment of the container II and III leaves 82.5 % and 57.6 % from the inflowing concentrations, respectively. On site 18 the outgoing amounts are 89.1 % and 36.9 % of the incoming. Especially in the treatment of site 18 the three treatment steps can reduce the concentrations even after the first carbon treatment container on a significant level, since treatment steps II and III leave 32.9 of the concentration after treatment step I. On site 9 47.5 % of the outflow from step I is left after step III.

A higher concentration in the outflow of the lagoon origins in PFOSA, which is a typical run-off substance [92], that likely caused the growing concentration. The concentrations of PFOSA are raising within the treatment steps of site 18, too. Degradation processes of precursor compounds must occur in the carbon container. See annex V and VI for information on the composition of these leachates.

6.7 Correlations of adsorption from PFCAs and PFSAs depending on the chain length and functional group

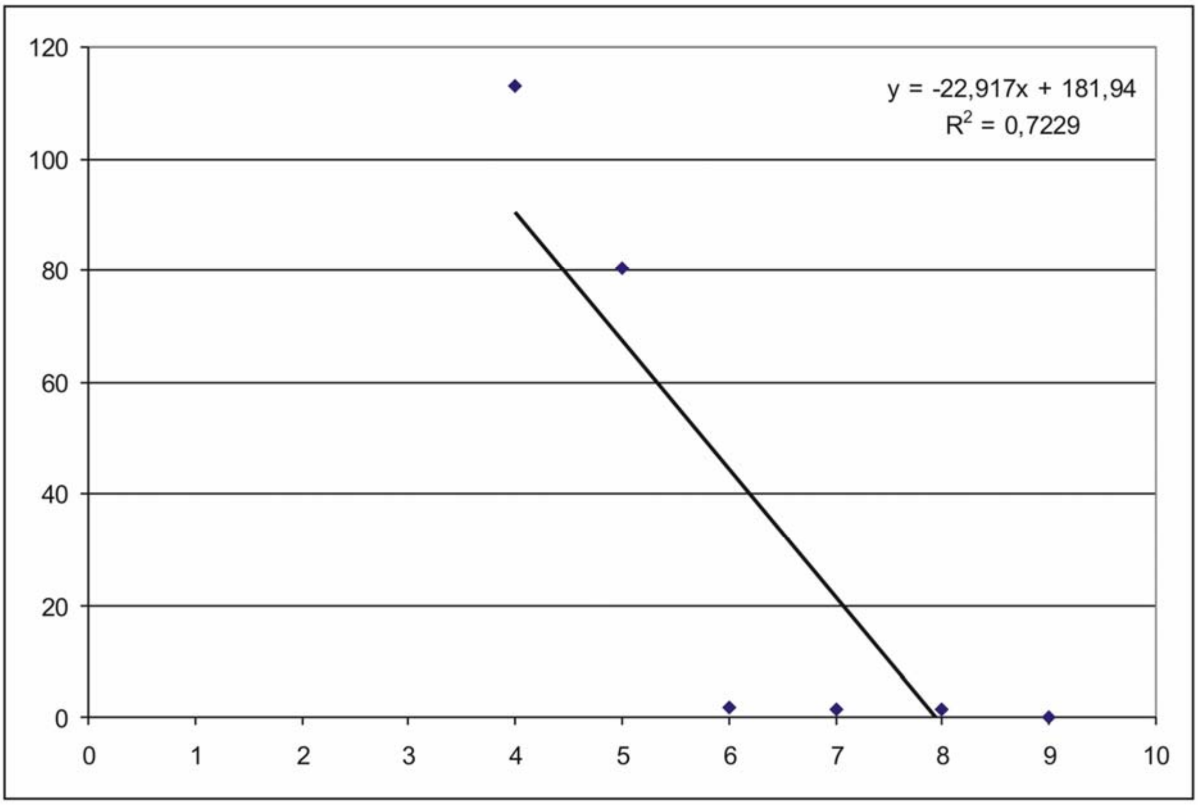
The change of concentrations in site 18, as shown in table 23, gives an idea if the cleaning of activated carbon depends on the chain length.

Table 21: Concentrations in leachate after each of three activated carbon treatment containers on site 18 for selected compounds in ng/L.

Compound	Step I	Step II	Step III
PFBS	2127	2108	136
PFPS	3.9	4.4	0.4
PFHxS	17	5.7	0.0
PFOS	9.8	2.8	1.6
PFBA	831	820	945
PFPA	412	324	331
PFHxA	678	515	11
PFHpA	91	56	1.3
PFOA	210	62	3.0
PFNA	4.0	0.0	0.0

The data suggest activated carbon treatment works better for longer chained compounds than for shorter chained compounds. For PFCAs coherences between the chain length and the remaining percentage for the influent and effluent of the containers seem to be existent. PFBA and PFPA are not affected by the carbon treatment on the whole; actually the concentration for PFBA is higher than the influent in two of three comparisons. The concentrations of carboxylic acids with more than five carbons in the chain are decreasing strongly. For PFSAs this behavior here is not observable. FOR PFCAs the results are comparable to results found in biota [63], where longer chained PFCs are adsorbing better.

A mathematical correlation between chain length and carryover from effluent of container I to effluent of container III for PFCAs leads to a correlation with $R^2 = 0.72$:



Graph 12: Correlation between chain length of the carbon chain in PFCAs and the leftover between effluent from activated carbon treatment container I and activated carbon treatment container III.

On sites 14 and 17 samples before and after the treatment could be taken, as described above. The remaining percentage of concentrations of selected compounds after the treatment system in comparison to the concentrations before the treatment system is shown in table 24.

Table 22: Comparison of remaining percentages of concentrations of selected compounds after the treatment system in comparison to the concentrations before the treatment system. All values are given in percent.

