National Institute for Public Health
and the Environment
Ministry of Health, Welfare and Sport

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RIVM report 2021-0143
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Colophon

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Synopsis

Per- and polyfluorinated substances in waste incinerator flue gases

By 2050, the Netherlands wants to produce as little waste as possible and to recycle products and materials as much as possible. However, these products and materials must be safe and free of hazardous substances. Some waste incinerators for instance recover carbon dioxide from their flue gases. Carbon dioxide can be used to promote the growth of crops in greenhouses.

RIVM has carried out a literature study to investigate whether and, if so, to what degree this carbon dioxide can contain PFASs. This is a first step of a risk assessment process. This study did not consider whether the presence of PFASs presents a risk for the human health or the environment.

As many types of PFASs exist, RIVM first described a definition of this group of substances. The next step was to examine whether these substances can be present in the flue gases of waste incinerators. In fact, that appeared to be the case.

Based on a literature review, RIVM expects that most of the PFASs will largely degrade during the incineration process and then be removed when the flue gases are cleaned. The remaining PFASs are expected to be removed during the recovery of the carbon dioxide. Some publications about measurements in the chimney of a waste incineration plant do not exclude the possibility that there may still be PFASs in the flue gases. At the same time it appears that a particular group of PFASs is formed during the incineration process and can be present in the cleaned flue gases. This involves strong greenhouse gases that contribute to global warming.

To our knowledge, no measurements have been made for PFASs in recovered carbon dioxide and only a few in cleaned flue gases. In view of the application, RIVM considers it desirable that both carbon dioxide and cleaned flue gas are measured for PFASs. Then the risks of the transmission of PFASs can be better understood.

It should be technically feasible to measure PFASs in the flue gases and the recovered carbon dioxide. RIVM recommends developing an effective measurement method for that purpose that can be used as a benchmark.

Keywords: waste incineration, PFAS, fluoropolymer, thermal degradation, flue gas, CO2 recovery, measurement

Publiekssamenvatting

PFAS’en in rookgas van afvalverbrandingsinstallaties

Nederland wil in 2050 zo min mogelijk afval produceren en producten en materialen zo veel mogelijk hergebruiken. Deze producten en materialen moeten dan wel veilig zijn en geen schadelijke stoffen bevatten. Sommige afvalverbrandingsinstallaties winnen bijvoorbeeld koolstofdioxide uit hun rookgassen. Dat kan gebruikt worden om gewassen in kassen beter te laten groeien.

Het RIVM heeft in een literatuurstudie verkend of, en zo ja in welke mate, PFAS’en in gewonnen koolstofdioxide kunnen zitten. Dit is een eerste stap voor een risicobeoordeling. In dit onderzoek is niet gekeken of de aanwezigheid van PFAS’en een risico vormt voor de gezondheid van mensen of het milieu.

Omdat er veel soorten PFAS’en bestaan, heeft het RIVM eerst de definitie van deze stofgroep beschreven. Daarna is onderzocht of deze stoffen in de rookgassen van afvalverbrandingsinstallaties kunnen voorkomen. Dat bleek het geval te zijn.

Uit literatuuronderzoek blijkt dat de meeste PFAS’en tijdens het verbrandingsproces grotendeels worden afgebroken. Door reiniging van het rookgas worden nog aanwezige PFAS’en er grotendeels uit verwijderd. De PFAS’en die nog overblijven worden naar verwachting tijdens de winning van de koolstofdioxide verwijderd. Enkele publicaties over metingen in de schoorsteen van een afvalverbrandingsinstallatie sluiten niet uit dat er toch nog PFAS’en in de rookgassen kunnen zitten. Ook blijkt uit de literatuurstudie dat een bepaalde groep PFAS’en tijdens de verbranding wordt gevormd en in het gereinigde rookgas zou kunnen voorkomen. Het gaat om sterke broeikasgassen die bijdragen aan de opwarming van de aarde.

Voor zover ons bekend zijn er geen metingen gedaan naar PFAS’en in gewonnen koolstofdioxide en maar enkele in gereinigde rookgassen. Gezien de toepassing vindt het RIVM het wenselijk dat zowel in koolstofdioxide als gereinigde rookgas wordt gemeten of er PFAS’en in zitten. Dan kunnen de risico’s van de verspreiding van PFAS’en beter in beeld komen.

Het zou technisch mogelijk moeten zijn om PFAS’en in de rookgassen en de gewonnen koolstofdioxide te meten. Het RIVM beveelt aan om hiervoor een geschikte meetmethode te ontwikkelen die als standaard kan worden gebruikt.

Kernwoorden: afvalverbrandingsinstallatie, PFAS, fluorpolymeer, thermische afbraak, rookgas, CO_2-afvang, meting

Contents

Summary

Background
In the Netherlands there are 13 waste incineration plants spread across the country that receive and incinerate different types of waste. In addition to household waste, municipal waste and non-hazardous industrial waste, some plants accept hazardous waste.
Waste incineration plants are licensed in accordance with the Dutch Activities Decree and must use the best available techniques. The plants have to comply with the requirements for incineration of non-hazardous waste by maintaining the temperature of the combustion gases at a minimum of 850 °C for at least 2 seconds after the last injection of combustion air, in the presence of at least 6% oxygen. For hazardous waste, the minimum temperature of the combustion gases must be 1100 °C. Emission limit values have been established for harmful substances in the flue gases in accordance with Article 5.19 of the Activities Decree.

There is a knowledge gap regarding whether and to what extent waste incinerators emit per- and polyfluoroalkyl substances (PFASs) via their flue gases and thereby contribute to PFAS contamination. Waste incinerators burn significant amounts of synthetic materials that also contain fluoropolymers and perfluoroalkyl substances. PFASs are known for their persistence, human toxicity and thermal stability. It is unknown whether and to what extent the PFASs present in household and industrial waste are effectively incinerated and converted into other substances in the flue gases. As well as potentially being present in the emitted flue gases, PFASs may occur in solid residues such as slag, and bottom and fly ashes, which are formed during the incineration process. These solid residues are collected at different stages from the incinerator and flue gas treatment system. Depending on the method of storage, as well as on the transport and processing of these incineration residues into useful applications such as building materials, there may be a risk of PFAS spreading.

Some waste incinerator companies in the Netherlands recover the carbon dioxide (CO_2) in the flue gases and make it suitable for various applications. Whether or not PFASs occur in flue gases largely determines the question of whether PFASs can also be expected in the recovered CO_2 and thus whether their presence should be considered for the intended applications. Knowledge about this is important in order to be able to make legal judgments for new applications of the CO_2 recovered from waste incinerator flue gases.

Against this background, Rijkswaterstaat (RWS) has commissioned RIVM to answer the following research questions on the basis of a literature study:

1) What is the precise definition of a PFAS and what connection is there between the advisory list of individual PFASs in the Temporary Action Framework and that in the Knowledge Document of the Expertise Centre PFAS?

2) Can PFASs be present in the flue gases of a waste incinerator as a result of not breaking down (completely)?
3) Can PFASs (not broken down or broken down into smaller molecules) be captured in flue gases after one or more cleaning steps?
4) Can PFASs (partly depending on the answers to questions 2 and 3 above) be present in the carbon dioxide recovered from waste incinerator flue gases?
5) Is the chemical analysis of fluoride sufficiently accurate to reveal the presence of PFASs in flue gases and carbon dioxide?
6) Can RIVM advise on the possible presence of PFASs in the carbon dioxide that is recovered from waste incinerator flue gases for applications such as growth improver in greenhouse horticulture?

RIVM study
RIVM has searched and studied the relevant literature in different libraries of scientific publications and reports as well as bibliographic literature databases such as Scopus, Pubchem, HSDSB and Google Scholar, and relevant internet pages.
The literature study covered a variety of topics, including:

- the definitions of PFAS;
- waste incineration processes/installations and the difference between several types of furnaces and flue gas treatment techniques;
- the different thermal chemical degradation reactions of PFAS components based on theoretical analyses and published experimental studies;
- the formation and emission pathways of PFAS degradation products resulting from waste incineration processes;
- PFAS, fluoride and total organic fluorine measurement methods;
- the effects of the CO_2 recovery process on the occurrence of PFASs in the recovered CO_2.

Conclusions
Based on published laboratory experiments and qualitative theoretical assessments, efficient thermal destruction is anticipated for the groups of PFASs considered.

Critical is the definition of complete thermal breakdown. Complete breakdown could refer to complete mineralisation of PFASs to hydrogen fluoride and CO_2. On the other hand, complete breakdown could mean that the original compounds are completely destroyed but without complete mineralisation. In practice, full mineralisation will hardly ever occur, as thermal degradation is always accompanied by the formation of various gaseous organic fluorine-containing products. If the minimum requirements for waste incineration plants are met, it is concluded that combustion by-products are mainly limited to the smallest members of the PFAS group perfluorinated carbons (PFCs), CF_4 and C_2F_6. Both are potent greenhouse gases, resistant to high temperatures and most likely (a) to be formed and (b) to survive the combustion process.

Fluorinated polymers such as polytetrafluoroethylene (PTFE) are also considered PFASs. PTFE is a fully fluorinated polymer that is one of the most thermally stable of all polymers. Based on experimental data found in literature, it is expected that PTFE will thermally degrade completely at the minimum required combustion temperature of 850 °C. However, for solid substances like polymers the conditions in the combustion bed are probably even more important than the temperature in the combustion chamber. The residence time and mixing of the incineration bed on the grate should be sufficient to allow for solid materials to burn out, that is to thermally degrade into smaller volatile components that will subsequently be incinerated in the combustion chamber. PTFE as such will not volatilise and then be burned in the combustion chamber. At the expected temperatures in the incineration bed, between 900 and 1100 °C, it is expected that PTFE and other fluorinated polymers will fully degrade into small fluorocarbon molecules.

For combustion by-products other than those previously mentioned, such as fluorinated dioxins and furans and perfluoroacetic acid, it is judged that their formation from PFASs is unlikely. The formation of fluorinated dioxins and furans, however, cannot be entirely ruled out because of the potential formation of fluorinated benzenes under unfavourable combustion conditions. Fluorinated benzenes could serve as precursors to the formation of fluorinated dioxins and furans. Ultimately, the formation of fluorinated dioxins and furans is not expected because they have not been detected at measurements that were done in order to reveal their occurrence.

From the qualitative assessment of the removal efficiencies of the flue gas treatment and CO_2 recovery processes it is concluded, for the PFASs considered, that:

1) the types of PFASs with the strongest tendency to pass through the flue gas treatment system are iodine-containing PFASs, fluorotelomer olefins (FTOs), the perfluoroalkanes (PFCs), the fluorotelomer alcohols with a short perfluorinated chain of 3 to 5 fluorinated carbon atoms (3-5:2 FTOH) and the fluorotelomer acrylates (FTACs) – assuming that these compounds survive the combustion process. Iodine-containing perfluoro compounds, for instance, are expected to be the least thermally stable of the perfluoro compounds and most unlikely to survive the incineration process;
2) due to the physical and chemical processes in the CO_2 recovery plant it is expected that none or very little of most of the PFASs considered will end up in the extracted CO_2. Of the substances considered, the PFASs with the highest tendency to end up in the recovered CO_2 stream are non-dissociating substances with a polar character, i.e. mainly fluorotelomer alcohols with a short perfluoro chain and the group of substituted perfluoroalkane sulphonamido ethanols (MeFASEs and EtFASEs).

These conclusions are based largely on published laboratory experiments and qualitative theoretical assessments. Published results from field measurements show that various PFASs have been detected in flue gas and incineration residues such as bottom ash and fly ash. The total PFAS concentration measured in flue gas was about 20 $ng.m^{-3}$. Measurements to detect the presence of PFASs in recovered CO_2 have not been conducted as far as we know.

The literature study further shows that no standardised methods are yet available for measuring the emission concentration of PFASs in the flue gases of waste incineration plants. However, it should be technically possible to sample different PFAS subgroups, such as gaseous, polar, water-soluble, dust-bound and dust-based (aerosols) PFASs, in the flue gases.

In sampling it is common practice to use a train of filters, adsorption columns and impinger absorption liquids connected in series. The collected filters, adsorption columns and impinger fluids can be chemically analysed in an accredited analytical laboratory after sampling. GC-MS and HPLC-MS/MS are particularly suitable for this purpose as analytical techniques. GC-MS lends itself well to the measurement of gaseous and non-polar to mildly polar PFASs, while HPLC-MS/MS is suitable for polar, dissociable and water-soluble PFASs. HPLC-MS/MS has been accepted in available standard requirements for the determination of the content of PFASs in soil, dredge, sediment, and ground and surface water.

A feasible limit of quantification (LOQ) for the measurement of PFASs in flue gases is estimated to be within an emission concentration range of 0.1 to 0.5 ng.m^{-3}. A sampling volume of approximately 4 m^3 of flue gas is assumed here.

The prescribed measurement method for fluoride in flue gas (NEN-ISO 15713) is not to be considered a suitable or replacement method for measuring PFASs. This is because the LOQ of fluoride is a factor of 1000 higher than the LOQ of a measurement method for determining individual PFASs and the fluoride measurement is not selective for the sum of PFASs.

The total organic fluorine (TOF) measurement seems to be a better method because the sum of PFASs is part of the TOF. So, if TOF is not being detected there is no PFAS. However, the feasible LOQ is expected be between 50 and 250 ng.m^{-3}, which makes this method less suitable for the detection of the sum of PFASs in flue gases.

With regard to the concentration of PFASs in recovered CO_2, as an order of magnitude estimate, 10 ng.m^{-3} could be used for the total concentration of PFASs. The total PFAS concentration measured in flue gas is about 20 ng.m^{-3}. However, the concentration is expected to be reduced substantially during the CO_2 recovery process.

Recommendations
In order to confirm whether PFASs are present in recovered CO_2 and to find out in what quantity they are present, measurements should be conducted. For a complete picture is recommended that measurements shall be taken in flue gases as well as in fly ash from incineration plants. Besides the standard set of PFASs according to the advisory list of the Temporary Action Framework, it is recommended in this report to include in the measurements the PFASs that are indicated in this study. It mainly concerns PFASs that are likely to survive or to be formed in the combustion process, to pass through the flue gas treatment system or to end up in the recovered CO_2. These include short-chain perfluoro

carbons, fluorotelomer alcohols and acrylates, and substituted perfluoroalkane sulphonamido ethanols.
It cannot be ruled out that differences in the results of PFAS emission measurements of the flue gases of waste incinerators are due to differences in the methods and laboratory tools used for sampling, sample pre-treatment and measurement. These factors could also explain the differences in the LOQ of up to a factor of 1000. It is therefore essential to standardise the measurement methods, including the sampling and the analytical techniques.

Final conclusion
Based on a review of the scientific literature and the theory about combustion processes and flue gas cleaning techniques, RIVM concludes that:

- PFASs present in household, municipal and industrial waste degrade into other substances when this waste is incinerated in compliance with the legal requirements for waste incineration plants in the Netherlands,
- at the same time, a new PFAS group is formed which are strong greenhouse gases such as perfluoromethane and perfluoroethane,
- some publications about measurements in the chimney of a waste incineration plant do not exclude the possibility that PFASs may still be present in the flue gases and that they can be emitted as a result.

The remaining PFASs are expected to be removed during the recovery of the carbon dioxide.

Due to the lack of sufficiently accurate PFAS measurements, it is uncertain what the composition and quantity of PFASs is in the cleaned flue gases and in the recovered carbon dioxide. In view of the application, RIVM considers it desirable to measure both carbon dioxide and cleaned flue gas in order to be able to determine the presence of the PFASs. The risks of the transmission of PFASs can then be better understood. This risk concerns both the flue gas emission from the chimney and the applications of the carbon dioxide extracted from the flue gases, such as the use as a growth improver in greenhouse horticulture.

It is also recommended that further research be conducted into the transmission of PFASs via waste streams from waste incineration, such as bottom ash, fly ash and waste water.

Samenvatting

Achtergrond
In Nederland zijn er verspreid over het land dertien afvalverbrandingsinstallaties die verschillende soorten afval in ontvangst nemen en verbranden. Naast huishoudelijk afval, gemeentelijk afval en niet-gevaarlijk bedrijfsafval, accepteren sommige installaties ook gevaarlijk afval.

Afvalverbrandingsinstallaties zijn vergunningplichtig conform het Nederlandse Activiteitenbesluit en moeten gebruikmaken van de best beschikbare technieken. De installaties moeten voldoen aan de eisen voor de verbranding van ongevaarlijk afval door de temperatuur van de verbrandingsgassen ten minste twee seconden op 850 °C te houden na de laatste injectie van verbrandingslucht in aanwezigheid van ten minste 6% zuurstof. Voor gevaarlijk afval moet de minimumtemperatuur van de verbrandingsgassen worden verhoogd tot 1100 °C. Voor schadelijke stoffen in de rookgassen zijn emissiegrenswaarden vastgesteld conform artikel 5.19 van het Activiteitenbesluit.

Er is een kennislacune over de vraag of en tot welke hoeveelheden afvalverbrandingsinstallaties via hun rookgassen per- en polyfluoralkylstoffen (PFAS’en) uitstoten en daarmee bijdragen aan de PFAS-verontreiniging. Afvalverbrandingsinstallaties verbranden aanzienlijke hoeveelheden synthetische materialen die ook fluorpolymeren en perfluoralkylstoffen bevatten. PFAS’en staan bekend om hun eigenschappen zoals persistentie, humane toxiciteit en thermische stabiliteit. Het is niet bekend of en in welke mate de PFAS’en die aanwezig zijn in huishoudelijk- en bedrijfsafval effectief worden verbrand en omgezet in andere stoffen in de rookgassen.

Naast PFAS-emissies via de rookgassen kunnen PFAS’en ook voorkomen in vaste reststoffen, zoals slakken en bodem- en vliegassen die ontstaan tijdens het verbrandingsproces en gescheiden worden opgevangen in de verbrandingsoven en het rookgasbehandelingssysteem. Afhankelijk van de wijze van opslag, transport en verwerking van deze verbrandingsresten tot nuttige toepassingen zoals bouwstoffen, kan er een risico op verspreiding van PFAS’en bestaan.

Enkele afvalverbrandingsinstallaties in Nederland winnen kooldioxide (CO_2) uit de rookgassen en maken deze geschikt voor verschillende toepassingen. Het mogelijk voorkomen van PFAS’en in de rookgassen bepaalt grotendeels de vraag of PFAS’en ook in het gewonnen CO_2 te verwachten is en of hun aanwezigheid voor de beoogde toepassingen in aanmerking moet worden genomen. Kennis hierover is van belang om rechtsoordelen te kunnen maken voor nieuwe toepassingen van het gewonnen CO_2 in de rookgassen van de afvalverbrandingsinstallaties.

Tegen deze achtergrond heeft Rijkswaterstaat (RWS) het RIVM opdracht gegeven om op basis van literatuuronderzoek de volgende onderzoeksvragen te beantwoorden:

1) Wat is de definitie van een PFAS en welk verband is er met de advieslijst van individuele PFAS'en van het tijdelijk handelingskader en die van het kennisdocument van het Expertisecentrum PFAS?
2) Kunnen PFAS'en in de rookgassen van een afvalverbrandingsoven aanwezig zijn, omdat ze niet (volledig) afbreken?
3) Kunnen PFAS'en die niet afgebroken zijn of afgebroken tot kleinere moleculen na één of meerdere reinigingsstappen in de rookgassen worden afgevangen?
4) Kunnen PFAS'en (mede afhankelijk van de antwoorden op vraag 2 en 3 hierboven) in kooldioxide aanwezig zijn bij de winning van dit gas uit de rookgassen van de afvalverbrandingsinstallaties?
5) Is de chemische analyse van fluoride voldoende nauwkeurig om de aanwezigheid van PFAS'en in de rookgassen en kooldioxide te kunnen aantonen?
6) Kan het RIVM adviseren over de mogelijke aanwezigheid van PFAS'en in de kooldioxide die uit rookgassen van afvalverbrandingsinstallaties worden gewonnen voor toepassingen als groeiverbeteraar in de glastuinbouw?

RIVM-onderzoek
Het RIVM heeft in verschillende bibliotheken naar relevante wetenschappelijke publicaties en rapporten gezocht en deze bestudeerd. Ook is er gezocht in bibliografische literatuurdatabases zoals Scopus, Pubchem, HSDSB, Google Scholar en relevante internetpagina's. De literatuurstudie omvatte een verscheidenheid aan onderwerpen zoals;

- de definitie van PFAS;
- de afvalverbrandingsprocessen/-installaties;
- het verschil tussen verschillende soorten ovens en de rookgasbehandelingstechnieken;
- de verschillende thermische chemische afbraakreacties van PFAS-componenten op basis van theoretische analyses en gepubliceerde experimentele studies;
- de vormings- en emissieroutes van PFAS'en en de afbraakproducten als gevolg van afvalverbrandingsprocessen;
- de meetmethoden voor PFAS'en, fluoride en totaal organisch fluor;
- de invloed van het CO_2 winningsproces op de aanwezigheid van PFAS'en in het gewonnen CO_2.

Conclusies
Op basis van gepubliceerde laboratoriumexperimenten en kwalitatieve theoretische beoordelingen wordt een efficiënte thermische afbraak verwacht voor de beschouwde groepen PFAS.

Cruciaal is de definitie van volledige thermische afbraak. Volledige afbraak kan verwijzen naar volledige mineralisatie tot waterstoffluoride (HF) en CO_2. Aan de andere kant kan volledige afbraak ook betekenen dat de oorspronkelijke verbindingen geheel worden vernietigd zonder volledige mineralisatie.
In de praktijk zal volledige mineralisatie bijna nooit optreden, aangezien thermische afbraak altijd gepaard gaat met de vorming van verschillende gasvormige organische fluorhoudende producten.

Als aan de minimumeisen voor afvalverbrandingsinstallaties wordt voldaan, wordt geconcludeerd dat de vorming van bijproducten tijdens de verbranding voornamelijk wordt beperkt tot de kleinste leden van de PFAS groep geperfluoreerde koolstoffen (PFCs), namelijk perfluormethaan (CF_4) en perfluorethaan (C_2F_6). Beide zijn krachtige broeikasgassen, die bestand zijn tegen hoge temperaturen en de meeste kans hebben om gevormd te worden en het verbrandingsproces te overleven.

Fluorpolymeren zoals polytetrafluorethyleen (PTFE) zijn eveneens PFAS’en. PTFE is een volledig gefluoreerd polymeer dat een van de meest thermisch stabiele polymeren is. Op basis van de in de literatuur gevonden experimentele gegevens wordt verwacht dat PTFE volledig thermisch zal degraderen bij de minimaal vereiste verbrandingstemperatuur van 850 °C. Echter voor vaste stoffen zoals polymeren zijn de omstandigheden in het verbrandingsbed misschien nog wel belangrijker dan de temperatuur in de verbrandingskamer. De verblijftijd en menging van het verbrandingsbed op het rooster moeten voldoende zijn om vaste stoffen te laten uitbranden, dat wil zeggen thermisch af te laten breken tot kleinere vluchtige componenten die vervolgens in de verbrandingskamer worden verbrand. PTFE als zodanig zal niet vervluchtigen en vervolgens worden verbrand in de verbrandingskamer. Bij de heersende temperaturen in het verbrandingsbed van tussen de 900 en 1100 °C, wordt verwacht dat PTFE en andere gefluoreerde polymeren volledig zullen afbreken tot kleine fluorkoolstofvebindingen.

Voor andere dan de eerder genoemde verbrandingsbijproducten, zoals gefluoreerde dioxinen en furanen en perfluorazijnzuur, wordt de vorming onwaarschijnlijk geacht. De vorming van gefluoreerde dioxinen en furanen kan echter niet volledig worden uitgesloten vanwege de mogelijke vorming van gefluoreerde benzenen onder ongunstige verbrandingsomstandigheden. Gefluoreerde benzenen zouden kunnen dienen als voorlopers voor de vorming van gefluoreerde dioxinen en furanen. Al met al wordt de vorming van gefluoreerde dioxinen en furanen niet verwacht, mede omdat deze bij metingen die verricht zijn naar hun voorkomen niet zijn aangetoond.

Uit de kwalitatieve beoordeling van het verwijderingsrendement in de rookgasbehandeling en het CO_2-winningsproces wordt voor de beschouwde PFAS’en geconcludeerd dat:

1. de soorten PFAS’en met de grootste kans om ongehinderd door het rookgasbehandelingssysteem te gaan zijn: jodiumhoudende PFAS’en , fluortelomere olefinen (FTO's), de perfluoralkanen (PFC's), de fluortelomeeralcoholen met een korte geperfluoreerde keten van drie tot vijf gefluoreerde koolstofatomen (3-5:2 FTOH) en de fluortelomeeracrylaten (FTAC's). Ten minste, als deze verbindingen het verbrandingsproces zouden overleven. Van jodiumhoudende perfluorverbindingen wordt bijvoorbeeld verwacht dat ze het minst thermisch stabiel zijn van de bekeken perfluorverbindingen. Het is voor deze verbindingen het meest onwaarschijnlijk dat ze het verbrandingsproces zullen overleven;
2. door de fysische en chemische processen in de CO_2-winningsinstallatie is het de verwachting dat de meeste van de

> beschouwde PFAS’en niet of nauwelijks in de gewonnen CO_2 terecht zullen komen. Van de beschouwde stoffen zijn de PFAS’en met de grootste kans om in de gewonnen CO_2-stroom terecht te komen niet-dissociërende stoffen met een polair karakter, zoals fluortelomeeralcoholen met een korte perfluorketen en de groep van gesubstitueerde perfluorsulfonamido-ethanolen (MeFASE's en EtFASE's).

Deze conclusies zijn grotendeels gebaseerd op gepubliceerde laboratoriumexperimenten en kwalitatieve theoretische beoordelingen. Uit gepubliceerde gegevens van praktijkmetingen blijkt dat verschillende PFAS’en worden aangetroffen in de rookgassen en verbrandingsresten zoals bodemas en vliegas. De totale PFAS concentratie in het rookgas na de rookgasreiniging is ongeveer 20 $ng.m^{-3}$. Voor zover bekend zijn er geen metingen gedaan naar de aanwezigheid van PFAS’en in gewonnen CO_2.

Uit de literatuurstudie blijkt verder dat er nog geen gestandaardiseerde methoden beschikbaar zijn om de emissieconcentratie van PFAS’en in de rookgassen van afvalverbrandingsinstallaties te meten. Het zou echter technisch mogelijk moeten zijn om verschillende PFAS’en zoals gasvormige, polaire, wateroplosbare, aan stof gebonden en stofgebaseerde (aerosolen) PFAS’en in de rookgassen te bemonsteren.