Compound	Site 14	Site 17
PFBS	2.4	0.1
PFPS	0.5	0.4
PFHxS	0.0	0.4
PFHpS	0.0	0
PFOS	0.1	0.9
PFBA	144	0.4
PFPA	113	0.1
PFHxA	18	0.1
PFHpA	2.2	0.1
PFOA	0.1	0.4

Here the correlations are for PFSAs in site 14 $R^2 = 0.71$ and in site 17 $R^2 = 0.27$. For PFCAs the correlations are $R^2 = 0.86$ and $R^2 = 0.00$. All together the correlations indicate, there might be a correlation between adsorption and chain length, but due to the small number of tested sites and the objecting results from site 17, the results cannot be proven.

6.8 Toxic effects of concentrations from landfills

Despite the lack of data on toxicities of all PFCs, there are only few data available on compounds with a chain length of C = 8, and even less for C = 4. However, due to the lack of better information, toxicity data for PFOS and PFOA are taken in the following discussion as mean toxicity values for all PFCs, to be able to discuss sum concentrations.

Effects in marine environments are reported to be acute toxic at levels beginning at low mg/L concentrations, at LD_{50} dose in 96 hours, the concentration in water where the dosage shows lethal effects on 50 % of the tested animals, of 3.3 mg/L for PFOS [97] and 9.1 mg/L for PFOA for fatheaded minnow (*Pimephales promelas*) [14]. The LD_{50} sinks to 7.2 ng/L in 28 days for PFOA [14]. These concentrations are not reached by the concentrations found in this study. The maximum value found is 0.08 ng/L and is therefore a factor of 100 away from a LD_{50}-dose.

Nevertheless NOEC, the lowest concentration where no effect was found on a group of animals compared to a control group, is 0.3 mg/L of PFOS for juvenile fatheaded minnow and 6.3 mg/L of PFOS for rainbow trout (*Oncorhynchus mykiss*). The LOEC, the lowest concentration observed where effects were noticeable, is 3.0 mg/L of PFOS for fatheaded minnow and 13.0 mg/L for rainbow trout, respectively [14]. Here the maximum value found in this study is only a factor of 3.6 lower the most sensitive NOEC. The average is about 22 times lower than the NOEC. Therefore it is safe to say, concentrations in treated leachate are close to affecting concentrations for sensitive species, since NOEC and LOEC are based on a test of 96h. Due to the lack of long term data and multi generation studies in aquatic environments these concentrations are too high to be neglected. Especially in combination with other compounds like pharmaceuticals local effects might occur.

Precautionary levels for drinking water, as stated by the commission for drinking water from the federal ministry of health (Trinkwasserkomission des Gesundheits-ministeriums) [98], stated levels of 0.1 μg/L as aim for drinking water, 0.3 μg/L as guiding value and 0.5 μg/L and 5.0 μg/L as precautionary action value for infants and adults, respectively, as Σ PFOA + PFOS. If the sum concentrations are not weighted for different toxicities, 8 μg/L (8060 ng/L) was the highest Σ PFC concentration found in this study. The highest concentration of Σ PFOA+PFOS was 3.1 μg/L. Treated leachate is unsuitable as drinking water, since the precautionary action value is exceeded.

Anyhow, it has to be taken into account, concentrations are only reached in outflows of the cleaning treatments and about half of the landfills are indirect dischargers; concentrations are diluted in WWTP and rivers. Normally undiluted leachates are not accessible for wildlife or human beings.

6.9 Concentrations compared to surface water and effluents of WWTPs

In aqueous environmental matrices a wide range of concentrations for PFCs can be found. In comparison the concentrations of landfill leachate are in a higher group. The smallest sum concentration found in this study is 4 ng/L, which is in the same field as the lowest concentrations in river water [93], sea water [40] or municipal WWTPs [54, 56]. The median concentration found in this study is 139 ng/L. This concentration is comparable to concentrations found in various WWTPs [54]. The mean concentration found in this study is 1336 ng/L. These concentrations can be found as well in few rivers in Europe [50] and industrial WWTPs [33, 56]. The highest amount found in this study is outbid by an industrial WWTP from a site used industrially, where metals are processed [33]. Actually the mean value of untreated leachate is smaller than the concentration from that particular WWTP. See table 13 for an overview. The concentrations of treated landfill leachate are, in the higher area of concentrations found. Nevertheless the mean concentrations are in the same range as industrial sources, and therefore not unusual to find.

Table 23: Concentrations of Σ PFCs in different aqueous environmental matrices in ng/L.

Aqueous sample type	Number of tested sites	Number of tested Substances	Min	Max	Mean or singular measurement	Source
Treated landfill leachate	20	43 ΣPFOS+PFOA	4 0.48	8,060 1117	1,335 176	This study
Treated landfill leachate	15	3–13	n.d.	5,227	1,456	[56, 86, 87]
Untreated landfill leachate	6	43	31	12,922	6,080	This study
Untreated landfill leachate	1	13	-	-	22,200	[87]
Rhine		43	4	268		[93, 100]
Rivers in Europe		PFOA PFOS		174 1371	12 39	[50]
WWTP NY-State	6	PFOA PFOS	58 3	1050 68		[54]
Industrial WWTP Municipal WWTP	4 6	7 6	12.7 n.d.	796.8 34.6	 24.0	[56]
north Sea		41	9.4	31.2		[40]
WWTP Printing industry	1	11			10.1	[33]
WWTP Textile industry	2	11	2.8	664		[33]
WWTP Laundry and cleaning	2	11	31.9	296.2		[33]
WWTP Paper industry	1	11			478	[33]
WWTP Electric industry	1	11			12.2	[33]
WWTP Metal industry	2	11	133.4	8472.0		[33]

6.10 Mass flows

Concentrations in landfill effluent are in a higher range, but not more than in other media, annual mass flows are a criterion to determine whether landfills are an important or minor source to the environment. The mass flows found in this study are between 0.03 g/year and 349 g/year. The mean mass flow is 49.4 g/year. The mass flows of Σ PFOS + PFOA is 0.06 g/year in mean.

Compared to the big German rivers Rhine and Elbe with estimated mass flows of 8500 kg/year [93] and 802 kg/year [52], respectively, the mean value of 49.4 g/year is in a per mille area of big rivers.

Bossi [56] found mass flows in industrial WWTPs between 10 and 147 g/year with an average of 96 g/year, and mass flows in municipal WWTPs <0.45 g/year. Becker found annual mass flows from WWTPs between 18 and 1825 g/year with an average of 551 g/year. Clara [33] found a mass flow up to 4.1 kg/year in one industrial WWTP for Σ PFOS + PFOA. The concentrations are comparable, even though a different number of compounds were tested, since the most abundant compounds are covered in all studies.

The number of landfills in Germany was 1725 in 1998 [94] and the number of 'class II' landfills was 162 in 2005 [95]. The numbers of landfills multiplied with the average concentration implies the annual mass flow is between 8 and 85 kg/year as a rough estimation. The annual mass flow for Σ PFOS + PFOA is between 0.9 and 10.35 g/year. The actual emission should be in a lower area of the calculated range, since 'class 0' and 'class I' landfills should have in average less polluted wastes and 'class III' and 'class IV' landfills should not emit at all to the environment, due to constructional reasons.

The number of WWTPs in Germany was 9,994 in 2004 [96]. The data by Bossi [56] suggest based on WWTP-concentrations from Denmark, emissions between 4.5 kg/year and 963 kg/year. The same calculation for data by Becker suggests emissions of 5507 kg/year ΣPFOS+PFOA from WWTPs. The Data by Becker seems more reasonable as estimation for Germany, since it would cover the data by Clara [33]. Therefore emissions from landfills are 0.14–1.5 % of the emissions from WWTPs. Compared to the one industrial WWTP in Germany that emits 4.1 kg/year ΣPFOS+PFOA [33] the summated concentration of 0.9–10.35 g/year Σ PFOS + PFOA from landfills is 0.02–0.25 % and therefore negligible. One industrial WWTP emits more than 400 times the amount PFOA + PFOS of all German landfills. Landfills therefore are no major source of PFCs to the environment.

Table 24: Mass flows of Σ PFCs per year from selected point sources and rivers.

If no other unit is given, all values are in g/year.

Matrix and compound	Quantity of tested Substances	Min	Max	Average or singular measurement	Source
Landfill effluent	43 ΣPFOS+PFOA	0,03 <<0.001	349 0.07	49.4 0.006	This study
Rhine	43			8500 kg/year	[93]
Elbe	40			802 kg/year	[52]
WWTP (n=4)	PFOA+PFOS	18.25	1825	551	[53]
Industrial WWTP Municipal WWTP	7 6	10.6 n.d.	147 1.8	96.4 0.45	[56]

6.11 Comparison to other data

6.11.1 Comparison to data from other landfills

The Σ PFC concentrations found in treated leachate in this study show a range of concentrations between a few ng/L and above 8,000 ng/L. Even though the highest concentration found in this study is larger than the highest amount found in other studies (i.e. 5,227 ng/L [87]), the mean concentration in this study is 1.3 ng/L and 1.5 ng/L in other studies, respectively, and therefore in the same range. See chapter 3.5 for a detailed overview.

6.11.2 Comparison to data on the same sites

A comparison of the values found in this study compared to non-published data by the federal state of North-Rhine Westphalia [99] shows good compliance, even though there is one of twenty-one values that varies more than one order of magnitude, another one varies by a factor of eight. These compounds are the short chain compounds PFBS and PFHxS, which are reported not to perform optimal under current methods [90]. Leachate can have changing concentrations of contaminants in short times, as shown later. For this reason, concentrations do not necessarily have the same concentrations in different measurements. A comparison is given in table 12. Anyhow the concentrations found in this study show similar results compared to other studies, both in peer reviewed literature on other sites, and in existing data on the same landfills.

Table 25: Concentrations of PFCs in treated landfill effluent of three landfills (i.e., 19, 21 and 22) compared to corresponding data from the federal state of North-Rhine Westphalia (LANUV) [99] on the same sites. All concentrations are in ng/L.

Landfill site	Substance	This study	LANUV
19	PFBS	99.0	45–200
	PFHxS	0.9	<25–30
	PFOA	8.6	<25
	PFBA	8.5	<25
	PFDA	0.7	<25
	PFHpA	3.1	<25
	PFHxA	2.7	<25
	PFNA	0	<25
	PFPA	3.1	<25
	PFOS	2.5	<25
21	PFBS	15.3	120
	PFHxS	3.5	110
	PFOS	8.2	<10
	PFBA	53.0	63
	PFPA	18.3	16
	PFHxA	19.0	20
	PFOA	22.7	16
	PFNA	0	<100
	PFDA	0.5	<100
22	PFOA	14.6	16–60.2
	PFOS	2.8	2.3–<50

6.11.3 Comparison to data on untreated leachate

Woldegiorgis reports a PFC concentration of 22,200 ng/L in untreated leachate at one tested site in Sweden. The number of compounds tested in that study is smaller, but covers the most abundant compounds of this study. In this study the maximum concentration found is 12,922 ng/L and the mean 6,080 ng/L. Since no data on the tested landfill site is available, there are three options to explain the difference: Either the high value is an outlier and coincidentally a non-representative landfill was sampled, or the high values result in different pre treatments of waste in different countries. In Germany pre treatment of waste is compulsory in order to get a chemical inactive material to deposit. The tested Swedish landfill site by Woldegiorgis [87] has not necessarily provided any treatment to waste before deposition and might therefore provide PFC into the leachate. On the other hand it doesn't seem impossible to find a landfill in Germany that shows concentrations higher than 20,000 ng/L, therefore the value found by Woldegiorgis [87] is higher, but likewise reasonable in Germany.