Bij het nemen van monsters is het gebruikelijk om een reeks filters, adsorptiekolommen en impinger-absorptievloeistoffen te gebruiken die in serie zijn geschakeld. De opgevangen filters, adsorptiekolommen en impingervloeistoffen kunnen na monstername chemisch worden geanalyseerd in een geaccrediteerd analytisch laboratorium. Als analytische technieken zijn hiervoor in het bijzonder GC-MS en HPLC-MS/MS geschikt. De GC-MS leent zich goed voor het meten van gasvormige en niet-polaire tot licht-polaire PFAS’en. De HPLC-MS/MS is daarentegen geschikt voor polaire, dissocieerbare en wateroplosbare PFAS’en. HPLC-MS/MS is geaccepteerd in beschikbare standaardmethoden voor de bepaling van het gehalte aan PFAS’en in bodem, bagger, sediment, grond- en oppervlaktewater.

Een haalbare bepalingsgrenswaarde (LOQ) voor het meten van de emissieconcentratie van PFAS’en in de rookgassen wordt geschat te liggen in een concentratiegebied van 0,1 tot 0,5 $ng.m^{-3}$. Hierbij wordt uitgegaan van een bemonsteringsvolume van circa vier kubieke meter van de rookgassen.

De voorgeschreven meetmethode voor fluoride in rookgas (NEN-ISO 15713) mag niet worden beschouwd als een geschikte of vervangende methode voor PFAS’en. De LOQ van het fluoride is een factor duizend hoger dan de LOQ van een meetmethode ter bepaling van individuele PFAS’en. Verder is de fluoridemeting niet selectief voor de som van PFAS’en.

De totale organische fluor (TOF) -meting lijkt voor een indicatie een betere meetmethode te zijn, aangezien de som van PFAS’en onderdeel is van de TOF. Met andere woorden als er geen TOF wordt aangetoond dan is er ook geen PFAS. Echter, de haalbare LOQ wordt verwacht te liggen in een concentratiegebied tussen 50 en 250 ng.m^{-3}, waardoor deze methode minder geschikt is om de som van PFAS'en in de rookgassen aan te tonen.

Wat betreft de te verwachten concentratie PFAS in de uit rookgassen gewonnen CO_2 wordt geschat dat deze in de orde van 10 ng.m^{-3} ligt. De totale gemeten PFAS concentratie in rookgas is ongeveer 20 ng.m^{-3}. Aan de andere kant wordt verwacht dat de concentratie aanzienlijk zal afnemen tijdens het CO_2-winningsproces.

Aanbevelingen
Om te achterhalen of PFAS'en aanwezig zijn in de gewonnen CO_2 en in welke hoeveelheden ze aanwezig zijn, moeten metingen worden uitgevoerd. Voor een compleet beeld is het aan te raden om aanvullend te gaan meten in zowel rookgassen als vliegassen van de verbrandingsinstallatie. Naast de in het Tijdelijk Handelingskader aanbevolen standaardset van PFAS'en die in het milieu worden gemeten, wordt aanbevolen om die PFAS'en op te nemen die in dit onderzoek naar voren zijn gekomen. Het gaat dan vooral om die PFAS'en waarvoor het waarschijnlijk is dat ze het verbrandingsproces zullen overleven of worden gevormd in het verbrandingsproces, niet door de rookgasbehandeling worden afgevangen of waarvoor het waarschijnlijk is dat ze in de gewonnen CO_2 terecht kunnen komen. Deze omvatten perfluorkoolstoffen met een korte keten, fluortelomeeralcoholen en acrylaten en gesubstitueerde perfluorsulfonamido-ethanolen.

Het valt niet uit te sluiten dat het verschil in de prestaties van de PFAS-emissiemetingen van de rookgassen van afvalverbrandingsinstallaties wordt veroorzaakt door verschillen in de methoden en laboratoriuminstrumenten die worden gebruikt voor monstername, monstervoorbehandeling en meting. Deze factoren kunnen de verschillen in de bepaalbaarheidsgrens tot een factor van duizend verklaren. Het is daarom essentieel om te komen tot een standaardisatie van de meetmethoden inclusief de bemonstering en de analysetechnieken

Slotsom
Op basis van een overzicht van de wetenschappelijke literatuur en de theorie over verbrandingsprocessen en rookgasreinigingstechnieken concludeert het RIVM dat:

- PFAS'en, aanwezig in het huishoudelijk, stedelijk en industrieel afval, tot andere stoffen afbreken bij de verbranding van dit afval onder verbrandingscondities die voldoen aan de wettelijke eisen voor afvalverbrandingsinstallaties in Nederland.
- tegelijkertijd een nieuwe PFAS-groep wordt gevormd die sterke broeikasgassen zijn zoals perfluormethaan en perfluorethaan.
- enkele publicaties over metingen in de schoorsteen van een afvalverbrandingsinstallatie niet uitsluiten dat er toch nog PFAS'en in de rookgassen kunnen zitten en ze daardoor kunnen worden geëmitteerd.

De PFAS’en die nog overblijven worden naar verwachting tijdens de winning van de koolstofdioxide verwijderd.

Vanwege het ontbreken van voldoende nauwkeurige PFAS metingen is het onzeker wat de samenstelling en de hoeveelheid van PFAS’en in de gereinigde rookgassen en de daaruit gewonnen koolstofdioxide is. Gezien de toepassing vindt het RIVM het wenselijk dat zowel in koolstofdioxide als gereinigde rookgas wordt gemeten om de aanwezigheid van de PFAS’en te kunnen vaststellen. De risico’s van de verspreiding van PFAS’en kunnen dan beter in beeld komen. Dit risico betreft zowel de rookgasemissie uit de schoorsteen als de toepassingen van de uit de rookgassen gewonnen koolstofdioxide zoals de inzet van een groeiverbeteraar in de glastuinbouw.

Verder verdient het aanbeveling nader onderzoek te doen naar de verdere verspreiding van PFAS’en via de afvalstromen van de vuilverbranding, zoals bodemas, vliegas en afvalwater.

1 Introduction

1.1 Background, issue and questioning

In the Netherlands there are 13 waste incineration plants spread across the country that receive and incinerate different types of waste. In addition to household waste, municipal waste and non-hazardous industrial waste, some plants process hazardous waste. According to the latest reported annual figures, a total of approximately 7.5 million tons of waste was incinerated in the Netherlands in 2018 (Rijkswaterstaat, 2020a).

In the period 1989 to 1995 the waste incineration plants were negatively reported by the media. The measurements of the National Institute for Public Health and Environment (RIVM) conducted in the context of the monitoring programme for food products revealed that the milk of cows feeding on grassland in the vicinity of the waste incinerators contained high levels of dioxins. It became clear that the waste incinerators were the main source of dioxin contamination. As a result, measures were taken to significantly reduce dioxin emissions by applying improvements in combustion conditions and flue gas cleaning. Outdated waste incinerators were taken out of production (Slob et al., 1993).

Waste incineration plants are licensed in accordance with the Dutch Activities Decree and must use the best available techniques (Infomil, 2020). Article 5.19 of the Decree sets emission limit values for various harmful substances in flue gases. The Decree is an implementation of the European Directive 2010/75/EU on industrial emissions (EURLEX, 2010).

Despite the successful reduction in emissions of dioxins and related compounds, there is a new gap in knowledge with respect to whether waste incinerators emit per- and polyfluoroalkyl substances (PFASs) via their flue gases and possibly contribute to the PFAS contamination of the environment.

Waste incinerators burn significant amounts of synthetic materials that also contain fluoropolymers and non-polymer per- and polyfluoroalkyl substances. In the Netherlands, 33% residual municipal solid waste, excluding paper, consists of synthetic materials, including textiles, plastics, electronics, rubber and carpet (Janmaat, 2020). PFASs are known for their persistence, human toxicity and thermal stability. Until recently little has been known about the extent to which flue gases from waste incinerators contain PFASs. In addition to their possible presence in flue gases, PFASs can occur in slag and in bottom and fly ashes, which remain as residues after the incineration of waste. Depending on the method of storage, as well as of the transport and processing of these incineration by-products into useful applications such as building materials, there may be a risk of PFAS spreading. It is important to know to what extent PFASs can be expected in bottom and fly ashes and whether there is a risk of their spreading to the environment.

PFASs can also be expected in the waste water from waste incinerators and therefore to constitute a source of emissions. Waste water is generated, for example, when water is used in flue gas scrubbing to remove acidic components from the flue gases.

In the context of the third National Waste Management Plan (LAP3), in which the Dutch policy framework for the prevention and management of waste was established, waste processing companies are encouraged by the national government to implement innovations for waste recycling in their processes (Rijkswaterstaat, 2020b). The recovery of the greenhouse gas carbon dioxide (CO_2) from flue gases is an example of this. The Dutch policy for the prevention and management of waste is based on the waste hierarchy, which, from highest to lowest, is:

- to limit or prevent the production of waste materials
- to prepare waste for reuse;
- to recycle materials from waste for their original function or equivalent;
- to recycle materials from waste for another function;
- to chemically recycle waste materials into raw materials for making new products;
- to treat waste for another useful application, including incineration with energy recovery;
- to remove waste by incineration;
- to landfill or discharge waste.

An important emphasis is placed in the LAP3 on the pursuit of waste management that is part of a transition to a circular economy. At the same time, a specific policy line has been drawn for the handling of waste containing substances of very high concern (SVHC). The transition to a circular economy therefore requires a responsible balance in waste management on the one hand and efforts that are necessary to keep SVHC out of our living environment as much as possible.

Some waste incinerator companies in the Netherlands recover the CO_2 in flue gases and make it suitable for different applications in the market, e.g. as a growth enhancer in the cultivation of crops for human consumption.

A schematic overview of the issue of the circular economy, waste handling and circulation of SVHC such as some individual substances within the group of PFASs is presented in Figure *1*. The focus in this scheme is on material circulation and the adjoining circulation of chemicals. The issue that is dealt with in this report is the useful application of the waste treatment side stream to growing crops, resulting in possible human exposure via food consumption (represented by the Waste Management stage in Figure *1*).

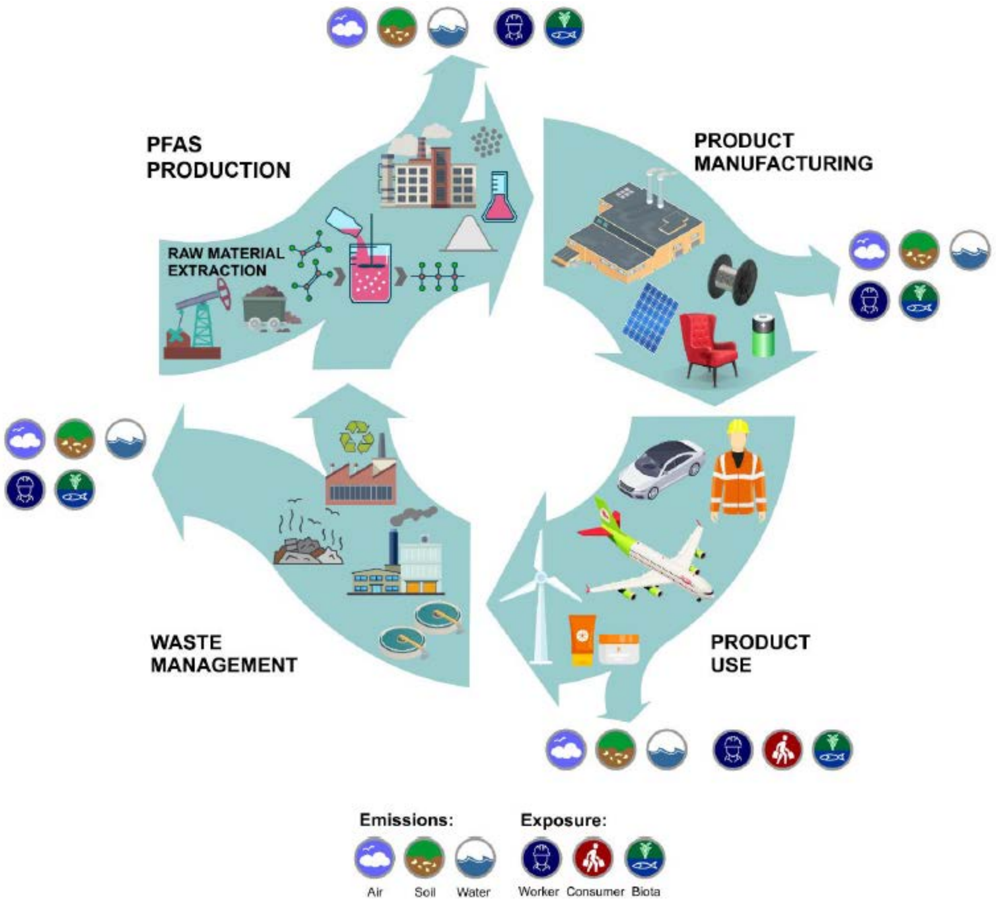

Figure 1 Emissions of and exposure to PFASs during their whole life cycle, including the waste management stage, in a circular economy.
Source: EEA-ETC report, Systemic view on fluorinated polymers, forthcoming 2020, as cited in EC (2020).

Crucially, the company that produces and supplies the CO_2 should provide sufficient evidence that its quality is such that its application will be safe. For this purpose, the company can submit a request to Rijkswaterstaat (RWS), an executive organisation of the Ministry of Infrastructure and Water Management, for a substantiated analysis confirming that the CO_2 is safe to use and that the product meets the end-of-waste criteria as set out in Article 6 of the European Waste Framework Directive 2008/98/EG (EURLEX, 2008). Whether or not PFASs can occur in flue gases is of importance to the question of whether PFASs can also be expected to be present as contaminants in the recovered CO_2. This knowledge can then be used to judge whether new applications of the recovered CO_2 from waste incinerator flue gases fulfil the legally required ‘end-of-waste-criteria’.

Against this background, RWS has commissioned RIVM to answer the following research questions on the basis of a literature study:

1. What is the precise definition of a PFAS and what connection is there between the advice list of individual PFASs in the Temporary Action Framework and that in the Knowledge Document of the Expertise Centre PFAS?

2. Can PFASs be present in the flue gases of a waste incinerator as a result of not breaking down (completely)?
3. Can PFASs (not broken down or broken down to smaller molecules) be captured in the flue gases after one or more cleaning steps?
4. Can PFASs (partly depending on the answers to questions 2 and 3 above) be present in the carbon dioxide recovered from the waste incinerator flue gases?
5. Is the chemical analysis of fluoride sufficiently accurate to reveal the presence of PFASs in flue gases and carbon dioxide?
6. Can RIVM advise on the possible presence of PFASs in the carbon dioxide that is recovered from waste incinerator flue gases for applications such as growth improver in greenhouse horticulture?

1.2 Objective

RWS is seeking to gain more insight into the behaviour of PFASs and the incineration of waste materials that contain or may contain these substances or their precursors. Attention is focused on the presence of PFASs in flue gases and the extent to which PFASs may be present in the CO_2 recovered from the flue gases. With this insight, RWS will be better able to provide legal judgments about the useful application of recovered CO_2 from the flue gases of waste incinerators.

The literature study should also generate more knowledge about the possible formation of PFASs and their emissions when household, industrial, municipal and hazardous waste are incinerated. This knowledge will provide a scientific basis for advising the national and regional policy and enforcement authorities on topics such SVHC, waste management, licensing, sustainability, risk assessment and circularity.

1.3 Literature study

RIVM has searched for information in its own library catalogue of publications and reports, in scientific publications of bibliographic literature databases such as Scopus, Pubchem, HSDSB and Google Scholar and from relevant internet pages. The following keywords have been used in this search:

- PFAS;
- incineration plants;
- air emissions;
- pyrolysis;
- thermolysis;
- combustion;
- incinerability;
- emission measurements;
- flue gas cleaning;
- fluorinated chemicals, compounds;
- waste.

1.4 Reader’s guide

The report starts with an extensive explanation of the definition of PFASs as defined in scientific publications, by different institutes and in various environmental policy contexts (Chapter 2). Characteristic main and subgroups are mentioned and distinguished within the PFAS group.

Chapter 3 examines the processes and techniques of burning waste and flue gas cleaning at waste incinerators. The chapter explains, among other things, different types of furnaces and provides information on typical incineration temperatures.

Chapter 4 deals with the chemical changes to PFASs that potentially occur in waste during combustion in relation to the incineration conditions. The chapter gives examples of possible PFAS combustion products.

Chapter 5 describes the processes and techniques of flue gas cleaning at waste incinerators and the behaviour of PFASs and combustion products during flue gas treatment. The chapter also discusses the availability of measurement methods to identify and quantify the concentrations of PFASs in flue gases and air emissions from those gases. Also presented in this chapter are the results of measurements of PFASs in flue gas and in fly and bottom ashes and estimates of the emissions from waste incinerators to air.

Chapter 6 elaborates on the technique of CO_2 recovery from flue gases and discusses whether PFASs can be expected to be removed during this production process or may still be present in the CO_2 that is recovered.

The final chapter concludes with answers to the study questions regarding the presence of PFASs before and after the cleaning of flue gases in a waste incinerator and the presence of PFASs in recovered CO_2.

2 General information on PFASs

In this chapter a general introduction will be provided on the definitions of PFASs that are currently used worldwide by different institutes and in various environmental policy contexts.

In addition, two ‘advice lists’ of PFASs to be measured in soil and sediment are discussed. These aim to facilitate the management of PFASs in soil and sediment and are discussed to determine their relevance for assessing the risk of PFASs in incineration gases later in this report.

2.1 Terminology and definitions of PFASs

This section describes which substances are considered to be PFASs, followed by a description of the subgroups of PFASs and relevant terminology.

In its attempt to build a PFAS list, OECD (2018) encountered several limitations in its PFAS definition and in the terminology recommended by Buck et al. (2011). Recently, OECD published a more inclusive description of the definition and terminology of PFASs (OECD, 2021).

In this OECD document PFASs are defined as fluorinated substances that contain at least one fully fluorinated methyl or methylene carbon atom (without any H/Cl/Br/I atom attached to it). In other words, with a few noted exceptions, any chemical with at least a perfluorinated methyl group ($-CF_3$) or a perfluorinated methylene group ($-CF_2-$) is considered a PFAS.

As a work in progress relevant to the definition of PFASs the REACH restriction proposal on PFASs should be noted. The Netherlands is working with Denmark, Germany, Norway and Sweden on a proposal for a European restriction on the use of PFASs. In this a clear definition of the PFASs to be restricted will be developed.

In this report we will consider a compound with at least one CF_2 moiety (i.e. $-C_nF_{2n}-$, $n \geq 1$) as a PFAS. This broad definition is chosen to ensure inclusion of the recent OECD definitions and the definition under consideration in the ongoing work on the REACH restriction proposal.[1]

In the sections below, the main non-polymeric and polymeric PFAS groups mentioned by Buck et al. (2011) and OECD (2021) are summarised.

Both non-polymeric and polymeric PFAS may be incinerated when discarded as waste, and are therefore relevant for the emission of PFASs from incineration plants.

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[1] ECHA/NR/20/13, Call for evidence. https://echa.europa.eu/nl/-/five-european-states-call-for-evidence-on-broad-pfas-restriction and https://www.reach-clp-biozid-helpdesk.de/SharedDocs/Downloads/DE/REACH/Verfahren/PFAS_RMOA_Supplementary_document.html

2.1.1 *Non-polymeric PFASs*

Within the non-polymeric PFAS group, 10 subgroups are defined by Buck et al. (2011):

- (aliphatic) perfluorocarbons (PFCs);
- perfluoroalkyl acids (PFAAs);
- perfluoroalkane sulphonyl fluorides (PASFs);
- perfluoroalkane sulphonamides (FASAs);
- perfluoroalkyl iodides (PFAIs);
- perfluoroalkyl aldehydes (PFALs) and aldehyde hydrates ($PFAL·H_2O$);
- perfluoroalkanoyl fluorides (PAFs);
- perfluoroalkane sulphonamido derivatives;
- fluorotelomer (FT)-based compounds, including semifluorinated n-alkanes (SFAs) and alkenes (SFAenes);
- per- and polyfluoroalkyl ether carboxylic acids (PFECAs).[2]

In OECD (2021) many more subgroups are added to these (see Figure 2). These subgroups are categorised into four main groups:

- perfluoroalkyl acids (PFAAs) including perfluoroalkylether acids (PFEAAs or PFAEs);
- polyfluoroalkyl acids and polyfluoroalkylether acids;
- PFAA precursors;
- other PFASs.

The per- and polyalkyl acid groups are also considered to cover per- and polyfluoroalkylether acids (Figure 2), i.e. those acids in which the acidic functional group(s) is directly connected to a per- or polyfluoroalkylether chain. Other PFAE- and all PASF- and PFAI-related substances were designated as PFAA precursors, i.e. substances that may be transformed into PFAAs, e.g. by (microbial) degradation, incineration or metabolism (Figure 2).

(Linear) PFCs (C_nF_{2n+2}), also known as greenhouse gases and notorious for their high global warming potential when gaseous, are considered as PFASs by Buck et al. (2011): 'Those PFCs that contain a $–C_nF_{2n+1}$ moiety are, by definition, members of the PFAS family'. However, Buck et al. also state that PFCs are chemically very stable substances, and it is uncertain whether any of them can actually degrade in the environment to give functionalised PFASs.

In Figure 2 OECD (2021) included PFCs in the group of 'other PFASs' as perfluoroalkanes.

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[2] Abbreviation not mentioned by Buck (2011), but by OECD (2015).

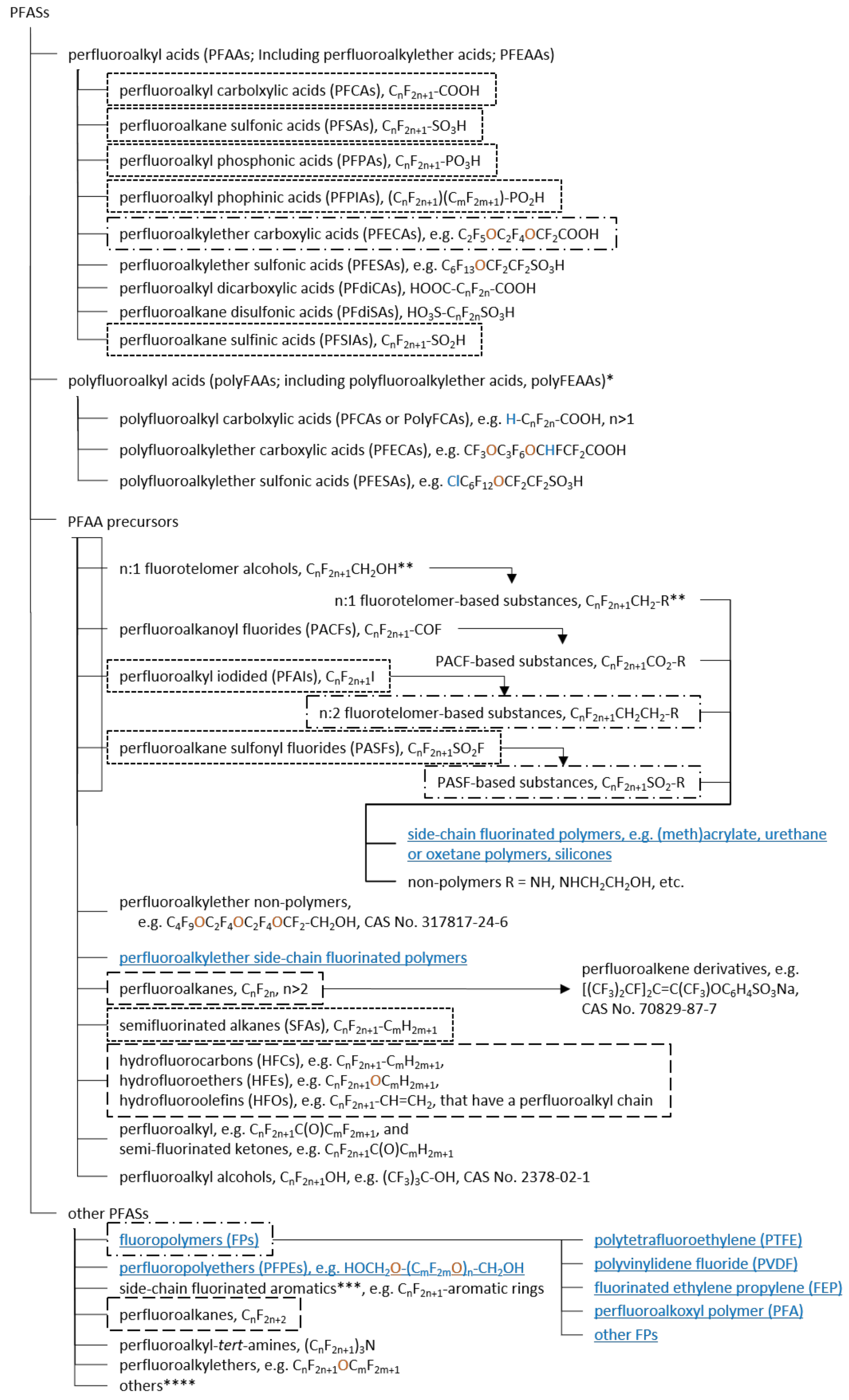

Figure 2 see next page for description of this figure.
Figure 2 cont.: A comprehensive overview of PFAS groups, their structural traits, examples and notes on whether corresponding common nomenclatures (including acronyms). Adapted from OECD (2021). Dotted box: Nomenclature

including acronyms well covered by Buck et al. (2011). Dash-dot box: Nomenclature including acronyms partially covered by Buck et al. (2011). Dashed box: Common nomenclature including acronyms exist. Arrows (→) indicate that it is a synthesis pathway, instead of examples. Blue underlined text indicates polymeric PFASs. Note that this figure is intended to be comprehensive, but not exhaustive; in other words, there are other groups of PFASs that are not captured in this figure.
** It is recommended that polyfluoroalkyl acids use the acronym PolyFAA to better distinguish from perfluoroalkyl acids.*
*** Strictly speaking, these substances are not fluorotelomers, as they are not derived from the telomerization process. Despite this, they are termed here "n:1 fluorotelomer-based" substances for readability.*
**** Depending on the type of linkages between fluorinated side chain(s) and aromatic ring(s), some side-chain fluorinated aromatics may act as precursors to PFAAs or PFEAAs*
***** Depending on the molecule structure, one may belong to PFAAs, PolyFAAs, PFAA precursors, or other groups that are not described here.*

2.1.2 Polymeric PFASs

According to Buck et al. (2011), the polymers considered as PFASs are: (1) those whose synthesis involves the incorporation of one or more PFASs as monomers; or (2) those whose manufacture requires the use of a PFASs as a production aid (Buck et al., 2011).
Within the group of polymeric PFASs, Buck et al. (2011) and OECD (2021) differentiate between (see Figure 2, blue text):

- Fluoropolymers: fluorinated polymers consisting of carbon-only backbone with fluorine atoms directly attached to this backbone. These fluoropolymers are synthesised from the following monomers or other starting substances e.g.:
  - polytetrafluoroethylene (PTFE);
  - polyvinylidene fluoride (PVDF);
  - fluorinated ethylene propylene (FEP);
  - perfluoroalkoxyl polymer (PFA);
  - other fluoroplymers.
- Side-chain fluorinated polymers: fluorinated polymers consisting of variable compositions of non-fluorinated carbon backbones with polyfluoroalkyl (and possibly perfluoroalkyl) side chains. The fluorinated side chains, including PASF- and fluorotelomer-based derivatives, are potential precursors of PFAAs (Liu and Mejia Avendano 2013). The following three side-chain polymers are mentioned:
  - fluorinated (meth)acrylate polymers;
  - fluorinated urethane polymers;
  - fluorinated oxetane polymers.
- Perfluoropolyethers (PFPEs): fluorinated polymers consisting of backbones containing carbon and oxygen with fluorines directly attached to carbon. They are not made from PFAAs or their potential precursors; and PFAAs or their potential precursors are not involved in the manufacturing of perfluoropolyethers.

2.2 Current advices on PFASs to be analysed in soil and water

In the next two sections (2.2.1 and 2.2.2) two Action Frameworks are discussed. It should be noted that the legal status of these frameworks differs. The Temporary Action Framework (Dutch: Tijdelijk

Handelingskader; 2.2.1) is an initiative of the Dutch Ministry of Infrastructure and Water Management and will eventually be incorporated into the existing Soil Quality Regulation. Because of the duty to prevent the spread of polluted soil and sediment, this Temporary Action Framework can already be used in anticipation of the amendment to the Soil Quality Regulation.

In contrast, the Knowledge Document and Action Framework of the Expertise Centre PFAS (Dutch: Expertisecentrum PFAS; Section 2.2.2) does not have a legal basis, but is intended as a practical and implementation-oriented framework that can help governments to develop policy, start research, interpret measurement data and determine the next steps in these areas. In addition, it should be noted that the documents discussed in this section date from before the most recent information on background values of PFASs in Dutch soil (Wintersen et al., 2020) became available.

2.2.1 *Temporary Action Framework (Dutch: Tijdelijk Handelingskader)*

PFASs are diffusely present in soil and sediments in the Netherlands and Europe and are found in many places at levels above the detection limit. As a result, the re-use of soil and dredged material stagnated. The Temporary Action Framework[3] published by the Dutch Ministry of Infrastructure and Water Management aims to eliminate this stagnation where possible, while at the same time applying the basic principle that risks to health and the environment and the spread of PFAS-containing soil and dredged material to areas that are not contaminated or contaminated to a lesser extend are prevented. The Action Framework is deemed temporary because it will eventually be implemented in the Dutch national Soil Quality Regulation (Dutch: Besluit bodemkwaliteit). The Temporary Action Framework considers only the reuse of PFAS-containing soil and dredging sludge and their application on dry land (soil) and in water. In addition, options for storing, cleaning and dumping soil and dredged material containing PFASs, including the acceptance options for the national dredging dumps, are described.

When analysing PFASs in soil and dredged material, the Temporary Action Framework recommends using the advisory list[4] of PFASs, version 12 (July 2019). If, on the basis of preliminary research, it is expected that PFASs other than those included in this advisory list may also occur in soil or dredged material, for example in the case of a point source, then the list of PFASs must be expanded to include the specific PFAS(s). It has been established that PFOS and PFOA are found diffusely throughout the Netherlands (and Western Europe) (Wintersen et al., 2020). These substances (both linear and branched) must therefore always be analysed.

The present advisory list of 30 substances (Table 1) is based on preliminary results showing that these PFASs occur diffusely in (aquatic) soil and sediment in the Netherlands. When determining the definitive

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[3] https://www.bodemplus.nl/onderwerpen/wet-regelgeving/bbk/grond-bagger/handelingskader-pfas/tijdelijk/

[4] https://www.bodemplus.nl/onderwerpen/wet-regelgeving/bbk/vragen/grond-baggerspecie-pfas-veldwerk-analyse-toetsing/faq/welke-pfas-verbindingen-geanalyseerd/

Action Framework, or as soon as possible on the basis of research results, it will be checked whether the advice list needs to be adjusted.

HFPO-DA (a GenX compound, Table 2) has mainly been found in the vicinity of locations where HFPO-DA is produced or discharged. In areas where no direct source or discharge has taken place there is therefore no need to measure HFPO-DA. There are indications that HFPO-DA occurs on more locations in the (aquatic) soil than expected. Some (Dutch) competent authorities therefore make the analysis of HFPO-DA mandatory in certain areas.

Table 1 Advisory list of PFASs to be measured in (aquatic) soil (12 July 2019) according to the Temporary Action Framework published by the Dutch Ministry of Infrastructure and Water Management. PFAS categories can be found in Figure 2

#	Compound	Abbreviation	Formula	CAS number
PFCAs				
1	Perfluorobutanoic acid	PFBA	C4HF7O2	375-22-4
2	Perfluoropentanoic acid	PFPeA	C5HF9O2	2706-90-3
3	Perfluorohexanoic acid	PFHxA	C6HF11O2	307-24-4
4	Perfluoroheptanoic acid	PFHpA	C7HF13O2	375-85-9
5	Perfluorooctanoic acid (linear)	PFOA	C8HF15O2	335-67-1
6	Perfluorooctanoic acid (branched)	PFOA-branched	-	NA
7	Perfluorononaoic acid	PFNA	C9HF17O2	375-95-1
8	Perfluorodecanoic acid	PFDA	C10HF19O2	335-76-2
9	Perfluoroundecanoic acid	PFUnDA	C11HF21O2	2058-94-8
10	Perfluorododecanoic acid	PFDoDA	C12HF23O2	307-06-7
11	Perfluorotridecanoic acid	PFTrDA	C13HF25O2	72629-94-8
12	Perfluorotetranoic acid	PFTeDA	C14HF27O2	376-06-7
13	Perfluorohexadecanoic acid	PFHxDA	C6HF31O2	67905-19-5
14	Perfluorooctadecanoic acid	PFODA	C18HF35O2	16517-11-6
PFSAs				
15	Perfluorobutane sulphonic acid	PFBS	C4HF9O3S	375-73-5
16	Perfluoropentane sulphonic acid	PFPeS	C5HF11O3S	2706-91-4
17	Perfluorohexane sulphonic acid	PFHxS	C6HF13O3S	355-46-4
18	Perfluoroheptane sulphonic acid	PFHpS	C7HF15O3S	375-92-8
19	Perfluorooctane sulphonic acid (linear)	PFOS	C8HF17O3S	1763-23-1
20	Perfluorooctane sulphonic acid (branched)	PFOS-branched	-	NA
21	Perfluorodecane sulphonic acid	PFDS	C10HF21O3S	335-77-3
Fluortelomer sulphonic acids				
22	4:2 fluorotelomer sulphonic acid	4:2 FTS	C6H5F9O3S	757124-72-4
23	6:2 fluorotelomer sulphonic acid	6:2 FTS	C8H5F13O3S	27619-97-2
24	8:2 fluorotelomer sulphonic acid	8:2 FTS	C10H5F17O3S	39108-34-4
25	10:2 fluorotelomer sulphonic acid	10:2 FTS	C12H5F21O3S	120226-60-0
FASA- and PASF-based derivatives				
26	N-methylperfluorooctane sulphonamidoacetic acid	N-MeFOSAA	C11H6F17NO4S	2355-31-9
27	N-ethylperfluorooctane sulphonamidoacetic acid	N-EtFOSAA	C12H8F17NO4S	2991-50-6
28	perfluoro-1-octanesulphonamide	PFOSA	C8H2F17NO2S	754-91-6
29	N-methylperfluorooctanesulphonamide	N-MeFOSA	C9H4F17NO2S	31506-32-8
Fluorotelomer phosphates				
30	8:2 polyfluoroalkyl phosphate diester	8:2 diPAP	C20H9F34O4P	678-41-1

Table 2 PFASs not in advisory list. To be measured when presence is suspected in (aquatic) soil (12 July 2019)

#	Compound	Abbreviation	Formula	CAS number
PFECA and PFAE or PFAA				
31	Hexafluoropropyleneoxide dimer acid	HFPO-DA or FRD-903 (a GenX compound)	C6HF11O3	13252-13-6

2.2.2 *Knowledge Document and Action Framework of Expertise Centre PFAS (Dutch: Kennisdocument en handelingskader van Expertisecentrum PFAS)*

The Expertise Centre PFAS (Dutch: Expertisecentrum PFAS) is a cooperation between the consultancy companies Witteveen + Bos, TTE Consultants and Arcadis. It was established to develop and share knowledge about PFASs.[5]

In June 2018, the Expertise Centre PFAS published two documents providing (local) governments with guidance on how to deal with PFASs in the soil and water (soil, groundwater, sediment and surface water): the PFAS Knowledge Document (Pancras et al., 2018) and the Action Framework PFAS (Slenders et al., 2018) (not to be confused with the Temporary Action Framework of the Dutch government; Section 2.2.1). The documents are intended as a practical and implementation-oriented framework that can help governments to develop policy, start research, interpret measurement data and determine the next steps in these areas. In addition, the documents provide information about the substance group PFAS and explains why these substances deserve attention.

Regarding a list of PFASs to be measured in soil and water, the Expertise Centre PFAS recommends analysing at least the C4–C10 perfluorinated compounds and the precursors 6:2 and 8:2 FTS (Table 3). High concentrations of C11 and C12 PFASs have also been found at some firefighting training sites and fire sites. Supplementing the package of the compounds to be measured can be useful for these sites. Other sources of contamination can also justify the expansion of the analysis package (e.g. GenX substances).

Precursors of PFASs may also be present in soil or water. In the environment, these precursors are degraded or transformed into persistent PFAAs such as PFOS and PFOA. According to the Expertise Centre PFAS, two analysis methods are suitable or can be used to measure precursors:

- total determinations of organically bound fluorine (AOF, PIGE or TOF);
- TOP analysis, in which almost all precursors are broken down into analysable PFASs (PFOS, PFOA and analogous compounds).

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[5] https://www.expertisecentrumpfas.nl/

Table 3 Advisory list of PFASs to be measured in soil and water according to the Expertise Centre PFAS. PFAS categories can be found in Figure 2.

#	Compound	Abbreviation	Chain length
	Perfluorocarboxylic acids	*PFCAs*	
1	Perfluorobutanoic acid	PFBA	4
2	Perfluoropentanoic acid	PFPeA	5
3	Perfluorohexanoic acid	PFHxA	6
4	Perfluoroheptanoic acid	PFHpA	7
5	Perfluorooctanoic acid (linear)	PFOA	8
6	Perfluorononaoic acid	PFNA	9
7	Perfluorodecanoic acid	PFDA	10
	Perfluorosulphonic acids	*PFSAs*	
8	Perfluorobutane sulphonic acid	PFBS	4
9	Perfluoropentane sulphonic acid	PFPeS	5
10	Perfluorohexane sulphonic acid	PFHxS	6
11	Perfluoroheptane sulphonic acid	PFHpS	7
12	Perfluorooctane sulphonic acid (linear)	PFOS	8
13	Perfluorodecane sulphonic acid	PFDS	10
	Precursors		
14	6:2 fluorotelomer sulphonic acid (1H,1H,2H,2H-Perfluoroctaansulphonzuur)	6:2 FTS (H4PFOS)	8
15	8:2 fluorotelomer sulphonic acid (1H,1H,2H,2H-Perfluordecaansulphonzuur)	8:2 FTS	10

2.3 Conclusions

PFASs are divided into two subgroups: non-polymeric and polymeric PFASs. Both of these groups may be present in discarded waste presented for incineration, and are therefore relevant for the emission of PFASs from incineration plants. With regard to the non-polymeric PFAS group, this report focuses on the main PFAS groups as defined by the OECD definition. Ozone-depleting substances matching the broader definition such as chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs) and bromine-containing Halons that are used as refrigerants, blowing agents, aerosol propellants, degreasing agents and fire-suppressing agents are not part of this study. These include the hydrofluorocarbons that do not have ozone-depleting properties but are known to act as greenhouse gases.

The two Action Frameworks discussed above aim to facilitate the management of PFASs in soil, sediment and water. It should be noted that the legal status of the two frameworks differs (Section 2.2). The PFASs that are to be measured and monitored according to these frameworks have been selected on the basis of their occurrence in soil sediment and (surface) water in The Netherlands. All the substances mentioned in the two action frameworks are generally regarded as PFASs according to all available definitions. (Section 2.1).
The listed PFASs are considered relevant when managing contamination in soil and sediment. However, their relevance to assessing the safety of incineration gases may not be sufficient because other PFASs not covered in the lists may be present in flue gases, since the incineration of PFAS-containing waste may produce different PFASs or fluor-containing gases, as will be discussed in the following chapters.

3 Waste incineration

This chapter deals with incineration techniques most commonly used in the Western World – and specifically in the Netherlands – for the treatment of hazardous, household and commercial waste. Specialist incineration techniques for the treatment of hospital waste and highly concentrated chemical waste other than that commonly treated in the post-combustion chamber of rotary kilns are not addressed in this chapter. Other waste-handling techniques, such as landfilling and composting, are also not discussed in this section.

So far, in the Netherlands, CO_2 recovery is carried out only at waste incineration plants that mainly treat biomass and commercial and household waste. Therefore, the most common techniques for incinerating these types of waste are discussed in this chapter. Whether and to what extent PFASs are thermally degraded and end up in recovered CO_2 depends on the process conditions at incineration, the subsequent flue gas cleaning and the CO_2 recovery process. The latter two subjects will be discussed in the following Chapters 5 and 6.

First, an overview is provided of waste incineration techniques in the Netherlands. This is followed by an explanation of the legal requirements relating to operating conditions at waste incineration plants. The most common waste incineration and flue gas treatment techniques will be briefly described in the next section. A more detailed description of the various techniques is included in Annex II. Special attention is paid to process parameters such as temperature, residence time and oxygen content. The physical and chemical techniques used in flue gas treatment, including the process conditions, will be also discussed in this chapter. This information is important in assessing the fate of PFASs at incineration and flue gas treatment, which are described in the following chapters.

Finally some information is included on the residues generated at waste incineration, the focus of this report being on the generated flue gas that serves as a source of CO_2 but which can also contain PFASs. Besides flue gases being a possible emission source of PFASs, residues such as fly ash and bottom ash might also contain PFASs and thus are also a potential source of emissions into the environment.

3.1 Waste incineration processes/installations

3.1.1 *Introduction*

There are various ways of treating waste streams, such as chemical treatment, physicochemical and biological treatment. Residues resulting from these treatment processes must be treated in a subsequent process such as incineration or need to be disposed of through landfilling or can be utilised directly in various applications. Besides landfilling, incineration is one of the most widely used waste treatment steps.

There are three main waste incineration processes, used for different types of waste. Household and related commercial waste is usually treated in waste incineration plants using grate kilns. For sewage sludge, fluidised bed firing is usually applied. However, sewage sludge can be combined with household waste for grate firing (Thomé-Kozminesky et al., 2012) and industrial or commercial waste can also be co-incinerated with dewatered sewage sludge in fluidised bed incinerators (Indaver, 2020). In some countries, including Japan and Sweden, fluidised bed furnaces are also used solely for processing municipal solid waste (Thomé-Kozminesky et al., 2012). Industrial and hazardous wastes are generally processed in rotary kiln ovens. Cement kilns are a type of rotary kiln in which certain types of waste such as rubber tyres are burned. However, in this document we do not include cement kilns when referring to rotary kilns. The types of waste treated in rotary kilns include solid and liquid residues containing organic matter from industrial production processes that cannot be reclaimed by physicochemical treatment. This group of wastes includes oils, greases, tars, paste-like and liquid residues (Thomé-Kozminesky et al., 2012). Organic liquid wastes are usually injected into and burned in the post-combustion chamber of a rotary kiln. If other methods fail or prove to be expensive, waste water can be treated by combustion of the organic constituents. Waste water can either be treated in specialised installations or be injected into the post-combustion chamber of a rotary kiln along with other liquid waste. Wastewater can also be incinerated in fluidised bed furnaces, though it often requires supplementary firing.

3.1.2 *Waste incineration in the Netherlands*

An overview of municipal solid waste incineration facilities in the Netherlands, 13 in total, is provided in Annex I, which also lists the facilities used for the combustion of waste water treatment sludges and those used for treating highly contagious hospital waste. All municipal and commercial solid waste incinerators in the Netherlands are moving-grate kilns. Some of them also process a small amount of hazardous waste (Rijkswaterstaat, 2020a; Agentschap NL, 2011). The only rotary kiln incinerator operating in the Netherlands was officially closed in 2005 (VROM-inspectie, 2006). From that year on, hazardous waste was mainly exported to surrounding countries like Belgium and Germany to be treated accordingly, mainly in rotary kilns. Currently, some hazardous waste is treated in moving-grate furnaces in the Netherlands though. To meet the legal obligations for hazardous waste incineration, specific requirements have been set for instance to the caloric value of the waste and deployment of auxiliary burners in order to reach the required minimum combustion temperature of 1100 °C in such installations. The facilities where hazardous waste is co-incinerated are EEW in Delfzijl, ARN at Weurt, AEB in Amsterdam and the AVR Rozenburg/Rotterdam-Botlek (Agentschap NL, 2011; STOWA, 2005). Annex I also contains information on the registered average and maximum combustion temperatures of the incineration plants during normal operation, types of ovens, number of incineration lines, types of waste burned, and company name and location.

In the Netherlands, there are currently three facilities using fluidised bed incinerators. Two of these are used for the combustion of sludges (Agentschap NL, 2011; STOWA, 2005). The sludges include sewage water treatment sludge and sludge from industrial waste water treatment plants. The fluidised bed incinerator at Duiven processes paper pulp from the paper industry. Part of the generated sludges are also co-fired in power stations, in the cement industry (ENCI) or in municipal solid waste incinerators (Rijkswaterstaat, 2020a; STOWA, 2005). As far as is known, none of the sludge incineration facilities processes solid municipal or commercial waste. The company EEW has advanced plans to build a sludge incineration installation next to their existing municipal solid waste incinerating lines at their site in Delfzijl.

Highly contagious hospital waste is thermally converted at the Zavin facility in Dordrecht. Zavin's two-stage incinerator consists of a moving-floor gasification section and a combustion chamber or afterburner (Zavin, 2021).

The company AVR-Afvalverwerking B.V. (AVR) at Moerdijk operates Vortex ovens in which industrial aqueous hazardous waste and high caloric petrochemical waste are incinerated.

With respect to CO_2 recovered from waste incineration flue gases in the Netherlands, there are currently two sites: AVR in Duiven and Twence in Hengelo. AVR is currently conducting a feasibility study to extract CO_2 from flue gases at its Rozenburg facility.

3.1.3 *Legal requirements in the EU*

According to Article 50 of the Industrial Emissions Directive 2010/75/EU, waste incineration plants must be designed to ensure that flue gases reach a temperature of at least 850 °C for at least 2 seconds in order to ensure the proper breakdown of toxic organic substances. The temperature should be measured near the inner wall of the combustion chamber after the last injection of air. In order to comply with this requirement at all times, it is necessary to install back-up auxiliary burners (often fueled by oil), which are fired into the boiler when the heating value of the waste is insufficient to reach this temperature. When hazardous waste containing more than 1% halogenated hydrocarbons is incinerated in a hazardous waste incinerator, the required temperature is at least 1100 °C. Incinerators are specifically designed and operated to meet these minimum conditions. By ensuring that the combustion gases are maintained at a minimum temperature for a minimum residence time at a minimum oxygen level, a good burnout of the combustion gases will be achieved.

In addition, the Directive requires the installation of measurement systems to monitor the temperature and oxygen level., Also relevant emissions to air and to water must be measured periodically and reported. Achieving the required residence time mainly is a matter of design of the incinerator. The residence time is determined by, among other things, the dimension of the post-combustion chamber, the secondary air flow rate, the number and position of the injection points and the temperature. These should be optimised to ensure the required residence time is achieved (Neuwahl et al., 2019). The residence time usually needs to be demonstrated during plant commissioning or licensing trials (Ellison and Hayes, 1997). Verification of the residence time is usually made indirectly by monitoring the appropriate parameters (Neuwahl et al., 2019).

In the following sections, the above-mentioned three main types of waste incineration installation will be described in more detail, with special attention to the typical operating temperatures. Section 3.2 will focus on the residues from waste combustion and the treatment of the exhaust gases.

3.1.4 *Description of waste incineration installations and the combustion temperatures*

Fluidised bed furnaces
Fluidised bed incinerators are widely applied to the incineration of finely divided waste with a relatively high water or liquid content, such as waste water treatment sludges and industrial sludges.

The fluidised bed furnace is a lined combustion chamber in the form of a vertical cylinder. In the combustion chamber, a sand bed on a grate or distribution plate is fluidised with air. The waste is continuously fed into the fluidised sand bed from the top or side. The temperature in the space above the bed is generally between 850 °C and 950 °C and the bed itself has a lower temperature, e.g. around 650 °C. Maximum operation temperatures are about 1200 °C. Additional information on fluidised bed furnaces and a schematic representation of a fluidised bed incinerator including flue gas treatment is provided in Annex II.1.

Rotary kilns
A rotary kiln consists of a cylinder inclined in the transport direction. The interior of the cylinder can be up to 20% filled with waste, which forms a moving bed. Rotation of the furnace turns over the contents and causes them to move toward the lower end. The rotary kiln is very versatile with respect to the type of waste that can be processed in it, ranging from solid materials to paste-like and viscous matter to contaminated liquids that are injected through simple burners in the combustion chamber (Thomé-Kozminesky et al., 2012).

The mean combustion temperature in the furnace is between 800 and 1400 °C, and residence times of the moving bed are ca. 60 min. Afterburning in a post-combustion chamber is provided to ensure complete burning of the combustion gases. The temperature in the post-combustion chamber typically varies between 900 and 1200 °C.

Additional information and a schematic representation of a rotary kiln incinerator including flue gas treatment is provided in Annex II.2.

Grate-fired furnaces
The typical incineration plant for municipal solid waste consists of a moving grate. It is the most widely used process for the thermal treatment of waste. In a moving grate-fired incinerator the grate conveys the waste in a horizontal or inclined direction towards the end of the combustion chamber. Secondary air is injected into the combustion space above the grate through nozzles to ensure complete combustion of the gases. Intensive mixing of the combustion gases should prevent the bypassing of unburned gases (Thomé-Kozminesky et al., 2012).

The maximum temperature in the fuel bed is reached at the end of the ignition zone. Here the temperature in the bed as well as that of the flue gas is about 900 to 1100 °C. After the addition of secondary air to the combustion chamber, the temperature of the flue gas lies in the range of 900–1050 °C (Gehrmann et al., 2013).

Additional information and a schematic representation of grate-fired furnaces including flue gas treatment is provided in Annex II.3.

Appendix I contains the recorded average and maximum incineration temperatures of the municipal solid waste incinerator (MSWI) plants in the Netherlands. Average temperatures are higher than the minimum required temperature of 850 °C, ranging between 890 and 1195 °C. Recorded maximum temperatures range from 974 to 1250 °C. In some facilities the average temperature is close to the maximum, but in general, the difference between the average and maximum temperature is between 150 and 250 °C.

3.2 Residues from waste incineration

Various kinds of residues are generated during the combustion process and the subsequent flue gas treatment. Besides the flue gases that are emitted through the stack, solid residues are formed such as fly and bottom ashes and slags from the kilns. During flue gas treatment, solid residues such as fly ash are collected in bags or by electrostatic filters. Besides these flue gas treatment residues, sludges are formed at the wet treatment when using scrubbers. In case of dry flue gas treatment solid gypsum is formed when using limestone as a desulphurisation agent. From the wet treatment of the flue gases also waste water is generated, from whose treatment waste water sludge is generated.

The possible presence of PFASs in these waste incineration residues is not further investigated and analysed. Measured concentrations in residue streams are discussed in Chapter 5 on emissions of PFASs from waste incineration plants. In the remainder of the report the focus is on the assessment of the presences of PFASs in the flue gases and in the CO_2 recovered from these flue gases.

3.3 Flue gas treatment processes

Typical combustion products from waste incineration are CO, CO_2, water vapour, sulphur dioxide and nitrogen oxides. Depending on the composition of the waste, other pollutants are produced, such as hydrogen chloride, hydrogen fluoride, dust, heavy metals, nitrogen oxides, dioxins, and furans. For many of these, such as CO, NO_x and dioxins, emission limits are set by regulation (Directive 2010/75/EU).

To fulfil these requirements, flue gases must be treated by a combination of cleaning processes, each specifically aimed at removing certain components from the flue gases. The flue gas treatment might vary from installation to installation. There are many components that can be configured in various ways. However, the flue gas treatment system usually consists of one or more of the following operations:

- dust collection using electrostatic filters, baghouses or cyclones;

- absorption of acids or acid-forming compounds such as SO_2, HCl and HF, usually in several steps through scrubbers or washing towers;
- sorption of trace organic compounds on activated carbon (AC) powder that is added as to the flue gas, with the optional addition of chalk, in combination with bag filters or the use of an AC filter bed, usually as a final flue gas cleaning step;
- catalytic and non-catalytic reduction of nitrogen oxides;
- catalytic oxidation of trace organics such as dioxins and furans.

In Annex III.1 the different flue gas treatment operations are discussed in further detail with a focus on the typical process conditions. As a further exemplification, Annex III.2 contains descriptions of the flue gas treatment at three waste incineration sites.

3.4 Conclusions

Three common processes for the incineration of hazardous, municipal and commercial wastes have been described. Essential for the assessment of the thermal destruction of PFASs in these installations are the legally required minimum temperature, the residence time and the typical operating temperatures. The typical operating temperatures are presented in Table 4. Three temperature zones can be distinguished: 1) the fuel bed, 2) the flame zone directly above the bed, and 3) the zone where secondary air is added, the afterburning section. The space above the fuel bed is usually referred to as the furnace. Usually, the temperature is measured in the zone after the injection of secondary air. Under normal operating conditions, incineration temperatures are usually somewhat higher than the minimum required temperature of 850 °C laid down in the Industrial Emissions Directive 2010/75/EU.