7 Conclusions and Outlook

This study was one of the first studies dealing with PFCs in landfills. Samples of leachate from 22 landfills were taken and analyzed for 43 different fluorinated compounds. The samples were prepared by solid phase extraction and analyzed by HPLC-MS/MS.

The main focus of this thesis was to determine if landfills are a source of PFCs into the environment. This question could be answered: Landfills are a minor source. Concentrations in untreated leachate are between 30.5 ng/L and 13,000 ng/L. Sum concentrations of PFCs in treated leachate are between 4 ng/L and 8060 ng/L and therefore in the same range as in other aqueous sources like WWTPs, but PFC mass flows are smaller compared to effluent of WWTPs. Mean annual mass flows from individual landfills are 49.4 g/year in average, and thus 50 % of the mean mass flows from individual municipal WWTPs. Due to the high Number of municipal WWTPs, total mass of landfills in Germany are estimated to be ~1 % of the total mass flows of municipal WWTPs in a conservative estimation. Individual industrial WWTPs show emissions up to 4 kg/year of Σ PFOA + PFOS. The emissions of Σ PFOA + PFOS are estimated to be between 0.9 g/year to 10.35 g/year for all landfills. Here all German landfills emit together maximum 0.25 % of that particular site and are therefore insignificant as source.

The concentration in effluents from landfills is depending on the cleaning treatment. Reverse osmosis showed lowest concentrations in treated effluent, followed by activated carbon and nano filtration. Wet air oxidation and biological treatment do not have effects on concentrations as a comparison to untreated leachate showed. PFC concentrations of leachates from closed sites show lower concentrations, in treated as well as in untreated leachate. Short chained compounds with a carbon chain length of $C < 8$ show higher shares than longer chained compounds with a carbon chain of $C \geq 8$ in treated and in untreated leachate. In activated carbon treatment a correlation between the adsorption and chain length could be observed for PFCA and PFSA in some cases.

For the characterization of landfill effluent it is inadequate if only the actual lead compounds, PFOA and PFOS are measured, since they show only small shares.

Nevertheless open questions remain. Some sites were sampled up to four times and concentrations were observed to vary in treated leachate. Knowledge on changes in short- and long term perspective could improve the estimations on mass flows, since they were made mostly by single measurements. One of the treatments, activated carbon treatment, showed a wide variation of results. Therefore more knowledge about adsorption behavior on activated carbon treatments should be gathered to explain the variation. Furthermore behavior of accumulation and breakthrough in activated carbon should be collected as well.

Gaseous emissions of volatile fluorinated compounds from landfills were no object in this study. Since it is suggested that landfills might emit precursor compounds, a study on this topic should be conducted as well.

Monitoring on a regular base seems to be more interesting for scientific reasons than for governmental or environmental protection reasons, since only knowledge on behavior can be gained and the database enhanced, but environmental concentrations concerning PFCs are occurring from other sources. Since individual industrial WWTP are shown to have higher mass flows of PFOA and PFOS than all German landfills together, more efforts should be taken on upgrading technologies in WWTPs. The beginning of reducing concentrations in aqueous environmental media starts by reducing mass flows from industrial WWTPs and not from landfills.

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Appendixes

Appendix I: Analytes, Acronymes, formula, supplier, purity, precursor and product ion and corresponding IS.

Substance	Acronym	Formula	Supplier and purity (%)	Precursor/ Product ion	Corresponding IS
Perfluorobutane sulfonate	PFBS	$C_4F_9SO_2O^-$	Fluka (97)	298.877/79.8	[^{18}O2]-PFHxS
Perfluoropentane sulfonate	PFPS	$C5F_{11}SO_2O^-$	n.a.	348.939/79.8	[^{18}O2]-PFHxS
Perfluorohexane sulfonate	PFHxS	$C6F_{13}SO_2O^-$	Fluka (98)	398.939/79.8	[^{18}O2]-PFHxS
Perfluorheptane sulfonate	PFHpS	$C_7F_{1}5SO_2O^-$	Well. Lab. (>98)	449.034/79.3	[^{13}C4]-PFOS
Perfluororcotane sulfonate	PFOS	$C_8F_{17}SO_2O^-$	Well. Lab. (>98)	498.971/97.7	[^{13}C4]-PFOS
Perfluorononane sulfonate	PFNS	$C_9F_{19}SO_2O^-$	n.a.	548.926/79.8	[^{13}C4]-PFOS
Perfluorodecane sulfonate	PFDS	$C_{10}F_{21}SO_2O^-$	Well. Lab. (>98)	598.896/79.5	[^{13}C4]-PFOS
6:2 fluorotemomer sulfonate	6:2 FTS	$C_6F_{13}C_2H_4SO_3$	ABCR (98)	426.925/406.7	[^{13}C4]-PFOS
Perfluoro-1-hexane sulfinate	PFHxSI	$C_6F_{13}SO_2^-$	Well. Lab. (>98)	382.865/319.0	[^{13}C4]-PFOSI
Perfluoro-1- octane sulfinate	PFOSI	$C_8F_{15}SO_2^-$	Well. Lab. (>98)	482.824/418.9	[^{13}C4]-PFOSI
Perfluoro-1-decane sulfinate	PFDSI	$C9F17SO2^-$	Well. Lab. (>98)	582.824/518.9	[^{13}C4]-PFOSI
Perfluorobutanoic acid	PFBA	C3F7COOH	ABCR (98)	112.900/168.7	[^{13}C4]-PFOSI
Perfluoropentanoic acid	PFPeA	C4F9COOH	Alfa Aesar (98)	262.825/218.9	[^{13}C4]-PFBA
Perfluorohexanoic acis	PFHxA	C5F11COOH	Fluka (97)	312.934/268.8	[^{13}C2]-PFHxA
Perfluoroheptanoic acid	PFHpA	$C6F^{13}COOH$	Lanc. Syn. (98)	362.950/318.9	[^{13}C2]-PFHxA
Perfluorooctanoic acid	PFOA	$C_7F_{14}COOH$	Lanc. Syn. (95)	412.987/368.9	[^{13}C4]-PFOA
Perfluorononaoic acid	PFNA	$C_8F_{15}COOH$	Lanc. Syn. (97)	462.908/418.9	[^{13}C4]-PFOA
Perfluorodecanoic acid	PFDA	$C_9F_{17}COOH$	Lanc. Syn. (97)	512.876/469.0	[^{13}C5]-PFNA
Perfluoroundecanoic acid	PFUnDA	$C_{10}F_{19}COOH$	ABCR (96)	562.865/519.0	[^{13}C2]-PFDA
Perfluorododecanoic acid	PFDoDA	$C_{11}F_{21}COOH$	Alfa Aesar (96)	612.991/568.9	[^{13}C2]-PFUnDA
Perfluorortridecanoic acid	PFTriDA	$C_{12}F_{23}COOH$	Well. Lab. (>98)	663.094/618.9	[^{13}C2]PFDoDA
Perfluorotetradecanoic acid	PFTeDA	$C_{13}F_{25}COOH$	Alfa Aesar (96)	713.036/669.0	[^{13}C2]-PFDoDA
Perfluorotridecanoic acid	PFPDA	$C_{14}F_{27}COOH$	n.a.	762.980/718.9	[^{13}C2]-PFDoDA
Perfluorohexadecanoic acid	PFHxDA	$C_{15}F_{29}COOH$	Alfa Aesar (96)	812.840/769.1	[^{13}C2]-PFDoDA
Perfluoroheptadecanoic acid	PFHpDA	$C_{16}F_{31}COOH$	n.a	862.980/818.9	[^{13}C2]-PFDoDA
Perfluorooctadecanoic acid	PFOcDA	$C_{17}F_{33}COOH$	Alfa Aesar (96)	912.870/869.0	[^{13}C2]-PFDoDA
Perfluoro-3,7-bis(trifluoromethyl)-octanoic acid	3,7m$_2$-PFOA	$C_6F_{19}COOH$	Alfa Aesar (97)	512.885/468.9	[^{13}C4]-PFOA
Perfluorohexlyphosphonic acid	PFHxA	$C_6F_{13}PO(OH)_2$	Well. Lab. (>98)	399.000/78.8	[^{13}C4]-PFOS
Perfluorooctylphosphonic acid	PFOPA	$C_8F_{17}PO(OH)_2$	Well. Lab. (>98)	499.000/78.8	[^{13}C4]-PFOS
Perfluorodecylphosphonic acid	PFDPA	$C_{10}F_{21}PO(OH)_2$	Well. Lab. (>98)	599.100/78.8	[^{13}C4]-PFOS
Perfluorooctane sulfonamid	PFOSA	$C_8F_{17}SO_2NH_2$	ABCR (97)	497.896/77.9	[^{13}C4]-PFOS

Substance	Acronym	Formula	Supplier and purity (%)	Precursor/ Product ion	Corresponding IS
N-methylperfluorooctane-sulfonamide	N-MeFOSA	$C_8F_{17}SO_2NH(CH_3$	3M (n.a.)	511.849/168.9	D_3-N-MeFOSA
N-methylperfluorooctane sulphonamide	N-EtFOSA	$C_8F_{17}SO_2NH(C_2H_5)$	ABCR (95)	526.008/169.0	D_5-N-EtFOSA
N-methylperfluorooctane-sulfonamidoethanol	N-MeFOSE	$C_8F_{17}SO_2N(CH_3)C_2H4OH$	3M (n.a.)	616.004/58.9	D_7-N-MeFOSE
N-ethylperfluoroctane sulfonamidedoethanol	N-EtFOSE	$C_8F_{17}SO_2N(C_2H_5)C_2H_4OH$	3M (n.a.)	630.109/58.8	D_9-N-EtFOSE
N-methylperfluorobutane sulfonamide	MeFBSA	$C_4F_9SO_2NH(CH_3)$	3M (n.a.)	311.914/218.8	D_3-N-MeFOSA
N-methylperfluorobutane sulfonamidoethanol	MEFBSE	$C_4F_9SO_2N(CH_3)C_2H_4OH$	3M (n.a.)	416.047/59.0	D_7-N-MeFOSE
2-perfluorohexylethanoic acid	FHEA	$C_6F_{13}CH_2COOF$	Well. Lab. (>98)	376.945/292.8	[^{13}C]-CFHEA
2-perfluorooctylethanoic acid	FOEA	$C_8F_{17}CH_2COOH$	Well. Lab. (>98)	476.909/392.9	[^{13}C]-FOEA
2-perfluorodecylethanoic acid	FDEA	$C_10F_{21}CH_2COOH$	Well. Lab. (>98)	577.011/493.0	[^{13}C]-FDEA
2H-perfluoro-2-octenoic acid	FHUEA	$C_6F_{12}CHCOOH$	Well. Lab. (>98)	356.885/293.0	[^{13}C]-FHUEA
2H-perfluoro-2-decenoic acid	FOUEA	$C_8F_{16}CHCOOH$	Well. Lab. (>98)	456.803/292.8	[^{13}C]-FOUEA
2H-perfluoro-2-dodecenoic acid	FDUEA	$C_{10}F_{20}CHCOOH$	Well. Lab. (>98	556.973/493.1	[^{13}C)-FDUEA

Appendix II: Internal Standards, Acronymes, formula, supplier, purity, precursor and product ion.