The required residence time and oxygen content have not been verified in this research. As well as temperatures, these parameters should be verified by the enforcement authorities to ensure the proper operation of the incineration process. Although it is recognised that all three parameters are essential for full burn-out of the combustion gases, in the further analysis on the incineration of PFASs the focus will be on combustion temperature.

Table 4 Typical incineration temperatures in the three most common types of waste incineration installation

Type of installation	**Temperature (°C)**	
	Typical	**Maximum**
Rotary kiln	900–1200	1200
Grate-fired	890–1100	1000–1250
Fluidised-bed	850–950	1200

Each process in the flue gas treatment process is designed to remove specific flue gas components. The flue gas treatment process usually consist of four steps:

- dust removal;
- removal of acid components;
- removal of trace organic pollutants, particularly dioxins and mercury;
- reduction of NO_x.

The cleaning of flue gas from waste incinerators is not specifically aimed at capturing PFASs. Depending on the properties of the different types of PFASs, they can be captured to a greater or lesser extent by the different cleaning steps. The flue gas cleaning efficiency depends not only on the physical and chemical properties of a chemical, but also on the cleaning steps applied (physical or chemical mechanism) and the process conditions at each cleaning step (acidity of the washing liquids, prevailing process temperature, filter efficiency, etc.). The most common unit processes are described together with their typical operating conditions.

4 Thermal degradation of PFASs and fluoropolymers

4.1 Introduction

One of the research questions addressed in this report is whether PFASs can be present in the flue gases of a waste incinerator because they do not break down (completely)?

To answer that question, it was investigated whether and, if so, to what extent and under what conditions PFASs, including fluoropolymers, are thermally degraded and what kind of incineration by-products are formed. To assess this, an overview of available key literature data on the thermal degradation of PFASs and fluoropolymers and the formation of by-products is presented in this chapter.

First, the process of combustion will be discussed, together with the description of various thermal decomposition experiments. This is followed by the description of various properties of chemical substances that could provide an indication of their thermal stability and incinerability. These sections will be followed by a presentation of the available theoretical and experimental information on the thermal degradation of PFASs and fluorinated polymers.

4.2 The combustion process and experiments

Before going into more detail on thermal degradation experiments it is useful to describe the terminology used, the combustion process and factors influencing the combustion process. After that, the differences between the various experimental methods and their relevance to the waste incineration process will be discussed.

4.2.1 The combustion process

Incineration (of waste) is the conversion of (waste) materials into ash, flue gas and heat through combustion.

Combustion is a complex sequence of chemical reactions between a substance (fuel) and an oxidising agent that releases heat, and results in a (limited) number of combustion reaction products. Heat is required to activate the chemical reactions and to generate combustible gases in the case of the combustion of solids. Once a combustion process has started, usually enough heat is generated to maintain the process. To support the combustion process and increase its efficiency, external heat can be applied, for instance through gas- or oil-fired burners.

Normally, combustion happens with oxygen as the oxidising agent. When single elements are burned, they yield oxides such as CO_2, sulphur dioxide and water. When molecules consisting of various elements are burned, other combustion products are generated as well; for instance, in the case of halogens, which react with hydrogen to form the associated acids, HF, HCl and HBr. In reality, combustion is never complete and side products are formed such as carbon monoxide, soot and aromatics in the case of the combustion of hydrocarbons.

Combustion and the associated breakdown of organic materials depends on temperature, residence time, oxygen content (fuel/air ratio) and turbulence in the combustion chambers (Moldenhauer and Mischer, 2012). For complete combustion, the various gas streams must be at the same temperature when they are mixed and to achieve a high degree of thermal degradation, the gases must have a sufficiently long residence time (2–5 seconds) at a sufficiently high temperature (850-950 °C) (Thomé-Kozminesky et al., 2012).

The thermal stability and incinerability of a substance also have an impact on breakdown efficiency. Properties such as the flashpoint, the autoignition temperature and the decomposition temperature can possibly be used as indicators for the thermal stability and the incinerability of a chemical. The appropriateness of these properties as indicators for incinerability will be discussed later in this section.

4.2.2 *Thermal decomposition experiments*

Thermolysis is the general term for chemical decomposition into at least two fragments by heat. Pyrolysis is the thermal decomposition (thermolysis) of organic materials at elevated temperatures in the absence of oxygen (vacuum) or in an inert atmosphere. Thermolysis and, specifically, pyrolytic reactions are an essential part of the combustion process.

Thermolysis experiments are essential to understand combustion reaction pathways. They show the intermittent breakdown products and final combustion products that are formed. Thermal stability and incinerability can be studied by different thermolysis methods. Such studies can be conducted under inert or oxidative atmospheres without applying a flame, so-called non-flame studies. Other experiments can be done by applying combustion in a flame, so-called flame mode studies (Licis, 1984; Dellinger et al., 1986a).

Depending on the experimental set-up, thermolysis experiments can provide an indication of thermal stability, reaction rate, possible side products being formed and possible combustion reaction pathways.

Both types of non-flame study are useful in investigating the incinerability of chemicals, as both oxygen-rich and oxygen-starved situations can occur during incineration (Taylor and Dellinger, 1987; Licis, 1984; Dellinger et al., 1986a, 2010). Key to understanding the significance of upset conditions is that only a very small fraction of the total volume of the waste needs to experience these less-than-optimum conditions to result in unfavourable destruction efficiencies, and that the post-flame chemistry controls incineration emissions (Dellinger et al., 1986a). In various studies it was shown that pyrolytic methods generated better results than other methods in predicting the (relative) incinerability of chemicals. However, in a later study it was concluded that oxidation kinetics-based ranking of the incinerability of chemicals was slightly superior to the pyrolysis-based ranking (Dellinger et al., 1993).

Furthermore, Yamada and Taylor (2003) state that emissions from incineration are controlled by the temperature in the post-flame zones and the residence time. Molecules entering the flame zone can be assumed to be completely destroyed and the small fraction escaping the flame zone can be emitted from the facility. Thus, flame zone failure modes may cause residual constituents to be emitted. The most prominent of these modes are thermal quenching and fuel (waste)/air mixing failure. Poor heat transfer at incinerator surfaces and poor gas phase mixing will thus result in conditions where the rate of destruction is low and the formation of by-products also called products of incomplete combustion (PICs) is favoured.

With respect to the relevancy of oxidising and non-oxidising gas-phase thermal stability experiments in determining the incinerability of chemicals, the combustion reactions between the fuel and the oxidizing agent should also be considered. Under non-inert atmospheres, chemicals react with oxidising agents usually oxygen. Abstraction by •O or •OH radicals dominates over addition reactions, as shown by the lack of oxygen-containing products even under oxidative conditions (Dellinger et al., 1986b). These abstraction reactions are relevant for hydrocarbons but not likely to be significant for halogen-containing compounds. It is most likely that for halogen-containing compounds such as PFASs decomposition appears through a unimolecular process (molecular bond breaking) followed by a reaction with radicals formed from the fuel (•H) or with oxygen-containing radicals (Dixon, 2001; Dellinger et al., 2010). According to Dellinger et al., (2010) this means that halogen-containing substances such as halon and CFCs exhibit the same stability under both oxidative and pyrolytic conditions (Dellinger et al., 2010). In conclusion, the oxidising and non-oxidising gas-phase thermal stability methods appear to be equally relevant in determining the incinerability of chemicals. For the potential emission of combustion by-products, often referred to as products of incomplete combustion (PIC), the results of pyrolysis experiments under inert conditions are valuable, although the chemical stability of any PICs formed also has to be taken into account when considering the degree of mineralisation and the possibility of being formed at and emitted from the waste incineration process.

Thermolysis experiments indicate at what temperature a chemical starts to decompose, The decomposition temperature provides a good indication of the potential destruction in waste incineration when comparing it with the minimum required and typical operation temperatures for the various waste incineration processes. If the kinetic parameters for the destruction reaction are also measured in these studies, the temperature and time needed to destroy a compound to a certain degree can also be derived (Licis, 1984; Tsang et al., 1998; Dellinger et al., 2010).

Gas-phase thermal stability such as the temperature for 99% destruction at 2 seconds' residence time may be used to predict relative incinerability. Thermal stability rankings based on laboratory experiments were published in early nineties (Taylor et al., 1990; Dellinger et al., 1993) for a number of chemicals. However, since then, to our knowledge, such information for other chemicals has not become available.

4.2.3 Other combustion related properties

If such data are not available, other data could possibly be used for an indication of the thermal stability and incinerability of a chemical. Several properties have been proposed thus far for ranking the relative incinerability of hazardous organic compounds, such as the heat of combustion, the autoignition temperature of the pure compound, flame destruction efficiencies and the previously mentioned thermal decomposition experiments (Licis, 1984; Dellinger et al., 1986a). The heat of combustion and the autoignition temperature are most relevant for destruction efficiencies achieved in the flame zone of an incinerator. As compounds can be assumed to be completely destroyed in the flame zone and relevant emissions appear to be generated in the post-flame/combustion stage, these parameters can be considered less relevant in relation to the overall incinerability according to Taylor and Dellinger (1987). As mentioned earlier when comparing the results of various experimental methods for ranking the relative incinerability of chemicals, thermal decomposition results provide the most consistent results.

The autoignition temperature is the temperature at which an air–vapour mixture spontaneously ignites without an external source in the presence of air and begins to self-heat at a sufficient rate to produce combustion. The autoignition temperature is actually the temperature required to supply the activation energy needed for combustion. The flash point is the lowest temperature at which there will be enough flammable vapour to induce ignition when an ignition source is applied. Therefore, there is a strong relationship with the vapour pressure. Furthermore, a prerequisite in estimating the flash point is that the chemical compound is flammable. Even if sufficient vapour is generated, a non-flammable compound will not ignite. Therefore, the flash point is thought not to be a good indicator for combustibility or thermal stability. The autoignition temperature, on the other hand, is thought to provide a better indication, although autoignition temperature is considered less relevant with regard to overall incinerability in terms of the rate of destruction (see previous paragraph).

Other information that can be used to better understand the thermal stability of substances are the bond dissociation energies of the different bonds between atoms in a molecule. In the combustion process, chemical compounds usually start to decompose at a specific temperature and then react with, for instance, oxygen. Decomposition reactions usually occur by bond scission and continue via a radical chain mechanism. Different bonds have different strengths and thus different dependencies on the temperature, the weakest bond breaking at the lowest temperature (Dixon, 2001). At sufficiently high temperatures several bonds will be broken and a broad range of radicals can be formed.

Data on the properties discussed in this section will be presented in the next section.

4.3 Thermal degradation of PFASs

4.3.1 Experimental studies on the thermal stability of PFASs

The thermal degradation of PFASs has been investigated in several studies. Dixon (2001) described the potential degradation pathways for fluorochemicals in the incineration process. The focus of that study was on perfluoroalkyl sulphonates and perfluoroalkyl sulphonamides. Dixon (2001) showed that the carbon–sulphur (C–S) bond is the bond most likely to break first, the carbon–carbon (C–C) and carbon–fluor bonds having higher bond energies in the perfluoro chain of PFASs considered.

The decomposition mechanism describe by Dixon (2001) is that, if a C–C or a C–S bond breaks, an oxygen molecule will react with the radical, leading to the formation of carbonyl fluoride and a perfluoroalkyl radical that is one carbon shorter. The chain decomposition will continue until finally a CF_3 radical is formed, which reacts with oxygen to finally form HF and carbonyl fluoride (COF_2) when abstracting a hydrogen atom from the hydrocarbon fuel. The main products formed from the decomposition of the fluorocarbon chain are therefore COF_2 and HF. COF_2 is an unstable substance that will react with water and decompose to CO_2 and HF (Farlow et al., 1960; Francisco, 1993).

$R_F\text{-}CF_2SO_2OH \rightarrow R_F\text{-}CF_2\bullet + \bullet SO_2OH$

$R_F\text{-}CF_2\bullet + O_2 \rightarrow R_F\text{-}CF_2OO\bullet \rightarrow R_F\text{-}CF_2O\bullet + O\bullet$

$R_F\text{-}CF_2O\bullet \rightarrow R_F\bullet + COF_2$

$CF_3\bullet + O_2 \rightarrow CF_3OO\bullet \rightarrow CF_3O\bullet + O\bullet$

$CF_3O\bullet + H \rightarrow CF_3OH \rightarrow COF_2 + HF$

$COF_2 + H_2O \rightarrow CO_2 + HF$

According to Dixon (2001) there is a concern regarding the formation of by-products such as CF4 and C2F6. Fluorinated by-products may be formed from the range of radicals formed, that can be re-joined to newly formed fluorocarbons before complete combustion occurs. As stated by Dixon (2001), this is not a temperature issue but rather a matter of mixing and temperature distribution in the incinerator, as this influences the residence time at sufficiently high temperatures.

Yamada and Taylor (2003) investigated the thermal degradation of PFOS and two perfluoroalkyl sulphonamides in a laboratory-scale simulation of a full-scale hazardous waste incinerator. The conditions were chosen to be representative of a full-scale incineration installation. In batch-charged continuous flow reactors, the organic materials are thermally stressed through combustion using methane as a fuel under controlled time, temperature and excess air level. The exit gas stream is analysed by GC-MS. Combustion tests were performed at 600 and 900 °C. Based on measurements of the reactor effluent, a high level of conversion of PFOS was observed from the incineration tests, which was concluded from the fact that PFOS was not detected in quantifiable amounts (DL 10 $ng.mL^{-1}$) at both temperatures. The authors concluded that the findings suggest that the C–S bond was completely destroyed. Furthermore, it was shown that PFOS was already thermally converted at a temperature of 450 °C and a high degree of degradation of PFOS and sulphonamides (PFASAs) is established at a temperature of 600 °C.

Fluorinated organic intermediates were observed in the reactor effluent, such as fluorobenzene C1 and C2 fluoroalkanes with likely products being CHF_3, CF_4 and C_2F_6. For C_2F_6, the concentration at 900 °C was much lower than at a combustion test temperature of 600 °C. Small amounts of 1,1-difluoroethene and 1,2-difluoroethene ($C_2H_2F_2$) were also observed at 600 °C. Higher molecular weight fluorinated polycyclic aromatic hydrocarbons were not detected (Yamada and Taylor, 2003). It can thus be concluded that mainly short-chained saturated and unsaturated perfluorinated carbons are formed.

Yamada and Taylor (2003) also concluded that incineration of PFOS and C8-perfluorosulphonamides is not likely to be a significant source of PFOS at incineration and that, with the exception of stable C1 and C2 fluorocarbons such as CF_4 and C_2F_6, fluorinated organic by-products are unlikely to be emitted from waste incineration facilities during the combustion of these substances.

In a paper by Vecitis et al. (2009) it was stated that the required decomposition temperatures of perfluorinated sulphonate salts are 100 to 200 °C higher than for the corresponding carboxylate salt. In the same paper it was mentioned that results from gas-phase NMR studies showed that for various PFOA salts the temperature at which more than 99% of the chemical is destroyed is in the range 300–350 °C. This temperature is lower than that reported by Stockenhuber et al. (2019), which showed that PFOA started to degrade at temperatures above 450 °C under an inert nitrogen atmosphere. The information provided by Vecitis et al. (2009) suggests a degradation temperature for PFSAs of about 450 °C, which is in line with the findings of Wang F. et al. (2015), which reported that degradation of PFOS and PFHxS starts at around 450 °C. Wang F. et al. (2015) also showed that the decomposition temperature of PFOA was around 100 °C, suggesting that PFOA underwent a self-decomposition mechanism, losing the carboxyl functional group under the formation of HF and leaving the fluorinated chain mainly intact. Furthermore, the experimental data from Wang F. et al. (2015) show that the decomposition temperature of FOSA was 150 °C and the data suggest that PFOS underwent a self-decomposition mechanism, while FOSA underwent a combustion mechanism, during the thermal treatment.

The thermal stability and decomposition mechanisms of seven perfluoroalkyl carboxylic acids, three perflouroalkyl sulphonic acids and one perfluoroalkyl ether carboxylic acid on spent granular activated carbon (GAC) was studied by Xiao et al. (2020) under different atmospheres. The decomposition of the PFCAs started at a temperature of 200 °C and PFECAs (such as HFPDO -DA) were even more readily decomposed at the same chain length. PFASs such as PFOS required a higher temperature of ≥450 °C. According to Xiao et al. (2020), this indicates that a perfluoro compound becomes less stable with the inclusion of an ether group. For the PFASs investigated, near complete decomposition (>99.9%) and high mineralisation rates occurred at a temperature of 700 °C or higher. On the basis of their data, the authors concluded that effective thermal destruction of PFASs during incineration or combustion is very likely. Volatile organofluorine species were the main decomposition products at temperatures below 600 °C. The results of Xiao et al. (2020) show that the carboxylic acid group of PFCAs is less thermally stable than the sulphonate group in PFOS, which is in line with the findings reported by Vecitis et al. (2009). Furthermore, Xiao et al. (2020) found that thermal decomposition decreased with increasing perfluoroalkyl chain length. According to the proposed degradation mechanism for PFOA, the following volatile products are formed: unsaturated compounds like CF_2, C_2F_4 and radicals like CHF_2, CF_3, C_3F_3 and fluorine atoms. As indicated by Dixon (2001) and Yamada and Taylor (2003), these compounds are not expected to be formed under normal combustion conditions in the presence of air and moisture though. Radicals will possibly recombine to form fluorinated hydrocarbon compounds or react with oxygen. Unsaturated compounds such as those mentioned above are not expected to occur at temperatures of >600 °C (Yamada and Taylor, 2003).

Yamada et al. (2005) investigated the thermal decomposition of a telomer alcohol at 200 and 600 °C. The experiments showed that decomposition of the telomer alcohol functionality occurred at 200 °C.

As part of a study on the fate of HFPO-DA (GenX) during the incineration of sewage sludge, Intertek Polychemlab (2018) investigated the thermal stability of HFPO-DA using both flash thermogravimetric analysis (TGA) under oxygen atmosphere and pyrolysis GC-MS (Helium atmosphere). The flash experiments indicated that initial degradation occurred between 323 and 353 °C. Analysis of the breakdown products formed showed the molecule breaks down in two major components and most likely breaks at the ether bond while the carboxyl group remains intact. The pyrolysis GC-MS experiments under inert conditions show that at 800 °C, besides CO_2 and hydrogen fluoride, a multitude of perfluoro radicals (CF_3, C_2F_3, C_3F_5, etc.) and several fluorinated products such as hexafluoropropylene, tetrafluoroethene and perfluoro-1-butene are formed. At this temperature, HFPO-DA molecule was not detected and was therefore assumed to be fully degraded. The findings from the experiments performed by Intertek Polychemlab (2018) are in line with the findings reported by Xiao et al. (2020).

Fully fluorinated perfluoroalkyl (PFC) compounds are the most stable of PFASs and require a high temperature for a high degree of thermal destruction. CF_4 is the most thermally stable compound composed of carbon and fluorine. The temperature at which 99.99% of the substance degrades in 1 second 1440 °C for CF_4 and 961 °C for the two-carbon PFC (C_2F_6). The 99% degradation rate temperatures in 2 seconds are 1380 °C and 930 °C, respectively (Tsang et al., 1998). However, thermal degradation starts at a lower temperature of about 1100 °C for CF_4 and 750 °C for C_2F_6.

Based on the above information, the following order of thermal stability, in terms of the approximate temperatures at which the compounds start to decompose, can be derived for individuals PFASs:

CF_4 > C_2F_6 > PFOS > PFOA ≈ HFPO-DA > FOSA

In more general terms, in line with Xiao et al. (2020) and the findings of Wang F. et al. (2015), the order of thermal stability for the groups of PFASs is:

PFCs> PFSAs > PFCAs > PFECAs > FTOHs > PFASAs

4.3.2 *Bond dissociation energy as a relative measure of thermal stability*

As described in the previous section, theoretical and experimental studies on the thermal stability of PFASs have been done for only a limited set of PFAS groups. There is a vast number of different types of PFASs in use, as discussed in Chapter 2, that have not yet been investigated. Following the degradation mechanism proposed by Dixon (2001), the thermal stability of PFASs is to a great extent determined by the bond dissociation energy (BDE) of the bond between the carbon of the perfluoro chain and the relevant atom of the functional group.

Dixon (2001) showed, on the basis of structure calculations, that, in the sulphonate group containing PFASs he investigated, the C–S bond has a BDE of 64 kcal·mol^{-1}. The bond between the fluorinated carbon directly attached to the sulphonate group and the remaining perfluoroalkyl chain fragment C_nF_{2n+1}-CF_2SO_2OH was calculated to have a BDE of 85 kcal·mol^{-1}. The average bond energies of C–C bonds in the perfluoroalkyl chain located further from the functional group are likely to be in the order of 95 kcal·mol^{-1} and the bond energy of the C–F bond in the perfluoroalkyl chain is about 120 kcal·mol^{-1}. Based on these bond energies, the C–S bond is the bond most likely to break (Dixon, 2001).

For the sulphonamido structures ($CF_3SO_2NH_2$ and $CF_3SO_2NHCH_3$) investigated by Dixon (2001), the calculated S–N bond energy for both the alkyl-substituted nitrogen (78 kcal·mol^{-1}) and unsubstituted nitrogen (79 kcal·mol^{-1}) and the C–N bond (94 kcal·mol^{-1}) are higher; thus, these bonds are thus stronger than the C–S bond (68 kcal·mol^{-1}) which is most likely to break first in the sulphonamido structures.Dixon (2001) concluded on the basis of bond energy calculations that temperatures in incinerators are high enough (about 1000 °C) for most decomposition processes readily to take place.

Following the line of reasoning presented by Dixon (2001), BDEs for the bond between the fluorinated chain and the terminal functional group can be used to assess the thermal stability of other PFASs. This is true if the bond breaking mechanism is homolysis, the breaking of a bond yielding two free radicals. Taylor and Dellinger (1987) applied the same reasoning in their analysis of the thermal stability ranking of a range of chemicals. However, they also indicated that other reaction pathways may exist that result in lower (and sometimes higher) energies than those that are required to break the bond with the lowest BDE.
If the different compounds are ranked according to their BDEs and the degradation temperatures are added for those substances for which it is known that the mechanism is homolysis, the BDEs could be used to check whether a certain temperature is high enough to break the bond between the perfluoro chain and a functional group.

In addition to the data on the BDEs and degradation temperatures for the PFASs previously presented, Table 5 contains two additional fluorine-containing chemicals (CF_2CL_2 and CCl_4), with homolysis as the reaction mechanism including their BDE and the temperature to establish 99% degradation at 2 seconds residence time ($T_{99,2}$). The degradation temperatures for PFOA and PFOS are also included in Table 5. It should be stressed however it is unclear to which extent these temperatures relate to homolytic bond breaking.

Table 5 Homolytic bond dissociation energies for fluorinated compounds

Bond	**BDE ($kcal\cdot mol^{-1}$)**	**Reference**	**$T_{deg\ start}$***	**$T_{deg\ 99}$^**
CF_3–F	131	1	1100	1380
CF_3–OH	115	1		
CF_3–H	106	1		
CF_3–CF_3	99	1	750	930
CF_3–COOH	89	1		
FCl_2C–F	80	2		790
C_8F_{17}–C(O)OH	~79	&	*200*	*~350*
CF_3–SO_2NHCH_3	78	4		
CF_3–SO_2OH; C_2F_5–SO_2OH	72.8; 70.7	3		
Cl_3C–Cl	71	2		670
CF_3–SO_2NH_2	68	4		
C_8F_{17}–SO_2OH; C_3F_7–SO_2OH	64	4	*450*	*600*
CF_3–I	54	1		
C_4F_9-I	49	1		

1) Luo (2007); 2) Taylor and Dellinger (1987); 3) Khan et al. (2019); 4) Dixon (2001). * $T_{deg,start}$ is the temperature in °C at which decomposition starts. $T_{deg,99}$ is the temperature in °C at which 99% of the substance is decomposed at 2 seconds residence time. & own assessment.

For PFOA ($C_8F_{17}COOH$), the binding energy is estimated to be 10 kcal lower than that for perfluoroacetic acid. This follows from the trend that the binding energy is strongest in the case of a single carbon atom (CF_3) 'fluorinated chain' and that the bond is weaker when one fluorine atom is replaced by another CF_3 group or a longer perfluorinated chain $CF_3(CF_2)n$. This can induce a lower bonding energy of 5–10 $kcal\cdot mol^{-1}$. This trend can be derived, for instance, from the available data for the different sulphonic acids provided by Dixon (2001).

Looking at the BDEs presented in Table 5, it is interesting to note that the bond strength between the perfluorinated chain and the carboxylate group is higher than that of the sulphonate group, which seems not to be in line with the data reported by Vecitis et al. (2009) and Xiao et al. (2020). Based on their findings it can be concluded that the carboxyl group is less stable than the sulphonate group.

The data in Table 5 also show that the BDE associated with 99% decomposition at the minimum residence time required (2 seconds) and a temperature of 850 °C, should be somewhere between 99 $kcal\cdot mol^{-1}$ and 80 $kcal\cdot mol^{-1}$, most probably around 90 $kcal\cdot mol^{-1}$. From this we could make the generalisation that, for PFASs with a bond strength between the perfluorinated chain and the functional group of less than roughly 90 kcal·mol^{-1}, 99% decomposition would be achieved at 850 °C and 2 seconds residence time.

Furthermore, the data on incineration temperatures presented in Chapter 3 show that in many facilities the average temperature for grate-fired furnaces in the Netherlands is above the minimum required and around $T_{deg,99}$ for the second-most recalcitrant PFAS.

Unfortunately, for other groups of PFASs the required BDEs are not available. However, it is likely that for many PFASs, BDEs will be lower than the BDE for the C-C bond in hexafluoroethane (99 kcal·mol^{-1}) and will be efficiently thermally degraded in grate-fire furnaces at average operating temperatures.

In several studies, alternative mechanisms to the thermal decomposition by detachment of the terminal functional group via direct bond breaking have been elucidated for both PFOS (Khan et al., 2019) and PFOA (Krusic and Roe, 2004; Stockenhuber et al.; 2019 and Xiao et al., 2020). These studies revealed a rather similar mechanism for both PFSAs and PFCAs involving a transitional state and the release of HF and SO_2 and CO_2, respectively, in the removal of the functional group. The activation energies for the reactions of the two compounds are 58 kcal.mol^{-1} (Khan et al., 2019) and 27 kcal.mol^{-1} (Stockenhuber et al., 2019), respectively. This indicates that PFOA is less recalcitrant than PFOS, which is in line with the results from the experimental studies discussed. This clearly shows that other mechanisms might exist that result in lower temperatures being needed to start thermal decomposition. However, using bond-breaking energies for the terminal groups could still be helpful for PFASs, as these could serve as a kind of worst-case estimate.

As stated before, the alternative decomposition mechanisms to direct bond breaking leave the perfluorinated chain nearly intact, producing different perfluoro compounds in the initial decomposition. Depending on the proposed mechanism, these could be 1-H-perfluoroheptane (Krusic and Roe, 2004) and perfluoroalkenes (Stockenhuber et al., 2019) for PFCAs and for PFSAs the initial decomposition products could be perfluoroalkylaldehydes (PFALs) and perfluoroalkenes (Khan et al., 2019). The decomposition proceeding from perfluorooctene-1 from the carboxyl and sulphonate elimination will follow the chain-shortening pathway and lead to the formation of CF_2, CF_3, C_2F_6, C_2F_4 and HF, among these the fluorocarbons compounds expected to transform into CO_x in the presence of oxidizing media except C_2F_6. Perfluoroalkyl aldehydes are known to rapidly hydrolyse to PFCAs (Khan et al., 2019).

In addition, Wang F. et al. (2015) suggested that PFOSA underwent a combustion mechanism at a relatively low temperature rather than a self-decomposition mechanism and started to decompose at a much lower temperature than PFOS. Based on the bond energy, however, PFOSA would have been assessed to be thermally more stable than PFOS.

The order of thermal stability based on the bond dissociation energies for direct bond breaking (of the terminal group) as presented amongst others by Dixon (2001), Luo (2007) and Khan et al. (2019) is as follows:

PFCs > PFCAs > N-alkyl FASAs > PFSAs> PFASAs > PFIs

4.3.3 *Flash point and autoignition temperature as indicators for incinerability*

The flashpoint and the autoignition temperature of a chemical could provide information on the thermal stability of a chemical. Not all of these are equally relevant indicators for incinerability, as previously discussed in section 4.2.3.

In their assessment of the degree of degradation on waste incineration, Houben and Boerleider (2020) collected information on the flashpoint of several PFASs. The data they collected on flashpoints was retrieved from the CompTox Chemicals Dashboard (US EPA, 2020). In addition to experimental information the database also provides predicted values for the flammability based on similar chemicals (consensus method). Although not all the details of the prediction method are known, it seems as if flammability is mainly or even completely based on the relationship between the rate of formation of vapour and the temperature, regardless of whether a chemical is flammable or not. As indicated in section 4.2, there is a strong relationship between the flash point and the vapour pressure, because the flash point is the temperature at which there is enough vapour to result in combustion when ignited. Results for the predicted flammability of perfluorocarbons provided in the Comptox database suggest that this relationship mainly affects the predictions. This is clearly shown by the predicted flash points for CF_4 and C_2F_6, predicted to be 7 and -13 °C, respectively. Perfluorocarbons, however, are thermally stable compounds (sections 4.3.1 and 4.3.2) and many perfluorocarbons are not flammable in air in any proportion (Kopylov, 2020; Wikipedia Contributors, 2021; Stacey et al., 1963), although some higher perfluorocarbons are flammable in pure oxygen. These predictions are therefore considered to be unreliable.

Although PFASs are generally known for their low or non-flammability, this does not mean that all fluorine-containing organic chemicals are non-flammable. This is, for instance, not the case for fluorocarbons containing a significant amount of hydrogen or a double bond. For example, C_2HF_3 has an autoignition temperature in the range of 450-500 °C and for C_2F_4 the autoignition temperature is 180 °C (Stacey et al., 1963).

The flashpoints and the autoignition temperatures of some familiar PFASs are presented in Table 6. Most of these data came from the ECHA database of REACH-registered substances (ECHA, 2021), but we did not extensively search the ECHA database, our focus was on the familiar PFCAs, PFSAs and FTOHs. For many of these well-known PFASs no information is available on flash point or autoignition temperature because, according to the registration dossiers, they are considered to be not flammable, these studies are not required according to the REACH and CLP regulation or the specific substances are not registered under REACH.

Table 6 Flammability characteristics of some PFASs

Compound	CAS	Flashpoint (°C)	Autoignition point (°C)	Reference
PFBS	375-73-5	177	649	ECHA
6:2 FTOH	647-42-7	> 200 Not flammable		ECHA
6:2 FTS	27619-97-2	Not flammable		ECHA
PFHpA	375-85-9	> 113		Pubchem
PFOSF	307-35-7	> 100		ECHA
PFAA	2043-47-2	Not flammable > 100		ECHA
6:2 FTAC	17527-29-6	94.5	360	ECHA
6:2 FTMAC	2144-53-8	110	385	ECHA
HHTVOP	1644-11-7	30	650	ECHA
Propion acid perfluoroalkyl ester	85631-54-5	Not flammable		ECHA
Perfuoro methyl pentanone	756-13-8	49	590	ECHA

ECHA: ECHA (2021); PubChem: PubChem.

From the data in Table 6 it is clear that some PFASs are flammable and can autoignite at a certain temperature. The autoignition temperatures are well below the legally required incineration temperature of 850 °C.

4.4 Thermal degradation of fluoropolymers

In addition to the various perfluorinated compounds, fluorine-containing polymers and elastomers may be present in waste to be incinerated. A distinction must be made between fluoropolymers consisting of a fully or partially fluorinated backbone of carbon atoms and polymers with fluorinated side chains attached to a non-fluorinated carbon backbone, so-called side-chain fluorinated polymers (SFPs), see Chapter 2. The first category is generally used to manufacture articles or fibres, but may also be used as (micro)powder in emulsions or mixtures or to coat, for instance, kitchen ware. The SFPs are usually applied to treat textiles or paper in order to make them water- and grease-repellent.

4.4.1 Decomposition temperatures

Fluoropolymers such as polytetrafluoroethylene (PTFE) have the reputation of being thermally stable. Indeed, they are one of the most thermally stable plastics. However, they start to generate toxic air contaminants due to thermal decomposition at or just above their recommended processing temperatures (Huber et al., 2009).

PTFE, also known as under the brand name Teflon, is a fully fluorinated polymer that is the most thermally stable of all fluoropolymers, including fluorine-containing polymers that are only partially fluoridated such as polyvinylidene fluoride (PVDF) and ethylene-tetrafluorethylene (ETFE), as shown by the results from the research by Giannetti (2005). According to this study, PTFE can be used for a long time at 260 °C and for a short time up to a temperature of 450 °C without loss of mass due to the formation of fluorine-containing gases. Significant mass loss does, however, occur at temperatures of >550 °C. For the other polymers studied, degradation occurred at temperatures of 470 °C for EFTE or lower (Giannetti, 2005). As far as weight loss is concerned, the order of relative thermal resistance is: PTFE > PFA> MFA> FEP> ETFE > PVDF ≈ PE > ECTFE > PCTFE (Gianetti, 2001, 2005). For PFA, MFA and FEB significant weight loss occurred at temperatures between 550 and 520 °C.

In addition to Gianetti (2005), several other studies investigated the thermal stability of PTFE. Garcia et al. (2007) found that, in spite of its thermal stability, PTFE decomposition begins slowly at 260 °C and noticeable decomposition occurs at temperatures above 400 °C.

According to Aleksandrov et al. (2019) thermal degradation of PTFE starts at about 500–550 °C and is complete at a temperature of about 650 °C;. Thermogravic analysis (TGA) performed by Aleksandrov et al. (2019) under a nitrogen and oxygen atmosphere resulted in estimated half-life times at 800 °C well below 0.1 s, which would result in complete thermal destruction within 1 second. On the basis of this information, it is expected that PTFE will thermally degrade completely at a minimum required combustion temperature of 850 °C (Aleksandrov et al., 2019). To show whether PTFE can be fully transformed into fluorine (F), a fluorine balance was generated including the formation of HF. No clear conclusions were drawn from the fluorine balance on the rate of conversion and mineralisation. It should be noted, however, that the TGA mainly provides insight into mass loss and gasification behaviour rather than the thermal decomposition profile including the formation of combustion by-products. It could be assumed that, for solid polymers like PFTFE, the polymer molecules are destroyed with the gasification of the polymer, but this does not provide information on the kind and degree of by-products formed and the rate of mineralisation.

Besides the above-mentioned fluoropolymers with a fluorinated carbon backbone, there is the category of side chain fluorinated polymers. This category of polymers does not have a fully or partially fluorinated backbone but rather a hydrocarbon backbone with (fully) fluorinated side chains attached to it. Yamada et al. (2005) conducted a study on the non-flame thermal degradation of a side-chain fluorinated polymer, a fluorotelomer-based acrylate polymer. The thermal degradation of the fluorotelomer and polyester-treated textile fabric was conducted under conditions (85% excess air, average temperature 1000 °C and residence time of 2 seconds). Gasification of the telomer-based polymer started around 100 °C and was nearly complete at 600 °C. The experiments showed that thermal decomposition of the telomer alcohol functional group occurred at 200 °C and a variety of combustion by-products and fluorinated radicals were formed at 600 °C. These included fluorobenzene and difluorobenzene, the $\bullet CF_3$ radical and a compound containing the $\bullet CF_2CH=CH_2$ fragment. The amount of formed ions decreased with increasing temperature. The relative amount of the two major radicals formed was less than 0.1% at a temperature of 1000 °C. At this temperature it was proven that 99.9% or more of the polymer had been mineralised. This temperature was slightly higher than that measured for other fluorotelomer-based materials in other studies, which may be related to the levels of excess air; previous tests employed considerably higher excess air levels, according to Yamada et al. (2005).

4.4.2 *Formation of perfluorocarbons*

Many analyses have been performed of the fumes formed at thermal degradation of PTFE under inert atmospheres, in air or using steam, as summarised by Garcia et al. (2007). In air, carbonyl fluoride (COF_2) was found and when using steam, the primary decomposition products were C_2F_4 and CF_2 radicals. It was found that CF_4 and CO_2 can be formed by secondary reactions such as through the reaction of C_2F_4 with oxygen. C_2F_4 can react to generate C_3F_6 and C_4F_8 above 600 °C under inert conditions.

Garcia et al. (2007) themselves determined the compounds generated in the degradation of PTFE at high temperatures (750–1050 °C), studying the influence of different atmospheres, going from pyrolysis to nearly total combustion conditions. In pyrolysis runs, only the perfluorocarbons C_2F_4 and C_3F_6 were found. Under oxidative conditions, C_2F_6, C_3F_6 and CF_4 were detected, the shares varying as a function of temperature and oxygen proportion in the atmosphere. At a temperature of 850 °C under inert conditions, C_2F_4 and C_3F_6 were formed and no other fluorocarbon compounds were detected. At increasing oxygen ratios, C_2F_4 and C_3F_6 began to disappear and decrease and fluorocarbons like C_2F_6 and CF_4 began to appear. From this Garcia et al. (2007) concluded that it seems that the presence of oxygen in combination with high temperature favours the combustion reaction of pyrolytic products. This is in line with the considerations on the reaction mechanism by Dixon (2001). Garcia et al. (2007) mentioned a third combustion reaction where C_2F_6 reacts with oxygen to produce CF_4 and CO_2 and noted that this reaction seems to become more significant as the oxygen fuel ratio increases. They derived conversion factors for CF_4 and C_2F_6 for different temperatures and oxygen/fuel ratios under fuel-rich conditions. Under typical incineration temperatures of 850–1050 °C, between 12.5% and 60.9% of the mass of PTFE incinerated was converted into C_2F_6 and between 5.5% and 9.3% was converted into CF_4. These figures indicate the large potential of the incineration of fluorinated polymers such as PTFE to contribute to emissions of the powerful greenhouse gases CF_4 and C_2F_6.

A literature survey on the emissions from incineration of fluoropolymer materials was conducted by Hubert et al. (2009), who listed the main decomposition products formed for a variety of fluoropolymers exposed at different temperatures. For waste incineration temperatures above 800 °C are most relevant. Many of these experiments were done under an inert atmosphere, mostly nitrogen. They also considered the result obtained by Garcia et al. (2007) performing thermal degradation experiments using air. For the fluoropolymers considered, at temperatures above 800 °C the main products formed under inert atmosphere are tetrafluoromethane (CF_4) hexafluoroethane (C_2F_6, HFE), CHF_3, trifluoroethylene (C_2F_3, TFE), hexfluoropropene (C_3F_6, HFP) and perfluoro isobutene (C_4F_8, PFIB).

4.4.3 *Formation of fluorinated dioxins and furans*

Although they do not fall under the definition of PFAS, we briefly discuss the possible formation of fluorinated dioxins and furans at waste incineration plants.

Huber et al. (2009) report that several fluoro-dioxins and fluoro-benzofurans besides other fluorinated aromatic compounds were identified by Herzke (1998) on the thermolysis of PTFE. Weber and Hagenmaier (1997), however, showed that the formation of PFDDs and PFDFs in industrial processes by 'de novo synthesis' does not occur. They explain that this is because the formation mechanism of PCDDs/PCDFs, where Cl_2 leads to the formation of C–Cl bonds, is impossible for fluorine due to its redox potential. Although formation of the C–F bond from carbon and fluorine ions occurs at 900 °C, dioxins are destroyed rather than formed at these temperatures. However, PFDDs/PFDFs can be formed from pre-dioxins such as fluorinated benzenes. The potential for formation of PFDDs/PFDFs at waste incineration thus depends on the formation of fluorinated pre-dioxins. Only in the study conducted by Yamada et al. (2005) on the non-flame thermal degradation of a side chain fluorinated polymer, fluorinated benzenes were found as products of incomplete combustion. Weber and Hagenmaier (1997) reported that in the burning of Teflon (PTFE) and Teflon-containing materials no formation of PFDDs or PFDFs could be detected, and the analysis of a number of fly ash samples from municipal waste incinerators revealed no PFDDs/PFDFs with detection limits of about of 0.01 $ng.g^{-1}$ for individual compounds.

Nakamura et al. (1999) report that PFDDs/PFDFs were not detected at a detection limit of 0.01 $ng.Nm^{-3}$ in flue gas at thermal destruction of CFCs in municipal solid waste incinerators. Their results confirm the differences in the formation characteristics of PFDD/PFDFs compared with chlorinated compounds.

4.4.4 *Formation of trifluoroacetic acid*

In Huber et al. (2009) reference is made to the possible formation of trifluoroacetic acid (TFA) and chlorodifluoroacetic acid (CDFA) and C3-C14 perfluorinated carboxylic acids (PFCAs) from fluoropolymer thermolysis at temperatures up to 500 °C, as reported by Ellis et al. (2001). However, the formation of these decomposition products as reported by Ellis et al. (2001) relates to the formation during the regular use of the fluorinated polymers at moderate elevated temperatures in a variety of applications such as ovens, cookware, industrial and car engines, and heat exchangers. Ellis et al. (2001) themselves state that incineration processes differ from thermolysis in that a source of fuel is used to induce complete decomposition, which is therefore unlikely to yield TFA due to the high temperatures and oxidising conditions, which will result in the cleavage of most carbon-fluorine bonds.

The findings from a study done by Ochi et al. (2008) are in line with those reported by Ellis et al. (2001). From the results of PTFE degradation at a temperature of 550 °C in an oxygen-rich atmosphere, many perfluorinated compounds were confirmed from both volatile and less volatile fractions. HFP, HFE and perfluorocyclobutane (PFCB) were identified in volatile fractions including PFIB and several Freon gases. The generation of PFCAs such as PFOA was suspected in less volatile fractions. These results relate to situations where fluoropolymers are exposed to moderate elevated temperatures in air, comparable to the circumstances described in Ellis et al. (2001). These conditions are different from those at incineration; therefore, the compounds formed cannot be considered representative of incineration of PTFE.

4.4.5 *Conclusion*

PTFE (Teflon) is the most stable fluorine-containing polymer. For PTFE it can be concluded that complete thermal decomposition is achieved at a temperature of about 800 °C. It can therefore be assumed that other fluorine-containing polymers also thermally decompose completely at a temperature of 800 °C. At thermal decomposition a variety of gaseous fluorine-containing products are formed. In order to determine the rate of mineralisation, supplementary information is needed on the amount and type of by- and end-products formed and their thermal degradation rates at waste incineration temperatures.

To evaluate whether and to what extent fluoropolymers degrade on incineration, the temperature in the combustion bed on the grates of the incinerator should considered rather than the temperature in the combustion chamber. Fluoropolymers are solids that do not evaporate with rising temperatures but rather start to decompose into volatile fluorinated compounds that will undergo combustion and thermal degradation in the flame zone and at secondary combustion. Temperatures at the pyrolysis front and the combustion front in the waste-burning bed range from 900 to 1100 °C (Ménard et al., 2006; Asthana et al., 2006), which is well above the temperature of 800 °C at which the complete thermal decomposition of PTFE is achieved.

During the combustion of PFASs and fluorine-containing polymers, various kinds of fluorine-containing combustion products can be formed. In addition to the aforementioned PFCs, these are in particular unsaturated PFCs (C_2F_4 and C_3F_6) and cyclic perfluorocarbon compounds, perfluoroisobutene (C_4F_8) and perfluorocyclobutane (C_4F_8). In general, it can be said that the higher the combustion temperature, the fewer by-products are formed, the smaller the absolute quantities and the smaller their molecular mass. The unsaturated compounds are generally unstable and are not expected to be formed in substantial amounts during waste incineration compared with the saturated PFCs.

4.5 Thermal stability of potential by-products

This section provides some information on the thermal stability of the fluorinated by-products that are most likely to be formed on the incineration of PFASs and fluorinated polymers. The thermal stability of most of these substances was not discussed in the previous paragraphs with the exception of the perfluoroalkanes.

All of the fluorocarbon by-products are fully fluorinated compounds that contain only carbon and fluorine. Fluorocarbons include perfluoroalkanes, perfluoroalkenes, perfluoroalkynes and perfluoroaromatic compounds.

4.5.1 *Perfluoroalkanes*

Kopylov (2002) investigated the flammability of several saturated fluorocarbons in oxygen. He concluded that three of the saturated fluorocarbons (CF_4, C_2F_6, C_3F_8) and CF_3H are non-combustible in the presence of oxygen. Kopylov (2002) found that this is in agreement with available literature data but also mentioned that C_4F_{10} is able to combust in oxygen in contrast with other findings.

Fully fluorinated compounds are rather resistant to high temperatures. As indicated in Section 4.3, Tsang et al. (1998) provide estimates of the temperatures needed to decompose 99.9% of a fluorocarbon in 1 second. For CF_4 this is about 1440 °C and for C_2F_6 about 930 °C. Based on this information, incineration temperatures have to be well above 1000 °C to decompose fully fluorinated compounds and prevent by-product formation

4.5.2 *Perfluoroalkenes*

Unsaturated fluorocarbons are far more reactive than perfluoroalkanes and many are highly toxic by inhalation, showing acute as well as chronic toxicity (Timperley, 2000; Tsai, 2009). Perfluoroisobutane and hexafluorocyclobutene, for instance, causing acute lung damage with symptoms that are very similar to those caused by inhalation of phosgene (Timperley, 2004). The toxicity of fluorinated olefins is apparently proportional to their reactivity towards nucleophiles (Siegemund et al., 2016).

C_2F_4

The main hazard associated with TFE is that of explosion, especially if oxygen is present. TFE reacts with oxygen at low temperatures to form an explosive oxide (Gozzo and Camaggi, 1966). Giannetti (2001) notes that TFE is thermodynamically unstable, breaking down into CF_4 and C. The autoignition temperature of C_2F_4 is 180 °C (Stacey et al., 1963).

C_3F_6

Although C_3F_6 is a non-flammable gas (ECHA, 2021), it reacts readily with hydroxyl radicals (Acerbonia et al., 2001), the main degradation product being CF_2O. In the combustion process large quantities of radicals are formed such as typical hydrocarbon radical pool and oxygen species (H, O, and OH). The reaction of hexafluoropropene with molecular oxygen was investigated. Measurements were conducted at a total pressure of 450 kPa and over the temperature range 190–220 °C, giving three major products, viz. hexafluoropropene oxide, carbonyl fluoride, and trifluoroacetyl fluoride (Lokhat et al., 2012). Although the above information is not based on pyrolytic or combustion experiments, it shows the potential of C_3F_6 to react with oxygen and hydroxyl radicals. According to Moore and Drobny (2006) hexafluoropropylene is thermally stable up to 400–500 °C and decomposes at about 600 °C.

In several studies on the thermal decomposition of tetrafluoroethylene it has been shown that at medium temperatures (550–700 °C), perfluoropropene and perfluorobutene are produced, which are finally converted into perfluoroethane, nonvolatiles and a low yield of perfluoromethane at temperatures above 700 °C (Matula, 1968; Atkinson and Trenwith, 1953; Atkinson and Atkinson, 1957).

Perfluoroisobutene, C_4F_8 (PFIB)

Perfluoroisobutene is highly reactive towards nucleophiles. It hydrolyses readily to give the relatively innocuous $(CF_3)_2CHCO_2H$, which readily decarboxylates to give hexafluoropropane (Timperley, 2000). At temperatures above 700 °C perfluoroisobutene is shown to disproportionate, giving perfluoroethane and various non-volatile products by a first-order mechanism (Atkinson and Atkinson, 1957).

4.5.3 *Cyclic perfluorocarbons*

Perfluorocyclobutane is indicated to be a non-reactive gas under normal atmospheric conditions. According to the REACH registration dossier, the compound is considered to be a non-flammable gas (ECHA, 2021). Perfluorocyclobutane undergoes a reversible decomposition to tetrafluoroehtylene and hexafluoropropene in the temperature range 360–560 °C. The formation of C_2F_4 is enhanced by traces of oxygen (Butler, 1962).

4.5.4 *General findings on the formation of fluorinated by-products*

Short-chain fluorinated products are mainly formed under pyrolytic oxygen-starved conditions. With the exception of perfluoroalkanes, most of them seem to be thermally – and some of them chemically – unstable. At normal incineration temperatures and levels of excess air it is unlikely that these compounds will be formed in substantial quantities as incineration by-products. Only in unfavourable conditions in the post-flame zone with low-temperature pockets and low oxygen levels these incineration by-products can be formed.

As indicated in Section 4.3, according to Dixon (2001) and Yamada and Taylor (2003), fully fluorinated unsaturated compounds and radicals are not expected to be formed under normal combustion conditions in the presence of oxygen and moisture. Radicals may recombine to form fully fluorinated hydrocarbon compounds or react with oxygen. Unsaturated compounds such as those mentioned above are not expected to occur at temperatures of >600 °C (Yamada and Taylor, 2003). Garcia et al. (2007) also concluded that the presence of oxygen in combination with high temperature favours the combustion reaction of pyrolytic products.

4.6 Conclusions

A literature search was conducted on the thermal stability of PFASs and fluorine-containing polymers and the formation of fluorine-containing combustion products.

From the literature studied, it can be concluded that at the minimum combustion temperature of 850 °C required by Directive 2010/75/EU for municipal waste incinerators, the studied PFASs thermally degrade. Thermal degradation usually starts at relatively low temperatures and a high degree of degradation is achieved at 600 °C, which is well below the minimum required combustion temperature. An exception to this is fully fluorinated saturated short-chain PFCs, which are thermally very stable. Considering their use, it is unlikely that saturated short-chain PFCs will occur in the waste that is to be incinerated. However, they can be formed as by-products during the combustion of PFASs. For a high degree of thermal degradation, temperatures higher than the minimum required temperature are required. This certainly applies to the most stable compound perfluoromethane (CF_4), for which a temperature of approximately 1400 °C is needed. For C_2F_6 this is about 950 °C, which is close to the typical combustion temperatures.

On the basis of experimental thermal degradation data and bond dissociation energies (BDEs) of the functional groups attached to the perfluorinated chain that were found in the literature study, PFASs were ranked according to their thermal stability.

The ranking of PFASs based on the BDE between the functional group and the perfluorinated chain shows to be a worst-case approach, since different decomposition mechanisms requiring lower energies have been identified.

Based on the BDEs for the direct bond breaking of terminal groups, PFASs can be ranked as follows:
PFCs > PFCAs > N-alkyl FASAs > PFSAs > PFASAs > PFIs

Based on experimental data PFASs can be ranked according to their thermal stability as follows :
PFCs> PFSAs > PFCAs > PFECAs > FTOHs > PFASAs

The experimental data show that, with the exception of PFCs, decomposition temperatures are far below the minimum required incineration temperature for non-hazardous waste incinerators.

Additional information on autoignition temperatures for some PFASs shows that they are all below the minimum required incineration temperature of 850 °C for municipal solid waste incinerators.

Polytetrafluoroethylene (PTFE or Teflon) is the most stable fluorine-containing polymer. For PTFE it can be concluded that complete thermal decomposition is achieved at a temperature of about 800 °C. It can therefore be assumed that other fluorine-containing polymers also thermally decompose completely at a temperature of 850 °C.

To evaluate whether and to what extent fluoropolymers degrade on incineration, the temperature in the combustion bed on the grates of the incinerator should be considered rather than the temperature in the combustion chamber. Temperatures at the pyrolysis front and the combustion front in the waste-burning bed range from 900 to 1100 °C, which is well above the temperature of 800 °C at which the complete thermal decomposition of PTFE is achieved.

During the combustion of PFASs and fluorine-containing polymers, various kinds of fluorine-containing combustion products can be formed. In addition to the aforementioned PFCs, these are in particular unsaturated PFCs (C_2F_4 and C_3F_6) and cyclic perfluorocarbon compounds, perfluoroisobutene (C_4F_8) and perfluorocyclobutane (C_4F_8). In general, it can be said that the higher the combustion temperature, the fewer by-products are formed, the smaller the absolute quantities and the smaller their molecular mass. The unsaturated compounds are generally unstable and are not expected to be formed in substantial amounts during waste incineration compared with the saturated PFCs.

Other fluorine-containing combustion products such as fluorine-containing dioxins and furans, and perfluoroacetic acid have also been mentioned as possible combustion products. Closer examination leads to the conclusion that incineration temperatures are unfavourable to the formation of these compounds. Fluorinated dioxins and furans can however be formed from precursors such as fluorobenzenes. In one study fluorobenzenes are reported to be formed. All in all, formation of fluorinated dioxins and furans is judged to be unlikely but cannot be completely ruled out.

The literature search shows that a number of PFASs have already been extensively researched. However, much is still unclear about the different reaction mechanisms that lead to degradation and the formation of by-products. The amount of research in this area is increasing, but the picture is not yet complete. In addition, information on the thermal degradation of many types of PFASs is still lacking.