Internal Standard	Acronym	Formula	Supplier and purity (%)	Precursor/ Product ion
Perfluoro-1-hexane[$^{18}O_2$]sulfonate	[$^{18}O_2$]-PFHxS	$C_6F_{13}S[^{18}O_2]O^-$	Well. Lab. (>98)	402.981/83.9
Perfluoro-1-[1,2,3,4-$^{13}C_4$]octanesulfonate	[$^{13}C_4$]-PFOS	$C_4F_9[1,2,3,4\text{-}^{13}C_4]\text{-}F_8SO_2O^-$	Well. Lab. (>98)	502.899/79.5
Perfluoro-1-[1,2,3,4-^{13}C]perfluoro-octanesulfinate	[$^{13}C_4$]-PFOSi	$C_4F_9[1,2,3,4\text{-}^{13}C_4]\text{-}F_8SO_2^-$	Well. Lab. (>98)	486.859/422.9
Perfluoro-n-[1,2,3,4-$^{13}C_4$]butanoic acid	[$^{13}C_4$]-PFBA	$2,3,4\text{-}^{13}C_3]F_7{}^{13}COOH$	Well. Lab. (>98)	216.823/171.8
Perfluoro-n-[1,2-$^{13}C_2$]hexanoic acid	[$^{13}C_2$]-PFHxA	$C_4F_9[2\text{-}^{13}C]F_2{}^{13}COOH$	Well. Lab. (>98)	314.891/269.9
Perfluoro-n-[1,2,3,4-$^{13}C_4$]octanoic acid	[$^{13}C_4$]-PFOA	$C_4F_9[2,3,4\text{-}^{13}C_3]F_6{}^{13}COOH$	Well. Lab. (>98)	416.978/371.8
Perfluoro-n-[1,2,3,4,5-$^{13}C_5$]nonanoic acid	[$^{13}C_5$]-PFNA	$C_4F_9[2,3,4,5\text{-}^{13}C_5]F_8{}^{13}COOH$	Well. Lab. (>98)	467.907/423.0
Perfluoro-n-[1,2-$^{13}C_2$]decanoic acid	[$^{13}C_2$]-PFDA	$C_8F_{17}{}^{13}CF_2{}^{13}COOH$	Well. Lab. (>98)	514.944/469.8
Perfluoro-n-[1,2-$^{13}C_2$]undecanoic acid	[$^{13}C_2$]-PFUnDA	$C_9F_{19}{}^{13}CF_2{}^{13}COOH$	Well. Lab. (>98)	564.959/519.8
Perfluoro-n-[1,2-^{13}C]dodecanoin acid	[$^{13}C_2$]-PFDoDA	$C_{10}F_{21}CF_2{}^{13}COOH$	Well. Lab. (>98)	614.9^{13}/569.9
N-methyl-d$_3$-perfluoro-1-octanesulfonamide	D_3-N-MeFOSA	$C_9D_3HF_{17}NO_2S$	Well. Lab. (>98)	514.920/168.8
N-ethyl-d$_5$-perfluoro-1-octanesulfonamide	D_5-N-EtFOSA	$C_{10}D_5HF_{17}NO_2S$	Well. Lab. (>98)	530.984/168.8
2-(n-deuteriomethylperfluoro-1-octanesulfonamido)-1,1,2,2-tetradeuterioethanol	D_7-N-MeFOSE	$C_8F_{17}SO_2N(CD_3)C_2D_4OH$	Well. Lab. (>98)	623.058/58.9
2-(n-deuterioethylperfluoro-1-octanesulfonamido)-1,1,2,2-tetradeuterioethanol	D_9-N-EtFOSE	$C_8F_{17}SO_2(C_2D_5)C_2D_4OH$	Well. Lab. (>98)	639.054/58.9
2-perfluorohexyl-[1,2-^{13}C2]ethanoic acid	[$^{13}C_2$]-FHEA	$C_6F_{13}CH_2{}^{13}COOH$	Well. Lab. (>98)	378.912/294.0
2-perfluorooctyl-[1,2-^{13}C2]ethanoic acid	[$^{13}C_2$]-FHOEA	$C_8F_{17}{}^{13}CH_2{}^{13}COOH$	Well. Lab. (>98)	478.911/393.8
2-perfluorodecyl-[1,2-^{13}C2]-FDEA	[$^{13}C_2$]-FDEA	$C_{10}F_{21}{}^{13}CH_2{}^{13}COOH$	Well. Lab. (>98)	579.017/494.1
2H-perfluoro-[1,2-$^{13}C_2$]- 2-octenoic acid	[$^{13}C_2$]-FHUEA	$C_6F_{12}\ {}^{13}CH^{13}COOH$	Well. Lab. (>98)	358.907/294.0
2H-perfluoro-[1,2-$^{13}C_2$]-2-decenoic acid	[$^{13}C_2$]-FOUEA	$C_8F_{16}{}^{13}CH^{13}COOH$	Well. Lab. (>98)	458.903/393.8
2H-perfluoro-[1,2-$^{13}C_2$]-2-dodecanoic acid	[$^{13}C_2$]-FDUEA	$C_{10}F_{20}{}^{13}CH^{13}COOH$	Well. Lab. (>98)	558.955/494.0
N-deuterioethylperfluoro-1-octanesulfonamidoacetic acid	D5-EtFOSAA	$C_8F_{17}SO_2N(C_2D_2C_2D_3)C_2H_2CO_2H$	Well. Lab. (>98)	589.015/418.7

Appendix III: Concentrations of each Compound in treated leachate.