5 Emissions of PFASs from incineration plants

This chapter deals with the question whether PFASs and their combustion products are captured effectively by the available flue gas cleaning techniques at waste incineration plants. It provides insight into the different physical and chemical PFAS properties to explain the expected behaviour of the PFASs and their combustion products. A theoretical assessment of the removal of PFAS from flue gas is made.

This chapter also describes measurement methods to characterize the PFAS emission concentrations. The main question to be answered is whether the chemical analysis of fluoride is sufficiently accurate to detect the presence of PFASs in flue gases. Different techniques and methods of sampling and chemical analysis of flue gas are mentioned.

Finally, the chapter covers the different emission pathways from a waste incineration plant. These include the emission of PFASs via flue gas and fly and bottom ashes, and their migration from the source through ambient air and leaching.

5.1 PFAS properties

5.1.1 Introduction

As indicated in Chapter 2, there are a large number of substances with a perfluoroalkyl moiety, which can be subdivided into a number of groups according to their chemical structure. There is a wide variety of physical and chemical properties among PFASs and their various subgroups.

To assess the fate of PFASs in the flue gas treatment process and in the recovery of liquefied CO_2 from incineration flue gases (see Chapter 6), information on the physical and chemical properties of the individual PFASs and their combustion by-products is required.

For PFASs with a functional group that can be ionised, the pH of the washing solutions is an important factor in assessing the distribution. The degree of ionisation is determined by the acid dissociation constant (pKa) of the compound of concern. In addition to the pKa, the air–water distribution coefficient and the octanol–air distribution coefficient are also required in the assessment. These coefficients will be used in determining the extent to which substances are absorbed from the flue gases into the washing liquids and adsorbed by AC, respectively. The extent of adsorption of PFASs to AC and which properties are important in this respect is still subject to discussion. In this study, the octanol–air partition coefficient is used as an indicator to assess the degree of absorption by AC. Research shows that, in the assessment of possible binding to fly ash and AC, the melting and boiling point are also relevant properties, as will be discussed later in this chapter.

Physical and chemical property information for a substantial number of well-known and commonly referenced PFASs has been collected or generated in several studies. Our assessment is based on the information from these data collections. In case essential information was lacking, however, the data were completed with information from additional sources such as publicly available databases and other scientific publications. In addition, the physical and chemical properties of the fluorinated substances generated as by-products of incomplete combustion were needed because these were either not or only partly included in the various data collections consulted. Therefore, an additional literature search was conducted, the results of which are presented in Section 5.1.3. It should be stressed that the PFASs included in our study are obtained from publicly available information sources and cover only a fraction of all the commercially available PFASs known.

No effort has been undertaken to review the data obtained from the sources mentioned below. The key properties in relation to the operational conditions for the different processes units will be discussed in Section 5.3.

5.1.2 *Information on physical and chemical properties*

The following collections of physical and chemical data on PFASs have been consulted in assessing the removal of PFASs in the flue gas treatment of waste incinerators and in the carbon recovery processes.

Concawe (2016) provided a review of published literature on the environmental fate of PFASs, describing the main types of PFASs and their physical and chemical properties, including melting and boiling points, acid dissociation constants (pKa) and sorption coefficients. Another source of information that was consulted is a database composed by ITRC (2020) as part of a guidance document to support stakeholders wishing to gain a working knowledge of the current state of PFAS science and practice. The data cover melting and boiling points, organic carbon partition coefficients and pKa values.

Additionally, data gathered and generated by Wang Z. et al. (2011) was consulted. Wang Z. et al. (2011) provided estimates of various physicochemical properties, including air–water portioning coefficients and pKa values, of 134 individual PFASs using a quantum-chemical model. The data provided by Wang Z. et al. (2011) lacked information on the pKa for various groups of PFASs such as FASAs, Me- and EtFASAs, FASEs and Me- and EtFASEs, FASAAs and the group of fluortelomer phosphate esters and fluortelomer sulphonates. pKa values for these groups were obtained from Field and Seow (2017), Barzen-Hanson et al. (2017), Gao et al. (2017), Wang Z. et al. (2014), Ahrens et al. (2012), Riddell et al. (2011), Rayne and Forest (2009a, 2009b, 2009c) and the 2018 Human Metabolome Database (Wishart et al., 2018). Physical and chemical properties for the perfluoroalkane sulphonamido acetic acids (FASAAs) have been generated from EPI Suite version 4.11 (US EPA, 2012). For FTCAs and FTUCAs no pKa values were found in literature. Not accounting for dissociation can be considered as a worst case when assessing the removal.

In addition to the physical and chemical properties of the 134 PFASs provided by Wang Z. et al. (2011), Gomis et al. (2015) provided physicochemical properties of an additional 22 emerging and novel per- and polyfluoroalkyl substances, some of which are used as alternatives to PFOA, PFOS and 8:2 FTOH. Finally, the set of substances was completed with 6:2 fluortelomer acrylate and 6:2 fluortelomer methacrylate, for which most of the information was obtained from the registration dossiers (ECHA, 2020).

pKa values for many PFAs have been published by Wang Z. et al. (2011), Gomis et al. (2015) and ITRC (2020). However, there was little information on the pKa values of some specific PFASs such as perfluoroalkyl phosphinic acids and the perfluoroalkyl phosphate esters. Additional information was found in literature and public internet sources for perfluoroalkyl mono phosphate esters. According to Riddell et al. (2011) and Jackson (2013), perfluoroalkyl monophosphate esters have pKa values of ≤3. Similar to Lee (2013) we applied read-across for the remaining phosphate-based PFASs using the information on pKa values for alkylphosphate esters (Kirby and Nome, 2015; Vipperla et al., 2017). From this information it is concluded that for these groups of PFASs the pKa is expected to be lower than 2.

Overall, it can be concluded that for nearly all PFASs with acid functional groups (PFAAs), including phosphate-based PFASs, the pKa values are lower than 3, in some cases substantially lower.

According to Ahrens et al. (2012) and Wang Z. et al. (2014), the estimated pKa for perfluorotelomer acrylates is about -5, as calculated by the SPARC tool. However, the SPARC pKa results for 6:2 FTMAC and 6:2 FTAC appear to have been misinterpreted. Acrylates do not contain an acid group and are weak bases. Most likely the pKa values represent those of the conjugated acid. This becomes clear when looking at the pKa values of some acrylates. For example, the pka of ethyl acrylate is -6.8 (HMDB, 2021). However, it is important to note that the reported pKa in HMDB (2021) is the strongest basic pKa. The strongest basic pKa is that of the protonated molecule. In our assessment we therefore assume that acrylates do not dissociate and are present only in the protonated form at very low pH values (50% at a pH of -6.8) and thus consider them as neutral compounds at positive pH values.

For perfluoralkyl sulphonamides (PFASAs) additional estimated pKa values were provided in the papers by Rayne and Forest (2009b) and Ahrens et al. (2012). The reported values for individual compounds differ by about 3 units. This is due to the fact the branching of the perfluoroalkyl chain was expected to have substantial impacts on amide moiety acidity in these PFAS groups, although the results were not conclusive with respect to the branching effect and direction (Rayne and Forest, 2009b). As with the PFSAs and PFCAs, sulphonamides have also been historically produced by the electrochemical fluorination method, which leads to a potentially large, and presently undefined, suite of linear and branched congeners that could be present in the environment. In the light of the above information, in this study we used the pKa value of the linear congener, which has the lowest value. For other perfluoralkyl sulphonamides, such as the methyl- and ethyl-substituted and sulphonamido ethanols, the reported pKa values are higher, in the range 8–14. Estimated pKa values for the carboxylate groups of sulphonamidoacetates (PFASAAs) range from 3.86 to 4.04 (Rayne and Forest, 2009b). The HMDB 2018 (Wishart et al., 2018) gives lower estimates, with pKa values of about 1 for EtFOSAA and MeFOSAA. As a worst case we used the higher pKa values in estimating the degree of ionisation.

Not all categories of PFASs might be equally relevant for waste incineration. The set of substances taken from Wang Z. et al. (2011) also includes categories that do not have a commercial application. These categories are mostly substances that are formed during biotic and abiotic degradation in the environment. According to Buck et al. (2011), these include environmental transformation products such as:

- fluorotelomer aldehydes (FTAL) and unsaturated aldehydes (FTUAL);
- fluorotelomer carboxylic acids (FTCA) and unsaturated carboxylic acids (FTUCA);
- perfluoroalkane sulphinic acids (PFSIA);
- perfluoroalkyl aldehydes (PFAL);
- perfluoroalkane sulphonamido acetic acids (FASAA).

It is expected that these substances are not present (or present only in small quantities) in waste to be incinerated. However, in the case of the combustion of (industrial) waste water treatment sludges, these conversion products may be more relevant. The outcome of the calculation for these PFAS categories is included in the report (see Appendixes V and VI). However, we did not consider them in the further analysis of our findings.

5.1.3 Properties of perfluorinated products of incomplete combustion

Wang Z. et al. (2011) included in their study information on four perfluoroalkanes with carbon chain lengths ranging from C4 to C10. The lighter perfluoroalkanes and alkenes that may be formed on incineration are not included in their study. In this section, the physical and chemical properties of perfluorinated products of incomplete combustion relevant to this study are presented.

Fully fluorinated saturated substances, or perfluorocarbons, are known greenhouse gases with a high global warming potential that do not deplete the ozone layer. Perfluoroalkanes are gases up to C4. Nearly all other fluoroalkanes are liquids or solids (Siegemund et al., 2016; Wikipedia Contributors, 2021).

CF_4 is a vapour that is slightly soluble in water. CF_4 is a greenhouse gas with a Global Warming Potential (GWP) of 6,630 (Myhre et al., 2013). It does not deplete the ozone layer (EEA, 2020). C_2F_6 has a GWP of 11,100 (Myhre et al., 2013). At ambient temperatures and atmospheric pressure C_2F_6 is a gas.

An overview of the Henry's Law constants and log K_{OW} values is presented in Table 7. The data are based on Mackay et al. (2006) and public information on substances registered under REACH (ECHA, 2020). For perfluoroisobutene the data comes from Chemspider (2021).

Table 7 Some environmental properties of perfluorocarbons: Henry's law constant, air-water distribution coefficient (K_{AW}) and octanol-water partition coefficient (K_{OW}).

Compound	**Molecular formula**	**Henry's Law constant (Pa.m^3/mol)**	**Log K_{AW}**	**Log K_{OW}**
Tetrafluoromethane	CF_4	539,961	2.4	1.18
Hexafluoroethane	C_2F_6	1,715,432	2.9	2.00
Perfluorocyclobutane	C_4F_8	391,925	2.2	1.60*
Tetrafluoroethene	C_2F_4	61,981	1.4	1.21*
Hexafluoropropene	C_3F_6	349,397	2.2	1.95*
Perfluoroisobutene	C_4F_8	179,649^	1.9	3.03^

Source: ^ Chemspider (2021) reports a Henry's Law constant of 1.773 atm.m^3/mol at 25 °C.
* ECHA (2020); otherwise Mackay et al. (2006).

As stated by Mackay et al. (2006), fate calculations show that, when released into the environment, virtually the total mass of volatile fluorinated alkanes and alkenes will partition to the atmospheric compartment.

5.2 Assessment of collection efficiency

A qualitative assessment is made of the extent to which PFASs are removed from flue gas before it is emitted or further processed in the CO_2 recovery installation. The assessment is based on the materials used in the flue gas cleaning process, the process conditions at the different stages of the cleaning process and the physical–chemical properties of the compounds. The physical–chemical properties are essential in this because they significantly determine how the substances behave under the specified process conditions. The most relevant parameters are the Henry's Law constant, the log K_{OW} the boiling point and the melting point and the acid dissociation constant pKa.

The effect of the process conditions and materials used on the removal of PFASs from incineration flue gas will be discussed for each step in the flue gas treatment process, starting with the binding to fly ash, followed by the removal of acid compounds and ending with the removal of trace organics by AC.

5.2.1 Binding to fly ash

In assessing the adsorption and binding of PFASs to waste incineration fly ash, the chemical composition, as well as the physical form, of the fly ash is important.

Adsorption to fly ash is determined by the total available surface area of the particles, which is in turn determined by the concentration of the particles in the gas stream, the specific surface area of the particles and the porosity of the particles. On the substance side, the degree of adsorption is correlated to the boiling point and the vapour pressure. With respect to physical adsorption, Ma et al. (2021) found that the removal by AC exhibited good linear relationships with the boiling point and saturated vapour pressure. They concluded that the boiling point was the key factor affecting the efficiency of the removal of volatile organic chemicals (VOCs). For an explanation of this they referred to Zhang et al. (2017). Zhang et al. (2017) stated that the physical adsorption process of the chemical being adsorbed (adsorbate) on porous adsorbent is similar to vapour–liquid phase transitions, where the adsorbates with higher boiling points would be adsorbed in preference to those with a lower boiling point because of the stronger intermolecular forces. Additionally, liquid-like condensation plays an important role in VOC adsorption onto AC; thus, the boiling point of is a crucial factor in the adsorption process (Zhang et al., 2017).

As well as physical adsorption, chemisorption plays a role, depending on the composition of the fly ash particles. Chemisorption involves the formation of chemical bonds between the adsorbate and adsorbent. Here especially, the chemical groups at the surface of the adsorbent are important, as they can form chemical bonds with certain functional groups of the chemical compounds to be adsorbed. This is, for instance, the case for silica and alumina, which are known as polar adsorbents, as they have a high surface polarity. This surface polarity corresponds to affinity with polar substances such as water, alcohols and carboxylic acids. Besides silica (gel) and (porous) alumina, other examples of polar adsorbents are zeolites and silica–alumina (Filho and Do Carmo, 2004). This affinity is also illustrated by the experimental results reported in a paper by Arp et al. (2006). The results show that non-polar perfluorinated compounds bind less to activated alumina, quartz and calcium carbonate than polar perfluorinated compounds. For the non-polar compounds the binding differentiates little between the substrates, while for the polar compounds the highest binding is achieved by calcium carbonate.

With respect to the composition of fly ash, fly ash from waste incinerators contains a high share of soluble salts, in contrast to fly ash from coal combustion, which contains a higher share of minerals such as silica and alumina. Fly ash also contains carbon. As regards its form, fly ash from waste incinerators usually consists of particles with a variety of forms, while fly ash particles from coal combustion are generally spherical and often glass-like with the carbon fraction encapsulated. Based in the limited content of minerals in fly ash, physical adsorption is expected to prevail. On the other hand, polar perfluorinated substances show an equal or slightly higher affinity with carbonate salts like calcium carbonate; thus, chemisorption could also play a significant role in adsorption to fly ash.

Because of the good linear relationship with the boiling point and the physical adsorption process, chemicals with higher boiling points will be adsorbed in preference to those with a lower boiling point. To provide a first indication of the degree of adsorption of the various PFASs to fly ash, the boiling points of PFASs in relation to the temperature of the flue gas are discussed next.

The temperature of the flue gas that exits the steam boilers is about 200–230 °C. As mention in Section 3.3, typical operating temperatures for electrostatic precipitators are 160–260 °C. Fabric filters used in large-scale waste incineration plants are operated at temperatures ranging from 170 to 200 °C.

At these operating temperatures most of PFASs are liquids or gases. Only within some of the PFAS categories the molecules with long perfluoro chains have melting points well above these temperatures. In particular, sulphur-containing PFASs such as perfluorosulphonic acids and phosphorous containing PFASs, even those with shorter perfluorinated chains, have relatively high boiling points, well above 200 °C. The more volatile PFASs with boiling points below the temperature in the dust filters, exist in the vapour phase. PFOA for instance has a boiling temperature of 188–192 °C and exists in the vapour phase at a temperature of 200°C. The same holds for PFCAs with a shorter perfluoro chain. PFCAs with longer perfluorinated chain have boiling points above 218 °C.

To conclude, PFASs that are in liquid or solid form at typical process temperatures are expected to be most strongly adhered to fly ash particles. For PFASs that are liquid and near their boiling point the binding to fly ash particles is less and it is more likely that they will pass to the next flue gas cleaning stage.

The adsorption of a chemical to aerosols in the atmosphere can be calculated using the Junge-equation (Pankow, 1987) The Junge-equation is based solely on the saturated vapour pressure. The Junge-equation is in line with the findings presented by Zhang et al. (2017) and Ma et al. (2021) with respect to the physical adsorption to particles in air or a gas stream.

As a measure of the adsorption of PFASs to fly ash we use the Junge-equation (Pankow, 1987) because the same physical principles hold for both aerosols and fly ash. The Junge-equation assumes that partitioning involves mainly physical adsorption, thus not explicitly including chemical adsorption. When the adsorption of reactive chemicals by chemisorption or electrostatic attraction onto mineral surfaces would make a significant contribution to the adsorption, then the adsorption calculated according to the Junge-equation is likely to underpredict the actual adsorption.

Although the mineral content of fly ash is limited, by neglecting chemical sorption to minerals with a high surface polarity, the actual adsorption of polar chemicals to fly ash is most likely higher than the Junge-equation will predict.

The fraction associated with aerosols according to the Junge-equation is calculated as follows:

$$\phi = \frac{c \cdot \theta}{P_L + c \cdot \theta}$$

In which:

Φ	fraction associated with aerosols (-)
Θ	aerosol surface area ($m^2.m^{-3}$)
P_L	(sub-cooled) liquid phase saturated vapour pressure (Pa)
c	constant (Pa.m).

According to Takaoka et al. (2016) fly ash concentrations range from 1.4 to 3.4 g.m^{-3}. Based on that range we use a typical concentration of 2 g of fly ash per cubic metre of flue gas. Kao et al. (2000) reported that the specific area of fly ash is in the range 5–42 m^{2}.m^{-3}. In our calculations, a value of 20 m^{2}.m^{-3} is applied. For the constant in the Junge-equation, a value of 0.002 atm.cm is used, which is a relatively high value applicable to polycyclic aromatic hydrocarbons. The constant is substance-dependent; a value of $1.7 \cdot 10^{-4}$ atm.cm is usually used for organic substances. For chlorinated organic chemicals like dieldrin and DDT the constant has a value of about $1.3 \cdot 10^{-4}$ atm.cm (Noordijk and de Leeuw, 1991).

Because of the elevated temperatures in the flue gas, the vapour pressure should be corrected using the enthalpy of evaporation. For several PFASs the heat of evaporation can be obtained from Zhang M. et al. (2020), their publication contains data on the heat of sublimation (ΔHsub) and the heat of fusion (ΔHfus). The difference between the heat of sublimation and the heat of fusion is the heat of evaporation, which is then used to calculate the vapour pressure of the substance at 200 °C. Additionally, the heat of evaporation for perfluoroalkanes was obtained from Dias et al. (2005) and Tsai (2009). The vapour pressures at 25 °C were taken from Wang Z. et al. (2011) except for perfluorodecaline (PFDF), where we used hte higher (measured) value of 910 Pa (Dias et al., 2005).

Using the vapour pressure at 200 °C in the Junge-equation shows that high molecular FTOHs and PFCAs with 10 or more carbon atoms could still significantly bind to fly ash at a temperature of 200 °C (Table 8). For the non-polar perfluoroalkanes the vapour pressures are higher compared with the polar analogues, resulting in lower binding to fly ash.

Table 8 Calculated fraction (Φ) of the selected PFASs bound to fly ash at a temperature of 200 °C applying the Junge-equation

Substance	**ΔHvap (kJ.mol^{-1})**	**ΔHsub (kJ.mol^{-1})**	**ΔHfus (kJ.mol^{-1})**	**log P_L (Pa)[1]**	**log $P_{L,}$ 200 °C (Pa)**	**Φ (-)**
8:2 FTOH	73.6	85	11.4	0.56	5.6	2%
10:2 FTOH	76.9	94.3	17.4	-0.26	5.0	8%
PFHxA	51.4	68.5	17.1	2.66	6.1	<1%
PFHpA	59.9	77.9	18.0	2.2	6.3	<1%
PFOA[1]	64.7	88.9	24.2	1.73	6.1	<1%
PFNA	64.7	88.7	25.2	1.27	5.7	2%
PFDA	58.1	101.5	43.4	0.82	4.8	12%
PFHxF	32.5[3]			4.43		<1%
PFOF	41[3]			3.40		<1%
PFDF	41.5[2]			2.96[2]		1%

ΔH_{vap} = heat of vaporisation; ΔH_{sub} = heat of sublimation; ΔH_{fus} = heat of fusion; P_L = sub-cooled liquid vapour pressure. [1] Data from Wang Z. et al. (2011); [2] data from Dias et al., (2005); [3] data from Tsai (2009).

5.2.2 *Removal of acid components*

In the first stage of the wet flue gas cleaning process, acid components such as HCl and HF are removed using water as a scrubbing agent. The operating temperature is below 80 °C. The temperature is low in order to protect the equipment. The pH of the scrubber water has a typical value of 1.

Depending on the acid dissociation constant (pKa) of the chemical and the acidity (pH) of the solution, deprotonating PFASs such as PFCAs (perfluorocarboxylic acids) will dissociate to their anions in an aqueous solution. Ionised forms in aqueous solutions behave differently. For instance, the perfluorooctanoate anion is highly water-soluble and has negligible vapour pressure, whereas the neutral form of PFOA has very low water solubility and a sufficiently high vapour pressure to partition out of water into air (Buck et al., 2011). As a general rule, it can be assumed that the ionised fraction in the solution will not volatilise and therefore the air–water partition coefficient needs to be corrected (Schwarzenbach et al., 1993).

PFASs with acid functional groups such as PFSAs and PFCAs are not the only ionising PFASs. Primary and secondary substituted amide protons of perfluoroalkyl sulphonamides (FASAs) and perfluoralkane sulphonamido ethanols (FASEs) are also acidic at near neutral pH values, n-FOSA having a pKa of between 6.2 and 6.5 (Rayne and Forest, 2009c; Buck et al., 2011).

PFASs with a pKa lower than 1, such as many PFCAs and PFSAs, exist for more than 50% in the dissociated form at a pH of 1 in the scrubber solution. At the second washing stage, where SO_2 is removed, alkaline agents are added to enhance the removal of SO_2, the pH of the scrubbing solution being in the range 5–7. At these pH values, all the acid group containing PFASs with a pKa below 3 are expected to be fully (>99%) deprotonated. When the pKa is lower than 4, the fraction dissociated is at least 90%. As shown in Figure 3, a chemical with a pKa of 3 is 99% dissociated at a pH of 5 and 50% at a pH of 3. Only perfluoroalkane sulphonamides having a pKa of between 6 and 7 are 50–90% dissociated at a pH of 3 and only 10% at a pH of 5.

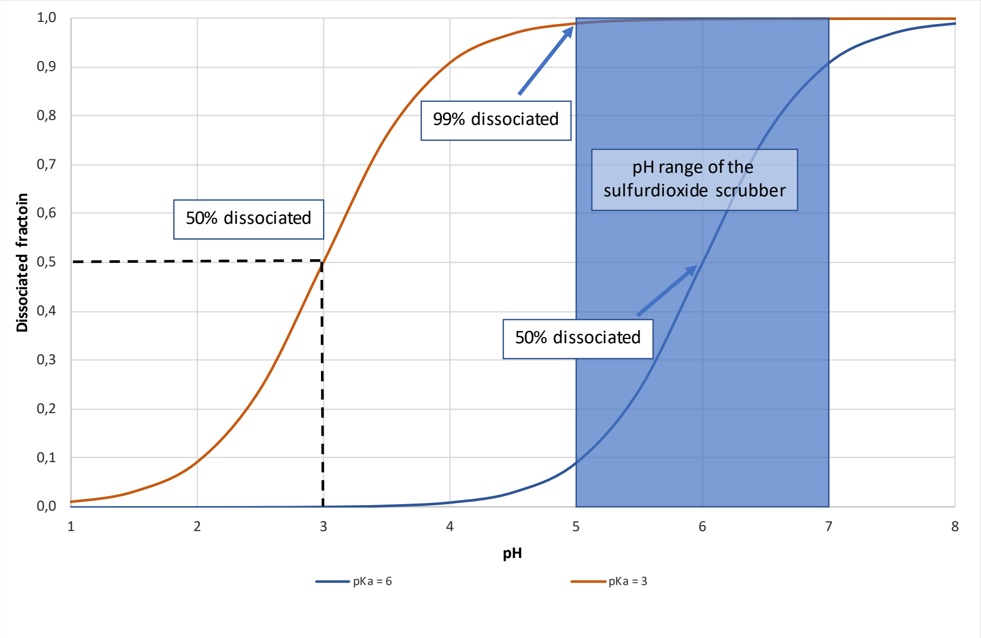

Figure 3 Fraction of the ionising substance dissociated in the SO_2 scrubber as a function of the pH and the acid dissociation constant, pKa

Most of the PFASs with acid functional groups are fully deprotonated in the SO_2 scrubbing solution and therefore do not volatilise but remain dissolved in the scrubber solution once absorbed. Those PFASs can be more effectively removed at the washing stages.

For PFASs with non-dissociating groups, the degree to which a substance tends to partition between the flue gas and the scrubber solution is determined only by the Henry's Law constant. The dimensionless form of the Henry's Law constant is the air–water partition coefficient (K_{AW}).

PFASs with non-dissociating, non-polar groups such PFIAs, FTIs and PFCs have relatively high K_{AW} values (log K_{AW} 2–5) and are likely to mainly remain in the gas phase and pass the flue gas washing stages. Non-dissociating PFASs with a monopolar group, such as FTOHs, have intermediate K_{AW} values (log K_{AW} -2–1).

PFASs such as FASAs and FASEs also have acidic moieties and will be substantially ionised at environmental pH values (Rayne and Forest, 2009b). At lower pH values, however, these PFASs are only partly ionised, as mentioned above. These PFASs, with two polar functional groups have log K_{AW}-values between -2 to -4, thus expected to remain in the scrubber solution once dissolved.

It is interesting to note that within the same functional group, the K_{AW} increases with increasing perfluorinated chain length and that the introduction of a CH_2 group between a bipolar functional group and the perfluorinated chain, as in the case of telomer compounds, decreases the K_{AW} values (Wang Z. et al., 2011).

The potential removal of PFASs by the washing stages is qualitatively assessed from the absorption factor. The absorption factor indicates to what extent PFASs can be absorbed by the applied washing liquids. Key in this assessment are the pH of the solution, the ratio of the washing liquid flow rate to the flue gas flow rate, the G/L ratio, the pKa and the air–water partition coefficient. The air–water partition coefficient needs to be corrected for the fraction of the chemical that is ionised in the washing solution (Schwarzenbach et al., 1993):

$$\alpha = \frac{1}{1 + 10^{pH - pKa}}$$

$$D_{AW} = K_{AW} \cdot \alpha$$

In which:

α	non-dissociated fraction of the substance (-)
pH	acidity of the solution (-)
pKa	acid dissociation constant of the substance (-)
K_{AW}	air–water partition coefficient ($m^3_{air}.m^3_{water}$)
D_{AW}	air–water distribution coefficient ($m^3_{air}.m^3_{water}$).