	2	3	4	5	6	7	8	9	10	12
PFBS	827,82	12,46	1056,78	1355,62	244,43	0,47	0,86	0,41	251,58	305,76
PFPS	n.d.	0,50	76,41	61,07	54,73	n.d.	n.d.	n.d.	7,34	12,99
PFHxS	36,43	0,44	177,50	82,41	84,78	n.d.	n.d.	0.07	12,35	43,34
PFHpS	1,90	n.d.	7,62	7,81	5,00	n.d.	n.d.	n.d.	n.d.	1,00
PFOS	45,01	0,66	192,06	234,99	88,55	0,29	0,29	0,01	7,99	27,69
PFNS	24,94	n.d.	n.d.	1,67	n.d.	n.d.	n.d.	n.d.	8,23	n.d.
6:2 FTS	74,76	n.d.	56,19	82,08	17,44	n.d.	n.d.	n.d.	20,96	9,40
PFHxSi	8,05	n.d.	0,51	1,80	0,59	n.d.	n.d.	n.d.	0,46	0,11
PFOSi	12,63	n.d.	0,46	9,33	n.d.	0,03	n.d.	n.d.	2,38	n.d.
PFDSi	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFBA	990,12	6,88	1302,77	1720,23	558,78	173,84	3,59	1.64	n.d.	392,32
PFPA	123,81	n.d.	201,84	828,74	154,54	2,06	n.d.	0,77	14,73	94,04
PFHxA	935,00	1,28	154,31	2508,66	334,30	0,83	n.d.	n.d.	185,45	198,39
PFHpA	201,03	n.d.	253,83	280,29	147,14	0,14	0,08	n.d.	32,20	39,40
PFOA	708,05	1,16	925,59	720,50	284,60	1,19	1,37	0,68	76,24	119,95
PFNA	13,14	n.d.	80,06	45,05	6,33	n.d.	n.d.	n.d.	n.d.	1,26
PFDA	6,59	n.d.	51,33	55,09	1,93	0,30	0,11	0,07	n.d.	1,61
PFUnDA	0,58	n.d.	2,82	2,98	0,36	n.d.	0,06	0,08	n.d.	0,21
PFDoDA	1,05	n.d.	1,29	2,45	0,63	n.d.	0,20	0,21	n.d.	0,51
PFTriDA	n.d.	n.d.	0,34	0,62	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFTeDA	n.d.	n.d.	n.d.	0,39	n.d.	0,41	n.d.	n.d.	n.d.	n.d.
PFPeDA	n.d.	n.d.	0,10	0,42	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFHxDA	1,51	n.d.	n.d.	1,91	n.d.	n.d.	n.d.	n.d.	n.d.	0,60
PFHpDA	n.d.	n.d.	n.d.	1,04	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFOcDA	2,92	n.d.	n.d.	2,96	2,56	n.d.	n.d.	n.d.	n.d.	0,90
Me2PFOA	n.d.	n.d.	n.d.	27,06	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFOSA	5,22	0,35	8,22	13,99	5,82	0,62	2,70	0,78	1,86	1,18
NMeFOSA	n.d.	n.d.	n.d.	1,04	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
NMeFOSE	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
MeFBSA	n.d.	n.d.	n.d.	9,72	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
MeFBSE	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
FHEA (6:2 FTCA)	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	6,57
FHUEA (6:2 FTUCA)	2,56	n.d.	1,66	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
FOUEA (8:2 FTUCA)	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFHxPA	n.d.	n.d.	39,72	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFOPA	n.d.	n.d.	19,47	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFDPA	n.d.	n.d.	n.d.	n.d.	n.d.	9,93	n.d.	n.d.	n.d.	n.d.
summation	4023	23,7	4611	8060	1993	190	9,26	3,97	622	1257
leachate in m^3/year	46000	26280	7000	8000	175200	28700	9000	8000	200	55000

Appendix III: Continuation.

	13	14	15	16	17	18	19	20	21	22
PFBS	8,83	75,00	2,53	0,86	2,26	135,76	99,89	n.d.	15,30	4,10
PFPS	n.d.	0,33	n.d.	n.d.	0,62	0,37	0,08	n.d.	0,96	n.d.
PFHxS	0,25	0,03	n.d.	0,03	1,08	0,03	0,87	n.d.	3,46	0,43
PFHpS	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFOS	0,22	0,27	1,07	0,76	2,54	1,60	2,52	0,49	8,23	2,78
PFNS	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6:2 FTS	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFHxSi	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFOSi	0,26	0,01	0,16	0,70	0,10	2,65	0,20	n.d.	0,59	0,66
PFDSi	n.d.	n.d.	0,04	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFBA	n.d.	2967,82	4,86	1,12	6,50	945,10	8,50	22,99	52,97	1,04
PFPA	n.d.	688,71	0,57	0,62	0,63	331,53	3,12	n.d.	18,36	0,66
PFHxA	1,43	327,33	2,75	0,56	1,23	11,08	2,66	n.d.	19,07	n.d.
PFHpA	0,22	9,31	1,45	0,35	0,32	1,30	1,67	n.d.	5,57	n.d.
PFOA	2,96	1,88	5,17	1,18	4,80	2,99	8,55	n.d.	22,68	14,55
PFNA	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFDA	0,26	0,13	n.d.	0,27	0,22	n.d.	0,63	n.d.	0,46	0,65
PFUnDA	n.d.	0,06	n.d.	0,06	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFDoDA	n.d.	0,01	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFTriDA	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFTeDA	n.d.	0,27	n.d.	0,02	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFPeDA	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFHxDA	n.d.	0,48	n.d.	0,09	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFHpDA	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFOcDA	n.d.	0,54	n.d.	0,02	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Me2PFOA	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0,04	n.d.
PFOSA	0,83	0,24	n.d.	1,52	0,16	9,87	n.d.	n.d.	0,90	1,09
NMeFOSA	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
NMeFOSE	n.d.	0,04	n.d.	0,02	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
MeFBSA	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
MeFBSE	n.d.	0,08	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
FHEA (6:2 FTCA)	n.d.	0,60	n.d.	1,19	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
FHUEA (6:2 FTUCA)	n.d.	0,09	n.d.	0,11	n.d.	n.d.	n.d.	n.d.	n.d.	0,16
FOUEA (8:2 FTUCA)	n.d.	n.d.	n.d.	0,06	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFHxPA	n.d.	6,03	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFOPA	n.d.	n.d.	n.d.	0,46	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFDPA	n.d.	n.d.	n.d.	0,82	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
summation	15,25	4079,24	18,60	10,83	20,47	1442,27	128,70	23,48	148,58	26,13
leachate in m^3/year	10000	20000	8000	16500	19500	131400	27500	26500	29000	41100