The absorption factor is calculated using the following equation:

$$F_{abs} = 1 - \frac{G/L}{G/L + 1/D_{AW}}$$

In which:

F_{abs}	the absorption factor (-)
G/L	flue gas to washing liquid flow rate ($m^3_{flue\ gas}.m^{-3}_{wash\ liquid}$)
D_{AW}	air–water distribution coefficient ($m^3_{air}.m^3_{water}$).

The volume-based G/L ratios and the pH values for the different washing stages are shown in Table 9. According to Wang Z. et al. (2015), the value of L/G usually ranges from 8 $L \cdot m^{-3}$ to 25 $L \cdot m^{-3}$ to ensure desulphurisation efficiency. These values correspond to G/L ratios of 125 and 40, respectively. In the calculations, a conservative value of 250 for the G/L ratio was used. For the quench, a G/L value of 1000, based on the data provided by Jordan (1987), was used. For the Venturi wash the G/L ratio was set equal to that of the quench.

Table 9 Volume-based gas to liquid ratios (G/L) for the different washing stages in the flue gas treatment process

Stage	G/L ratio	pH	Range
Quench	1000	1	0.3–1
SO_2 trap	250	5	5–7
Venturi	1000	4	4–7

The results of the qualitative assessment of the removal of the different PFASs in the flue gas washings are presented in Appendix V. In the qualitative assessment the following gradations are used, which are indicated by colours in Appendix V: red refers to poor removal, orange to average, yellow to good and green to very good. For a more quantitative interpretation, indicative removal efficiencies are provided here for the different classes: green >99%; yellow 90–99%; orange 90-75% and red <75%. These indicative values are an expert judgement based on the measured removal efficiencies achieved for well-known and studied flue gas components such as HCl, HF, SO_2 and particulate matter (see Section 6.2).

In conclusion, PFASs with non-dissociating, non-polar groups such as PFIAs, FTIs and PFCs, have high K_{AW} values (log K_{AW} 2–5) and are likely to remain mainly in the gas phase and pass through the different flue gas scrubbing stages. PFASs with polar functional groups, PFASs such as the FTOHs, FTMAC, PFPiAs, PFSAs, FASAs and FASEs, including the alkyl-substituted and the novel PFASs Novec 1230 and PFOTSi, also have the tendency to remain in the gas phase and are thus expected to be removed from the flue gas only to a limited extent.

5.2.3 *Removal of trace organics by activated carbon*

After the removal of acid pollutants in the preceding washing stages, AC adsorption is applied for the fine cleaning of flue gas. This can be done by leading the flue gas through a fixed bed adsorber or by injecting carbon powder into the gas flow, after which the carbon powder must be filtered out using, for instance, bag filters or cyclones.

Different types of AC have different adsorption efficiencies for different types of pollutant. The adsorption efficiency is very much influenced by the AC manufacturing process. Like fly ash particles, the adsorption efficiency of AC is influenced by the particle size, the specific surface area, the pore volume, the pore size distribution and the chemical composition of the AC surfaces (Ma et al., 2021; Zhang et al., 2017). The removal efficiency is enhanced by a smaller AC particle size, longer AC residence time, and greater AC feeding rate (Ma et al., 2021). The adsorption efficiency generally decreases with increasing temperature.

Adsorptive capacity often tends to increase with the gas phase concentration, molecular weight, diffusivity, polarity, and boiling point of the pollutant (Ma et al., 2021; Zhang et al., 2017). AC can adsorb a wide range of VOCs; however, there are some limitations. AC is less effective for compounds that are highly polar or volatile or have small diameters.

As discussed in Section 5.2.1, removal efficiency exhibits good linear relationships with boiling point and saturated vapour pressure. Ma et al. (2021) concluded that boiling point was the key factor affecting the efficiency of the AC in removing VOCs. Thus, boiling point is a crucial factor in the adsorption process (Zhang et al., 2017).

Rao et al. (2002) found that the order of adsorption efficiency from aqueous solution onto GAC for the investigated pharmaceuticals and personal care products correlated well with their log K_{OW} values.

Ridder (2012) found that hydrophobic partitioning was an important mechanism, which especially dominated the removal of relatively hydrophobic solutes. For more hydrophilic solutes, hydrogen bond formation between the solute and the AC surface strongly affected solute removal. Aromatic solutes showed slightly better adsorption than aliphatic solutes, due to the potential to form pi–pi bonds with the basal planes of AC. This clearly shows that different types of bonding are relevant for different types of chemicals.

Studies comparing the sorption of PFASs from aqueous solution to GAC and powder active carbon (PAC) have shown PAC to be a better sorbent of PFASs than GAC (Schedin, 2013).

As mentioned in Concawe (2016), sorption of PFASs increases with increasing perfluorinated chain length, decreasing pH and increasing concentration of Ca^{2+}. Furthermore, it was stated that PFAS sorption to GAC is lower than for organics with similar molecular weights, and other co-contaminants will compete for, and preferentially utilise, the adsorptive potential of the GAC media. Sorption velocity is faster for longer-chained PFAS and smaller-diameter GAC particles and, therefore, GAC that is optimised for the removal of one PFAS will not optimally remove other PFASs.

From the above it is clear that a lot of factors influence the adsorption efficiency of AC. This makes it difficult to assess the removal of PFASs by AC. In this study we assume that adsorption to AC correlates with the solubility in octanol and that the saturated vapour pressure is also a key factor. The octanol–air partition coefficient (K_{OA}) – is therefore thought to be a reasonable indicator for the removal of PFASs from flue gas by carbonaceous materials such as AC, lignite or coke.

Ren et al. (2020) also indicated that the vapour/particle phase partitioning of organic chemicals in the atmospheric environment is usually described by octanol–air partition coefficients (K_{OA}), which are inversely proportional to the saturated vapour pressure of organic chemicals. They explored the relationship between flue gas-to-fly ash partition coefficient (Kp) values of chlorinated aromatic congeners and their K_{OA} values. The results were not fully conclusive, but they inferred that in the bag filter section, log Kp values of chlorinated aromatics were linearly correlated to their log K_{OA} values.

To assess the potential removal by AC, an adsorption factor is defined. The adsorption factor is calculated from the amount of AC added per cubic metre of flue gas and the octanol–air partition coefficient:

$$F_{ads-AC} = \frac{DOSE_{AC}}{DOSE_{AC} + 1/K_{OA}}$$

In which:

$F_{ads\text{-}AC}$	the activated carbon adsorption factor (-)
$DOSE_{AC}$	dose of activated carbon to flue gas ($m^3_{AC}.m^{-3}_{flue\ gas}$)
K_{OA}	octanol–air partition coefficient ($m^3_{octanol}.m^3_{air}$).

A dosing rate of 100 $mg.m^{-3}$ is used (Cabot, 2016) and for the bulk density we took an average value of 400 $kg.m^{-3}$ (Inaqua, 2021), leading to dosing of $2.5 \cdot 10^{-4}$ $m^3_{AC}.m^{-3}_{flue\ gas}$.

Using these values to calculate the adsorption factor it appears that substances with a log K_{OA} value higher than 2 are significantly bound to

AC. Based on the octanol–air partition coefficients derived by Wang Z. et al. (2011), all of the 134 individual PFASs included in their study had calculated log K_{OA} values of 2 or higher, the lower values applying to the smaller molecules. Only perfluoroaldehydes with a fluorinated chain of 4 and 5 carbons had a slightly smaller log K_{OA} of 1.68 and 1.93, respectively, the perfluoroalkanes having the lowest log K_{OA} values, 0.29 and 0.87 for C_4F_{10} and C_6F_{14}, respectively. For the PFASs included in the study by Gomis et al. (2015) only Novec 1230, had a log K_{OA} lower than 2; for all the other PFASs the log K_{OA} is at least two orders of magnitude higher.

The calculated adsorption factors are presented in Appendix V. From the calculations it is expected that the applied AC, coke or lignite has a strong potential to filter out most of the PFASs from flue gas. For those compounds that tend to pass through the scrubbing stages, it is expected that PFIAs, FTIs, PFCs, FTOHs, Novec 1230 and FTMACs are also not filtered out by treating the flue gas with AC, the smaller molecules with higher saturated vapour pressures having the lowest binding potential.

Expected to be adsorbed to a low degree by AC are: FTOs, FTIs, PFIAs, PFCs, FTOHs < 6:2 FTOH, Novec 1230 and FTMACs.

The adsorption factor only provides an indication of the potential binding to AC. As discussed, there are many factors that determine the actual removal efficiency that are not taken into account such as temperature, residence time and certain substance-specific properties. This model takes into account only the affinity of the chemical to carbonaceous material, with octanol as a surrogate and the tendency of a molecule in the gas phase to adhere to particulate material by means of the saturated vapour pressure. In this study the adsorption factor is used as a qualitative measure of removal efficiency in order to compare the different PFASs and indicate which PFASs are most likely not to be removed efficiently by AC treatment.

5.2.4 *Overall removal of PFASs in flue gas treatment*

The qualitative assessment of the overall removal of PFASs in the flue gas treatment system is presented in Appendix V. The overall removal factor combines the removal efficiency of each three individual flue gas cleaning step. The overall removal factor is calculated as follows:

$$F_{rem-overall} = 1 - (1 - F_{abs-quench}) \cdot (1 - F_{abs-SO_2}) \cdot (1 - F_{abs-venturi}) \cdot (1 - F_{ads-AC})$$

In which:

$F_{rem-overall}$	overall removal factor for the flue gas cleaning (-)
$F_{abs-quench}$	absorption factor for the quench (-)
$F_{abs-SO2}$	absorption factor for the SO_2 trap (-)
$F_{abs-venturi}$	absorption factor for the venturi wash (-)
F_{ads-AC}	adsorption factor for the AC cleaning (-).

From the calculated removal factors it can be concluded that the majority of PFASs are removed effectively from flue gas. Some groups of PFASs are more difficult to remove. Based on the calculated removal factors, the overall removal is expected to be limited for the following groups: FTOHs < 6:2 FTOH; FTOs; FTIs < 8:2 FTI; PFAIs; PFCs; the fluorinated aldehydes; NOVEC 1230 and the fluorotelomer acrylates.

5.3 PFAS measurements at incineration plants

To gain sufficient insight into the occurrence and emission routes of PFASs, measurement and monitoring at the different stages of the process at an incineration plant can be helpful.

First, attention is given to available methodologies for sampling and chemical analysis of the composition and emission of PFASs via flue gas.

In the remainder of this chapter, studies on various PFAS emission pathways are discussed in detail. The focus is on flue gases and bottom and fly ashes. Additional information is provided on PFASs in ambient air at or near incinerators, landfills and transfer stations of PFAS-containing waste and ashes. Also included is information on PFAS leaching and wastewater from these sites.

5.3.1 Introduction to the measurement of PFASs in flue gas

A perfect, complete combustion of PFASs results, in theory, in the emission of water, CO_2, HF and, depending on the functional groups in the PFAS, sulphur dioxide, phosphorus oxide and nitrogen dioxide. These combustion products are not specific to the combustion of PFASs, but are also formed by the combustion of other chemicals that are present in municipal and industrial waste materials. HF, for example, originates from the incineration of various inorganic and organic fluorine compounds that are found in waste, including PFASs. More insight into the presence of PFASs and their relationship with HF in flue gases is obtainable by the availability of validated and standardised measurement methods for the quantification of the emissions of PFASs to the air.

This RIVM study looked at the availability and the validity of methods for the determination of air emission of PFASs from the flue gases emitted by waste incineration plants. Currently, there is a lack of standardisation of measurement methods. This has partly to do with the absence of legal standards for the emission of PFASs to the air. There are, however, emission standards for PFOA and PFOS (Risks for Substances, 2020). An overview of these can be found in Table 10, which also includes the emission limit values for hazardous substances in the flue gases from waste incinerators obtained from the Dutch Activities Decree (Infomil, 2020). Unlike PFASs, there are standardised measurement methods for HF and polychlorinated dioxins, furans and dioxin-like PCBs. The substances mentioned present comparably problematic environmental and health issues that made it necessary to regulate these substances. They triggered the development of methods for sampling, sample preparation and chemical analysis in flue gases that could be valid for PFAS as well, e.g. parts of the standardised methods for dioxin, C_xH_y and HF measurements may also be suitable for PFASs.

Table 10 Emission limit values and mass flows of the air emission of PFOA, PFOS, HF and 2,3,7,8-tetrachlorodioxin in the Netherlands and emission limit values for waste incinerators in milligrams per (normalized) cubic metre

Substance	**Emission limit [a] value**	**Mass flow**	**Substance[h] classification**
	milligrams per Nm^3	grams per hour	
PFOA	1	2.5	MVP2
PFOS	0.05	0.15	MVP1
HF	3	15	gA.2
2,3,7,8-TCDD [b]	0.1 [c]	20 [d]	ERS
	Emission limit values for waste incinerators[e]		
	half-hour and daily average		
PM	5		
C_xH_y	10		
HCl	8		
HF	1		
SO_2	40		
NO_x	180		
CO	30		
Hg	0.05		
Sum Cd and Tl	0.05		
Sum Sb, As, Cr, Co, Cu, Pb, Mn, Ni and V	0.5		
Sum dioxins and furans [f]	0.1 [g]		

a) Source: Risk for Substances (2020).
b) 2,3,7,8-tetrachlorodibenzodioxine(TCDD).
c) 2,3,7,8-TCDD has a toxicity equivalence (TEQ) factor of 1, which means that the given value, which should be expressed in nanogram TEQ per Nm^3, can also be expressed in nanogram per Nm^3.
d) 2,3,7,8-TCDD has a TEQ factor of 1, which means that the given value, which should be expressed in milligram TEQ per year, can be expressed in milligram per year.
e) Source: Infomil, 2020 (Dutch Activity Decree, article 5.19, table 5.19)
f) The sum of 17 congeners calculated in toxic equivalents to 2,3,7,8-TCDD with the help of the corresponding TEQ per congener.
g) The emission limit value expressed in nanograms TEQ per Nm^3
h) The emission values of SVHC are classified in order of increasing hazard: MVP2, MVP1 and ERS. MVP (in Dutch: minimalisatieverplichting) is a substance classification meant to take effort to minimise the emission of SVHC. ERS (in Dutch: extreem risicovolle stof) is the most critical hazard category of SVHC.

5.3.2 *Scientific literature on measurements of PFASs in flue gas*

There are many applications published about the use of analytical techniques to detect, identify and quantify PFASs. However, the measurement methods mainly concern the chemical analysis of environmental matrices such as soil, groundwater, surface water, sediment and drinking water. Only a few scientific publications on PFAS measurements for the determination of the PFAS concentration in the flue gases were found. On-site measurements of PFASs in ambient air and emission concentration measurements of PFASs in flue gases in particular have hardly been tested, but are now attracting worldwide attention.

In 2009, a Norwegian research group published a list of degradation products of different fluoropolymers on the basis of a review of various publications (Huber et al., 2009). The studies included in the review relate mainly experimental research on laboratory scale to the hypothesis about the reaction mechanisms and the identification of products of pyrolysis and combustion of fluoropolymers. They conclude that fluoropolymers such as PTFE-containing waste treated in incinerators cause the formation and emission of greenhouse gases. During combustion PTFE at a temperature between 750 and 1050 ºC, fluorocarbons such as CF_4, CHF_3, C_2F_6, C_3F_6 and C_4F_8 are formed. Huber et al. (2009) recommended developing and validating measurement methods to determine of the emission concentrations and emission loads of these substances.

Much later, it was established from a presentation by the US EPA that no standardised methods are yet available for measuring emissions of PFASs in the flue gases of waste incinerations (Ryan, 2019). The presentation mentions a series of interesting sampling and analysis techniques to measure polar, non-polar, non-volatile, semi-volatile and volatile PFAS compounds in the flue gases. For the discontinuous time-averaged measurements of the PFAS emission concentrations, the modified EPA MM5 method was used (EPA, 1986). The flue gases are isokinetically sampled with a (heated) probe placed in the chimney. The flue gases pass through the probe connected to a heated (glass fibre) filter unit, followed by an XAD-2 adsorbent column and three series-connected impingers. The first two are filled with deionised water or a 0.1 molar sodium hydroxide, sodium acetate or sodium borate water solution. The third and final impinger contains silica gel to retain the moisture still present before the flue gas leaves the sampling unit and is released into the ambient air. Optional is the placement of a second column of XAD-2 adsorbent between the second and third impinger for the purpose of identifying any breakthrough of PFAS from the first XAD-2 column. Ideally, there should be no breakthrough. If there is, the chemical analysis of the second XAD-2 column will help determine the correct final emission concentration PFAS. The sample materials such as filters, XAD-2 adsorbents, impinger fluids and methanol or ammonium sweep liquids are then chemically analysed for PFAS. The various samples can be measured with an HPLC-MS/MS after suitable work-up of extraction, purification and concentration. This analysis technique is now fairly standard in the chemical analysis of non-volatile, semi-volatile, non-polar and polar PFAS compounds in modified water measurement solutions. The volatile neutral PFAS compounds having boiling points below 100 °C may be sampled in a SUMMA canister. This is a metal vessel that can be brought to underpressure or overpressure and is equipped with connectors, valves, flow controllers and a pressure gauge. For the sampling of the flue gases the canister is connected in an identical manner to the train of XAD and impingers by a probe that is inserted into the chimney and is provided with a heated filter unit. The sampling into the canister, which is set under pressure, starts as soon as the valve is opened. In addition to sampling by underpressure, it is also technically possible to sample the flue gases by overpressure in the canister with the aid of a pump. The metal inner wall of the canister is specially treated to make it inert to PFAS and other substances. After completion of the sampling procedure, the canister is easily disconnected after closing of the valve. Thereafter, the canister is easily connected to a GC-MS to start the chemical analysis. The analysis is in accordance with EPA TO15 method, wherein the composition of the standard substance mixture should be adjusted in line with the choice of target PFAS substances (EPA, 1998).

The sampling method illustrated in the EPA presentation makes it possible to determine the emission concentration of both dusty PFASs and gaseous PFASs. Relevant performance characteristics of the measurement methods such as the limit of determination, measurement range and reproducibility are not presented. An overview of the measured values is also not presented.

A German research group has largely used the same sampling method for discontinuous HF and PFAS emission measurements (Aleksandrov et al., 2019). A pilot plant was used for this, which was equipped with the best available techniques for combustion and flue gas cleaning in accordance with German legislation. The measurements were performed with a train of serially coupled filter units, impingers filled with absorption liquids and XAD/PU adsorbent columns. The method differs from the EPA method in terms of the sample train configuration, in which the solid adsorbent column is placed after the second impinger instead of before the first impinger. A chemical analysis was performed to determine the emission concentration of 31 individual PFAS compounds. For this purpose, the filters, impinger fluids and XAD/PU adsorbent columns were analysed with HPLC-MS-MS on the content of the individual PFAS compounds. The researchers performed another chemical analysis to determine the total fluorine content in the fuels, the dust-like flue gas particles collected on filters, and the gaseous fluorine in impinger water solutions and the XAD/PU adsorbent columns. The gaseous part of total fluorine was analysed with an ion chromatographical measurement technique to determine the fluoride levels of the aqueous solution that remained after treatment the absorption media. The particulate fluorine fraction in the collected fly ash was chemically analysed after a pyrohydrolytic treatment with a potentiometric (fluoride ion-selective electrode) measurement in the resulting water solution. Based on an analysis of the fluorine balance, it was concluded that the contribution of dust-bound fluorine in flue gases is negligible compared with that of gaseous fluorine. It is not clear whether this means that the fraction of dust-bound/dust-like PFASs in the filter is also negligible, or not above the limit of detection (LOD) of the measurement method. The LOD is equal to three times the value of the standard deviation of a blank measurement. The limit of quantification (LOQ) equals ten times the value of the standard deviation of a blank measurement. Nothing about the experimental fluorine limit values was disclosed in the investigation. The LOQ of the chemical analysis of the 31 individual PFAS compounds amounts 0.3 µg.m^{-3} to the majority of the substances. The limit depends on the sample volume of flue gas emissions. In this study, 100 litres or 0.1 cubic metre was taken by isokinetic sampling at 4 litres per minute for a period of 25 minutes. The measurements show that the PFASs were not detected above their LOQ, so that they cannot be quantified. The LOQ of the gaseous fluorine as fluoride was also not reported. However, this can be derived from other publications and standard regulations (Ministry of the Environment of Japan, 2013; Standard Committee, 2009). Starting from the above-mentioned sampling method, an LOQ of gaseous fluorine of about 0.3 mg.m^{-3} can be derived. Taking into account the measurement uncertainty, this limit value is more than sufficiently low to be able to test whether the emission limit value of HF is exceeded. On the basis of the published results a relationship between the air emission of dust-bound/dust-like and gaseous PFASs on the one hand and dust-bound/dust-like and gaseous fluorine on the other hand is not sufficiently clear.

A course for environmental professionals on the topic of PFAS sampling presented several methods of air sampling and chemical analysis of PFAS (EPOC, 2019). The air measurements included both emissions of flue gases and ambient air concentrations of PFASs at locations near emission sources. These sources included industries that make and use PFASs and incinerate PFAS-containing waste. As explained, the methods of sampling PFASs in the flue gases of waste incinerators correspond to those of the EPA presentation and the research of Aleksandrov et al. (2019).

In Harlingen (the Netherlands) the Residual Energy Plant (REC) burns household waste for the production and supply of energy to companies and households in the region. In 2016, this plant carried out a project in which time-averaged measurements of chlorinated dioxins/furans, dioxin-like PCB, brominated dioxins, brominated diphenyl ethers and the sum parameters of PFOA and PFOS were measured. In January and February, a total volume of 461.7 m^3 of flue gases was sampled for 30 days. Afterwards, the collected sample media were chemically analysed for the aforementioned substances by a German laboratory with the aid of high-resolution HRGC-MS. An emission concentration of the sum of PFOA and PFOS of 0.0143 ng.m^{-3} was reported. This measurement value includes the determination limit value of 0.00108 ng.m^{-3} (Eurofins GfA Lab Service, 2016). We note that in this study a large volume of the flue gases was sampled compared with the 0.1 m^3 in the PFAS emission measurements of the pilot plant (Aleksandrov et al., 2019). This also deviates from the flue gas volume to be sampled according to standard measurement methods for determining dioxin emissions, which is approximately 4 m^3. The LOQ of the sum of PFOA and PFOS can be estimated on the basis of a calculation at 0.13 and 0.50 ng.m^{-3} if 4 or 0.1 m^3 of the flue gases, respectively, are sampled. Compared with the previously mentioned 0.3 µg.m^{-3} for individual PFAS compounds, the calculated LOQ is a factor of 600 lower. The large difference is probably due to differences in the methods of extraction, purification and concentration during sample pre-treatment in the laboratory. Detailed information on the emission measurements carried out on the sample before treatment was not made available.

Intermezzo

Half an hour to several hours of isokinetic flue gas sampling is common for discontinuous time-averaged emission measurements from stationary sources. A relevant example is the standardised measurement of dioxins and dioxin-like PCBs according to NEN-EN 1948:2006. Part 1 of the measurement standard describes three variants of the method to detect dioxins and (dioxin-like) PCBs in *the flue gases (Standard Committee, 2006a). This is very similar to published methods of PFAS emission measurement such as the EPA MM5 method (EPA, 1986). In order to maintain the performance characteristics of the measurement method for dioxins and PCB described in part 3 of the NEN-EN standard, the sample volume must be at least 4 m^3 (Standard Committee, 2006b). This can be achieved with an isokinetic gas flow rate in the range 0.5–5.0 m^3 per hour, depending on the sampling method chosen in part 1. In meeting these requirements an LOQ of the individual dioxins can be established in an emission concentration range from 0.1 to 8.8 picograms per (normalised) m^3.*

The international and Dutch measurement standard ISO-NEN 15713: 2011 is suitable for measuring the emission concentration of gaseous fluorine in stationary point sources (Standard Committee, 2011). The sampling method is the same as that of the EPA-MM5 method. The difference from the ISO-NEN method is the fact that it does not contain any columns with solid adsorbent in the sampling train.

In accordance with ISO-NEN 15173:2011, the measurement of hydrogen fluoride in the flue gases of incineration plants should determine the emission of HF to the atmosphere for assessing the exceedance of the emission limit value mentioned in table 10 This follows from the measurement obligation of Article 5.29 of the Dutch Activities Decree. The chemical analysis in the laboratory of the collected impinger fluids for fluoride content is carried out according to the measurement standard using a fluorine ion-selective electrode. Fluoride measurement is also possible based on an ion chromatographic analysis of anions and conductivity detection (NEN-EN-ISO 10304-1). The LOQ for fluoride converted to HF in flue gases for both analysis methods is set at 0.1 mg.m^{-3}. This is based on approximately 4 m^3 of sampled flue gases.

5.3.3 *Discussion and conclusions on PFAS emission measurement methods*

It cannot be ruled out that, due to differences in the methods and laboratory tools used for sampling, sample pre-treatment and measurement, other factors and circumstances may influence the comparability of the performance of the PFAS emission measurements of the flue gases of waste incinerations. At the same time, they can explain the differences in the LOQ up to a factor of 1000. This is therefore a reason to standardise the measurement methods. From the foregoing it is clear that larger sample volumes of flue gases result in a lowering of the LOD and LOQ.

A target list of PFASs can be used to screen for the detectability and emission concentration of selected PFAS compounds. The target list includes compounds for PFAS pure standard substances and their corresponding C^{13} labelled isotopes for laboratory tests. The preparation and chemical analysis of appropriate concentrations of standard mixtures of PFASs make it possible to quantify the emission concentrations of the individual PFASs of the target list in flue gases. Because of the broad spectrum of substance properties within the PFAS group, the target list serves best for statements about (the behaviour of) PFASs as a whole, and therefore all possible properties should be represented. A selection of only about 30 substances, such as in the advisory list of PFASs to be measured in (aquatic) soil (Table 1), implies that uncertainty is accepted because only some of the known PFAS groups are represented. This was extensively discussed in Chapter 2, on the definition and properties of PFASs.

The Knowledge Document of the Expertise Centre PFAS (Pancras et al., 2018) refers to a PFAS target list of approximately 30 standard substances that has been compiled on the basis of the latest insights. These substances are routinely offered by contract laboratories for the PFAS analysis. However, the list is mainly used for the accurate measurement of PFASs in liquid and solid environmental matrices. The list is also discussed in Section 2.2.2.