Appendix IV: Concentrations of each compound in untreated leachate in ng/L.

	1	6	8	11	14	17
PFBS	3657,14	247,00	0,41	37,04	3081,49	1572,85
PFPS	0	35,80	n.d.	19,95	63,58	175,35
PFHxS	123,71	66,26	n.d.	59,81	348,68	244,11
PFHpS	n.d.	10,02	n.d.	n.d.	35,49	18,95
PFOS	98,38	47,91	n.d.	63,81	473,06	298,63
PFNS	n.d.	n.d.	n.d.	2,16	n.d.	n.d.
TH-PFOS	n.d.	n.d.	n.d.	n.d.	1343,48	n.d.
PFOSi	184,14	n.d.	n.d.	n.d.	96,66	n.d.
PFBA	2787,61	695,49	28,25	2276,91	2058,33	1673,78
PFPA	339,48	214,21	1,33	95,96	608,82	940,62
PFHxA	1407,37	311,62	n.d.	283,64	1829,27	1565,47
PFHpA	230,84	92,21	n.d.	117,75	433,80	591,32
PFOA	512,12	162,43	0,55	273,37	2269,41	1280,28
PFNA	35,40	n.d.	n.d.	n.d.	39,65	4,00
PFDA	56,24	n.d.	n.d.	n.d.	42,66	3,34
PFUnDA	2,30	n.d.	n.d.	n.d.	6,06	n.d.
PFDoDA	n.d.	n.d.	n.d.	n.d.	3,27	n.d.
PFOSA	29,52	5,96	n.d.	4,84	36,00	1,75
NMeFOSE	44,44	n.d.	n.d.	n.d.	56,15	n.d.
NEtFOSE	87,79	n.d.	n.d.	n.d.	96,11	n.d.
MeFBSE	82,44	n.d.	n.d.	62,40	n.d.	n.d.
FHEA (6:2 FTCA)	86,32	n.d.	n.d.	23,36	n.d.	n.d.
FOEA (8:2 FTCA)	117,80	n.d.	n.d.	n.d.	n.d.	n.d.
FHUEA (6:2 FTUCA)	64,47	n.d.	n.d.	n.d.	n.d.	n.d.
FDUEA (10:2 FTUCA)	33,64	n.d.	n.d.	n.d.	n.d.	n.d.
Summation	9948,50	1894,90	38,53	3332,00	12935,96	8387,45

Appendix V: Detailed results of four samples from the 3rd activated carbon treatment container and from two samples from the outflow of the lagoon of site 9. All concentrations are in ng/L. Not shown compounds were not detected.

	AC3-1	AC3-2	AC3-3	AC3-4	Lagoon-1	Lagoon-2
PFBS	0.48	0.43	n.d.	0.72	n.d.	0.88
PFHxS	n.d.	n.d.	n.d.	0.14	n.d.	0.18
PFOS	n.d.	0.02	n.d.	n.d.	n.d.	n.d.
PFBA	n.d.	1.94	3.91	n.d.	3.91	n.d.
PFPA	n.d.	2.32	n.d.	n.d.	n.d.	n.d.
PFHpA	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFOA	n.d.	0.74	1.96	n.d.	1.96	n.d.
PFNA	0.36	n.d.	n.d.	n.d.	n.d.	n.d.
PFDA	n.d.	0.20	n.d.	n.d.	n.d.	n.d.
PFUnDA	0.18	n.d.	n.d.	0.15	n.d.	0.17
PFDoDA	0.43	n.d.	n.d.	0.40	n.d.	0.44
PFHxDA	n.d.	n.d.	n.d.	n.d.	n.d.	0.72
FOSA	0.23	0.67	1.69	0.54	1.69	4.89

Appendix VI: Detailed results of samples from three activated carbon containers from site 18. All concentrations are in ng/L. Not shown compounds were not detected.

	Ac-1	Ac-2	Ac-3
PFBS	2126	2108	136
PFPS	3.85	4.37	0.37
PFHxS	16.9	5.70	0.03
PFOS	9.70	2.75	1.60
PFHxSi	0.78	0.56	n.d.
PFOSI	n.d.	2.09	2.65
PFBA	831	819	945
PFPA	412	324	332
PFHxA	678	515	11.1
PFHpA	91.3	56.27	1.30
PFOA	210	62.34	2.99
PFNA	3.94	n.d.	n.d.
PFOSA	n.d.	7.03	9.87