The suitability of such a target list for the air emission measurements of stationary sources of waste incineration is open to discussion. As indicated above, short-carbon chain (≤C6), non-polar and gaseous PFASs are to be expected in the flue gases. These are suitable for measuring with GC-MS, with options for variation in the configuration of the MS instrumental part. The advantage is that these PFASs does not first have to be transformed into a water solution. However, effective adsorption or absorption and preferably a process of concentration of the PFAS must be carried out. This sample treatment must be developed and validated in a measurement method. The previously explained sampling technique with the use of canisters requires hardly any additional treatment before a chemical analysis with GC-MS takes place.

It is possible to search for non-target PFAS substances. These are PFAS compounds that do not occur in the standard substance mixtures of the chemical analysis, but can be characterised and identified by applied mass spectrometric detection methods with the help of smart software data processing techniques. A common technique is HPLC-ESI-tandem-MS. For the GC-MS analysis, a 'hard' ionisation method by electron impact of the MS is suitable for the characterisation of the PFAS compounds. The ionisation method is fairly standard for the detection and identification of organic compounds in environmental samples. The choice for 'soft' ionisation methods such as positive or negative chemical ionisation are also applicable.

Relationship between measured PFASs versus total fluorine and total organic fluorine (TOF) in flue gases
If we compare the LOQ of the HPLC-ESI-tandem-MS or GC-MS analysis of individual PFAS compounds with that of the ion chromatographic or potentiometric analysis of fluoride, it is clear that the LOQ of the fluoride analysis is intrinsically a factor of 1000 higher. This implies that the detection limits are also related in the same way. The LOD is by definition a factor of 3 lower than the LOQ. Due to the lower LOD for the PFAS measurement, we can expect that individual PFAS compounds can still be detected if the fluoride measurement does not exceed its LOD.

In addition to the measurement of fluorine, analytical methods have now been developed to determine the total content of the organic fluorine compounds. These are referred to as TOF (total organic fluorine) analyses. The Knowledge Document (Pancras et al., 2018) mentions, among other things, the combustion ion chromatographic TOF analysis method for determining the content of organic bounded fluorine compounds in environmental matrices such as groundwater and surface water, sediment and soil. Variants of the TOF analysis are further explained in various scientific publications (Abercron et al., 2019; Yeung et al., 2013; Miyake et al., 2007). These essentially involve solid phase extraction (SPE) or liquid extraction (LLE) of the organic bounded fluorine compounds from sample matrices. A measured volume of the organic extract of the sample is injected into an oven at a temperature of about 1000 °C. The TOF converts to inorganic hydrogen fluoride, which is then absorbed into a water liquid. A partial volume of the absorbing liquid is analysed by ion chromatography in which the anions such as fluoride, chloride, bromide, sulphate are fractionated and detected. The analysis technique largely corresponds to that of the standardised HF measurements in the flue gases. The LOQ of the TOF measurement depends on the maximum reconcentration step during the SPE or LLE. A limit of between 2 and 10 $\mu g.L^{-1}$ in the impinger fluids is achievable. This corresponds to a range of 50–250 nanogram TOF per m^3 in the flue gas, which is still well above that of the achievable LOQ of individual PFAS compounds. Although the TOF is more selective for the detectability of PFAS concentrations and on that basis is a better indicator measurement, the disadvantage remains that the expected LOQ of the TOF measurement still seems inadequate. This means that the TOF measurement is also a less suitable indicator for the detectability of PFAS in flue gases.

5.3.4 *Fly ash and bottom ash: PFAS composition and emission*

In addition to their emission via the flue gas from waste incineration plants, PFASs may also be present in bottom ash and fly ash. They can occur in ashes as a result of the incomplete combustion of municipal and industrial waste. Therefore, the ashes can form an additional emission source. Emissions depend on how the ashes are treated and used. Bottom ash and fly ash are used as secondary building materials in many construction applications. Where bottom ash and fly ash do contain PFASs, the storage, transportation, processing (to make the ashes suitable as building materials) and use (especially given their long presence in building and road construction sites) are potential sources of PFAS emissions. Emissions can, for example, result from the blowing-away of dust-bound PFASs and the leaching of water-soluble PFASs after contact with (rain) water.

Besides measurements of PFASs in flue gases, a few studies have measured PFASs in bottom ash and fly ash.
Particularly interesting is the experimental study on PFASs in bottom ash, fly ash, condensation water and waste water from four waste incineration plants in Sweden (Sandblom, 2014). All four plants were operating in line with the laws and regulations set by the EU and the Swedish government (European Parliament, directive 2000/76/EG; Miljöbalken, 1998: 808; Avfalsförordning, 2011: 927). This means that the waste is incinerated at a minimum temperature of 850 °C. Chemical analysis methods have been developed and validated in this experimental study. Table 11 provides an overview of the reported measurement values of a target list of eight

perfluorocarboxylic acids and one perfluorosulphonic acid with chain lengths of 4 to 12 carbon atoms. The best known are PFOA and PFOS.

Table 11 Average values of the PFAS acids in bottom and fly ash in µg.kg^{-1} *(ng.g*$^{-1}$*) and PFAS concentrations in condensation and waste water in ng.L*$^{-1}$ *in four incineration plants in Sweden*

PFAS	**Bottom ash**[a]	**Fly ash**[a]	**Condensate water**	**Waste water**[b]	**LOD Solid samples**	**LOD**[c] **Water samples**
PFBA	1.148	0.384	*3.74*–6.68	*3.74*	0.170	3.74
PFHxA	0.832	1.772	*0.312*–5.91	0.614	0.024	0.312
PFOA	0.196	0.395	*0.874*–1.88	*0.874*	0.013	0.874
PFNA	1.877	5.909	*0.932*–8.69	*0.932*	0.022	0.932
PFDA	0.141	0.318	*0.165*–9.71	*0.165*	0.114	0.165
PFUnDA	0.088	*0.085*	*0.244*–1.82	*0.244*	0.085	0.244
PFDoDA	*0.118*	*0.118*	*0.285*–2.90	*0.285*	0.118	0.285
PFHxS	0.014	0.027	*0.122*–0.298	0.158	0.003	0.122
PFOS	0.380	1.778	*1.52*–2.04	*1.52*	0.128	1.52

Note: The values in italic are concentrations at the LOD.

a) Refers to average values of chemical analyses of samples gathered from four waste incineration plants.
b) Relates to one sample from one of the four waste incineration plants.
c) LOD is 3 times the standard deviation of measurements at blank level and corrected for blank matrix effects.

Source: Sandblom (2014).

Particularly striking is the variation in measurement values of the condensation water. The variation might be assumed to be caused by taking samples at different points in the flue-gas cleaning process. The wastewater was sampled and chemically analysed only once at one of the four incineration plants. The research shows that the waste incineration installations do not fully destroy the PFAS. The sum value for the concentration of PFAS carboxylic acids with chain lengths from C4 to C12 are quantified at a level of 10 µg.kg^{-1} in bottom and fly ashes. The condensation water contained a level of 30 ng.L^{-1} of the sum value. The waste water in this study contained a sum value at the level of the LOQ.

The analytical methods developed are found to be valid and fit for the purpose of quantifying the individual target PFAS compounds in the solid and water samples. The methods for sample pre-treatment, such as digestion, extraction, purification and concentration, as well as for chemical analysis with HPLC-MS/MS are similar to other analytical methods. This applies to the chemical analysis of soil, fly ashes, condensation and waste water. The laboratory research was carried out with sufficient quality control and quality assurance. One plant used internal standards, C^{13} labelled standard PFAS compounds and the determination of a number of performance characteristics such as LOD, recovery, blank analysis procedure, precision and bias.

The limitation of this study is that the list of selected PFAS compounds does not fully represent PFASs as a group. As a result, there are uncertainties about the nature and quantity of the categories of PFAS not included in the study. There may thus be an underestimation of the actual PFASs issued, such as non-polar neutral PFASs, short-chain versus long-chain PFASs, volatile versus non-volatile PFASs and precursors of PFASs, the nature and size of whose influence is unknown.

The concentrations of PFASs in bottom ash and fly ash, measured at two sites owned by the AVR in the Netherlands, are available from a report by Houben and Boerleider (2020); see Annex IV. Concentrations in the fly ash from the Rotterdam-Botlek site were sampled only once and were all below the LOD of 0.1 μg.kg^{-1}. With regard to bottom ash, the highest concentrations were measured at the site in Duiven. At the Rotterdam-Botlek site only 4 of the 34 substances were found to be above the LOD, namely 6:2 FTS, PFBS, PFAS and 8:2 FTS. At Duiven, of the PFASs analysed, 19 were found to be above the LOD, 6:2 FTS having the highest concentration of 36 μg.kg^{-1}. The concentrations in the bottom ash varied considerably. Of the three measurements at the site in Duiven at least one was below the LOD of 0.1 μg.kg^{-1} for all 19 PFASs.

Using the highest measured concentrations per substance, the total concentration of PFASs in the bottom ash at the site at Duiven is 48.95 μg.kg^{-1}. Using the total annual amount of bottom ash generated at this site (125,000 tonnes; Houben and Boerleider, 2020), this results in a total amount of about 6.12 kg PFASs per year in the bottom ashes. This amount should be considered as a high estimate because the highest concentration for each substance was used for calculating the total amount of PFAS. Furthermore, the concentration is mainly determined by just one substance, 6:2 FTS. In many samples the concentrations were below the LOD for the same substance in different samples. Therefore, the numbers should be considered as indicative and additional measurements at other waste incineration sites are needed to obtain a representative picture.

A recent study investigated PFAS emissions from bottom and fly ash via leaching at various landfills in Florida (Solo-Gabriele et al., 2020). The landfills studied included sites filled with mixed bottom ash and fly ash, sites filled with bottom ash, fly ash and (unburned) municipal waste and sites filled with bottom ash, fly ash, municipal waste and gas condensate. Landfills with exclusively municipal waste and landfills with construction and demolition materials were also included. A chemical analysis was performed for 11 individual PFAS compounds, including seven perfluorocarboxylic acids, three perfluorosulphonic acids and one precursor 5:3 fluorotelomer carboxylic acid. The findings showed that almost all PFAS compounds were above the LOD in the leachates. The lowest measurement values were found in the leachate from landfills with 100% mixed bottom ash and fly ash in a concentration range from 0.1 μg.L^{-1} to 0.6 μg.L^{-1}. For the other two types of landfills the measured concentrations were up to a factor of 10 higher for the majority of PFASs. The relevant PFAS compounds found in the leachates of the sites filled with only bottom ash and fly ash were quantified at 0.25 μg.L^{-1} (PFOA) and 0.12 μg.L^{-1} (PFOS). Solo-Gabriele et al. (2020) also looked at the measured values for the sum of the 11 PFAS compounds and the relationship of the leaching of PFAS from ashes formed with the different combustion temperatures. There appears to be a consistent relationship between the concentration of PFASs in the ashes available for leaching and the combustion temperature at which the ashes are formed. The ashes in landfills originating from the waste incinerations plants with the highest combustion temperatures, namely 930–980 ºC, contain sum levels of PFAS target compounds in the leachates up to a maximum of 3.4 µg.L^{-1}. The sum value increases to 8.4–8.7 µg.L^{-1} for ash originating from incineration plants with combustion temperatures of 815–870 °C. The highest values were found for ashes from plants with combustion temperatures of 760–870 °C, namely from 12.3 to 13.5 µg.L^{-1} for the sum of 11 PFAS target compounds.

The samples of leaching water from the landfills were taken onsite by drilling monitoring wells to a depth of a few centimetres and 10 metres. The water samples were collected in HDPE 0.5-litre bottles. The chemical analysis of the PFASs was performed by the laboratories of the EPA in Triangle Park in Raleigh, USA. Sample preparation consisted of an addition of internal standards and corresponding isotope-labelled substances. The filtration was carried out with a glassfibre filter, followed by solid phase extraction with SPE columns in two batches with Oasis WAX cartridges and Envicarb cartridges. The SPE was eluated with a mixture of ammonium hydroxide and methanol (1: 1000). After evaporation with nitrogen until dry, the residues were added with 2.5 molar ammonium acetate preparing measuring solutions for the chemical analysis of the PFAS. A time-of-flight HLPC/MS was used as the selected analysis technique. The LOQ was 300 ng.L^{-1} for the majority of the target PFAS compounds. This suggests that the LOD is 100 ng.L^{-1}.

It is noticed that the LOD of the analytical method of the Swedish study (Sandblom, 2014; see Table 11) is approximately a factor of 100 lower.

Intermezzo
In outline, the sample preparation and the technique of chemical analysis of various analytical methods for the determination of PFAS in water matrices such as surface water, drinking water, wastewater and groundwater are rather standard. The methods are available from a number of commercial and institute laboratories located in the Netherlands. Chapter 7.2.2 of the Knowledge Document of the Expertise Centre PFAS contains a description of the standard applied analytical technique of the HPLC-MS-MS for the determination of the PFAS content of water. Detection limits of 0.65 to 1.0 ng.L^{-1} are achievable for these measurement methods. In wastewater, the detection limits are slightly higher according to the Knowledge Document. The LOD of PFAS in groundwater of 5 ng.L^{-1} is sufficient low to measure PFAS, while for surface water it should be 0.5 ng.L^{-1}, according to the Knowledge Document. Standards developed worldwide for the determination of PFAS in water matrices include:
ISO 25101: 2009*. This method is suitable for the analysis of PFOS and PFOA in unfiltered drinking water, groundwater and surface water (fresh and salt water) and can be used in a concentration range of 2.0 to 10,000 ng.L^{-1} for PFOS and 10 to 10,000 ng.L^{-1} for PFOA (Technical Committee, 2009).*
US EPA method 537.1: *This modified method contains a target list of 18 PFAS compounds consisting of 11 carboxylic acids, 4 sulphonic acids, 2*

precursors of sulphonamide acetic acids and FRD-903 (HFPO-DA or a PFAS in the GenX process). Depending on the PFAS compound, the LOD lies in a concentration range of 0.53 to 6.3 ng.L^{-1} (EPA, 2020).
DIN 38407 -42*. This German method is suitable for the determination of the concentration of PFAS in drinking, ground, surface and waste water. The LOD lies between 10 and 25 ng.L^{-1}, depending on the matrix (National Committee, 2011).*

In their conclusion Solo-Gabriele et al. (2020) recommend further investigation of the contribution of precursor PFASs, which can increase the total of persistent PFASs. This recommendation also applies to research into the composition of ash, condensation and waste water (Sandblom, 2014). The Knowledge Document of the Expertise Centre PFAS (Pancras et al., 2018) contains an explanation of the total oxidisable precursor PFAS (TOP) analysis in chapter 7.2.4. The analytical method was developed to investigate the broad spectrum of PFASs, the principle being that a sample on the target list of PFAS is analysed before and after the oxidation step according to the method for the PFAS analysis of water samples. The difference calculated from the PFAS concentration analysed before and after the oxidation yields the concentration for the PFAS precursors. The oxidation takes place in the sample treatment through a thermolysis of persulphate to the formation of hydroxyl radicals, which, in turn, convert the precursors into stable perfluorocarboxylic acids.

In another recently published study the emission of PFASs from municipal waste was measured at three landfills, two temporary storage sites and two industrial waste incineration plants in Tianjin, China (Wang et al., 2020). The measurements were carried out for (1) air emissions due to evaporation of volatile PFAS and/or blowing-up of dust-bound PFAS and (2) leaching through contact of rainwater with the waste containing PFAS.

The air measurements were carried out per object at various strategic measurement locations by passive sampling with Sorbent Impregnated Polyurethane (SIP) foam disks. With an air flow rate of 4 m^3 per day, a total volume of 120 m^3 was sampled over a period of 30 days. The sample handling was carried out in accordance with good laboratory practice by packaging the disks in aluminium foil and preserving the storage conditions (frozen at -20 °C) until the start of the chemical analysis in the laboratory. Of the PFAS target list to be screened, 22 ionisable PFAS components were analysed with HPLC-MS/MS and 7 neutral PFAS components with GC-MS. The seven neutral PFAS are 6:2, 8:2 and 10:2 fluorotelomer alcohols; N-methyl and N-ethyl perfluorooctane sulphonamides (N-MeFOSA and N-EtFOSA); N-methyl and N-ethyl perfluorooctane sulphonamide ethanols (N-MeFOSE and N-EtFOSE). Of the ionisable PFAS there are 11 perfluorocarboxylic acids (C2-C12), 3 perfluorosulphonic acids (C4, C6 and C8), 6:2 and 8:2 fluorotelomeric unsaturated acids (6:2 and 8:2 FTUCAs), 6:2 and 8:2 Cl-PFAESs and 6:2 and 8:2 diPAPs. Depending on the individual PFAS compounds, the method detection limit is between 0.03 (N-MeFOSA) and 0.22 (N-EtFOSE and 6:2 FTOH) pg.m^{-3}. The analytical method for the determination the ambient air concentration of PFASs was developed and validated several years earlier (Tian et al., 2018).

Approximately 0.5-litre water samples of the leachates (n = 14) and the effluents (n = 8) were taken in duplicate and collected in polypropylene bottles (Wang et al., 2020). The effluent is the leachate that has undergone a biochemical treatment. Good laboratory practice of packaging, coding, preservation, transport and transfer to the analysis laboratory was performed. All samples of leachates and effluents were also chemically analysed for the concentration contribution due to the presence of precursor PFAS compounds. A previously developed TOP analytical method was used for this. The oxidation step, as explained in the Knowledge Document, was carried out with potassium persulphate at a temperature of 85 ºC for a period of 6 hours. The water samples were chemically analysed before and after oxidation using solid phase extraction over oasis WAX SPE cartridges. The sample treatment and measurement are largely in accordance with other published analytical methods using HPLC-MS/MS. The performance characteristics of the analytical method used are also in line with those of other analytical methods.

Wang et al. (2020) conclude that PFAS emissions occur particularly through the leaching of PFASs from municipal waste dumps, transfer stations and industrial waste incinerators. They found surprisingly high PFAS leaching through the contribution of precursor PFAS compounds. An underestimation of the actual PFAS emissions of approximately 6 to 49% is found if only the target list of PFAS is considered.

5.3.5 *Flue gas: PFAS composition and emission*

The study by Wang B. et al. (2020) investigated the air emission of neutral PFASs. Measured air concentrations were in the range 393-19.000 pg.m^{-3}, or 0.393–19 ng.m^{-3}. Of the neutral PFASs, the fluorotelomer alcohols are dominant in the total air emissions. The ambient air concentrations of the proportion of anionic PFASs vary from 0.458 to 13 ng.m^{-3}. The perfluorocarboxylic acids are dominant here. The total air concentration of PFASs at the central measurement locations of the investigated objects was a factor of 2 to 30 higher than the measurement locations upwind per object examined. Figure 4 shows the calculated emissions of the total of neutral and anionic PFASs in kilograms per year per location (landfill site, temporary storage site and industrial site of combustion installation).

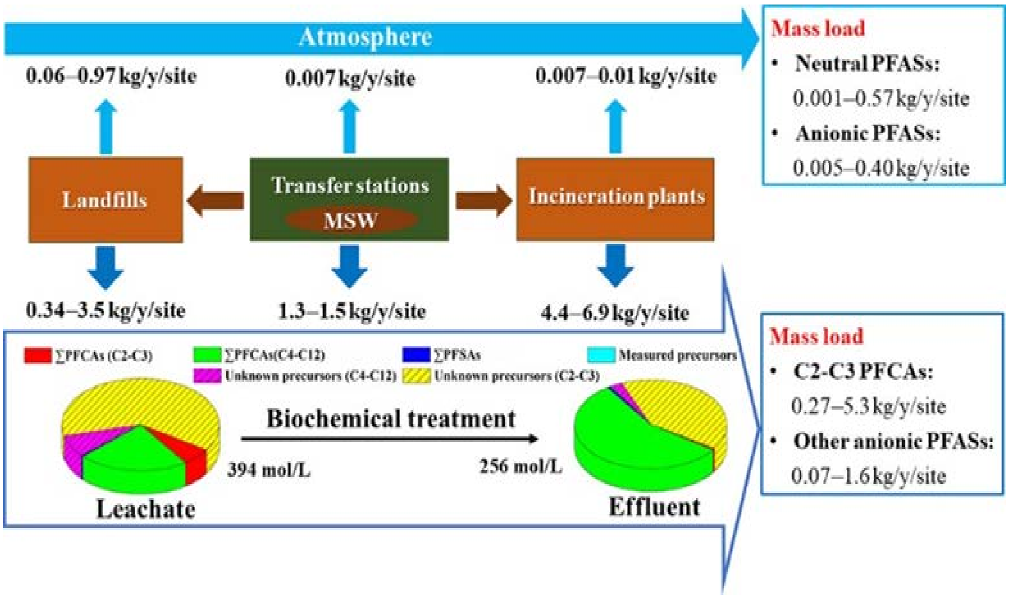

Figure 4 Mass flows for the different emission routes and waste treatments
Source: Wang et al. (2020).

PFAS measurements were also performed on flue gas at the AVR site in Rotterdam-Botlek and the results were published by Houben and Boerleider (2020). The data are provided in Annex IV. The flue gas concentrations presented are the average values of single measurements at four different stacks. The measured flue gas concentrations at the AVR site in Rotterdam-Botlek show that the highest concentration of 8.9 ng.Nm^{-3} was measured for PFOA (linear and branched). The total concentration of detectable PFASs (n = 19) was 20.26 ng·Nm^{-3} excluding the concentrations below the detection limit. Most of the 30 PFASs listed in Table 1 were included in the measurements at the site in Rotterdam-Botlek, except PFPeA. From the measured concentrations at the Rotterdam-Botlek site and the amount of flue gas produced by the three MSW incineration lines at the AVR site in Duiven (~107 000 Nm^3·hour^{-1} per line; Houben and Boerleider, 2020), a yearly emission to air of 56.8 g PFAS is calculated. The amount of flue gas relates to 394,082 tonnes of waste incinerated. These numbers result in an emission factor of 0.14 mg PFAS per tonne of waste burned. Applying this emission factor to the AVR site at Botlek, with an annual amount of 1,322,937 tonnes of waste burned, would result in emissions to air of ~191 grams PFAS per year. Th Rotterdam-Botlek site is the second largest MSWI in The Netherlands after the AEB in Amsterdam. The amounts of waste burned include not only municipal and commercial waste, but also non-hazardous and hazardous industrial wastes and filter residues (Rijkswaterstaat, 2020a). Because the information from two different sites is combined, the calculated emissions in this section should be considered with care and should be taken as indicative. Additional measurements at other waste incineration site are needed to obtain a representative picture.

Wang B. et al. (2020) estimated the total emissions to the atmosphere of measured neutral and anionic PFASs from waste incineration plants in China to be in the range of 7–10 grams per year per site (Wang et al., 2020: Figure 4). Emission factors are calculated from the estimated loads to air and the reported incineration capacity (see Table 12). The emission factors of the incineration plants in China are a factor of 3-5 lower comparted to the estimated emission factor for the site at Rotterdam-Botlek. The difference in the emission factors can mainly be explained by the difference in the set of PFASs included in the measurements. Back calculation of the emissions from surrounding air measurements introduces additional uncertainty, in contrast to direct measurements in the flue gases.

Table 12 PFAS release factors from the estimated loads to air and incineration capacity. Air loads are from Wang B. et al. (2020).

	Incineration plant	
	IP1	**IP2**
Air load (kg.year-1)		
Total neutral PFASs	2.5×10^{-3}	4.3×10^{-3}
Total ionizing PFASs	4.6×10^{-3}	7.1×10^{-3}
Total PFASs	7.1×10^{-3}	11.5×10^{-3}
Incineration capacity (tonne.day-1)	600	1200
Release factor (g PFAS/tonne waste)	$3.2.10^{-5}$	$2.6.10^{-5}$

As described above, Wang B. et al. (2020) measured 20 PFASs in leachate, and determined air emissions from landfills and stored waste and concentrations in air upwind of and in the central area of two incinerator facilities. The set of PFASs included several PFASs not measured at the AVR sites and also not included in the advisory list of PFASs to be measured in soil and water (Table 1). Those not included are 8:2 FTUCA (environmental transformation product), the 6-10:2 fluortelomer alcohols, N-EtFOSA, N-MeFOSE and N-EtFOSE. The last two were not detected in air upwind and downwind of the incineration plant, but N-MeFOSA and N-EtFOSA were. Of the anionic PFAs, PFPeA and PFHpA were detected in only a few cases (in the leachate of one landfill and in the air and leachate of one of the two incineration plants investigated). All in all, the investigated PFASs were detected at each stage, i.e. landfill site, transfer station and incineration plant, and could therefore be regarded as relevant. It should also be noted that N-MeFOSE and N-EtFOSE, PFHpA were not detected in the air samples at the incineration sites.

5.4 Conclusions

Removal from flue gas

Perfluorinated acids such as perfluoroalkyl sulphonic acids, carboxylic acids are strong acids that are expected to be highly deprotonated in the washing and absorber solutions and thus to be removed from the flue gas.

PFASs with a non-dissociating, non-polar terminal groups such PFIAs, FTIs, PFCs and FTACs have relatively high K_{AW} values (log K_{AW} 2–5) and are likely to remain in the gas phase and pass through the flue gas scrubbing stage. FTOHs also have this tendency, especially FTOHs with a perfluorinated chain consisting of eight or more carbon atoms.

The octanol–air partition coefficient (K_{OA}) is used as an indicator of binding to AC. It is expected that a number of PFAS groups will not be captured (or captured only to a limited extent) by AC. This is mainly the case for iodine-containing PFASs, fluorotelomer olefins (FTOs), the perfluoroalkanes (PFCs), the fluorotelomer alcohols with a short perfluoro chain of 3 to 5 carbon atoms (3-5:2 FTOH) and the fluorotelomer acrylates (FTACs). With respect to the PFCs, this also includes the main perfluorinated by-products formed during incineration, as indicated in the previous chapter.

Overall, if present in the flue gas that comes from the combustion chamber, the substances most likely to pass through the flue gas treatment system are iodine-containing PFASs, FTOs, PFCs, the fluorotelomer alcohols with a short perfluoro chain of 3 to 5 carbon atoms (3-5:2 FTOH) and the FTACs.

PFAS emission measurement methods
In publications from 2009 and onwards, scientists have emphasised a trajectory of development, validation and standardisation of new measurement methods for determining PFAS emission concentrations, but our literature study shows that no standardised methods are yet available to measure the emission concentration of PFAS compounds in the flue gases of waste incineration plants.

It is nevertheless concluded that, among other things, volatile fluorinated gases are most likely to be formed on incineration and to be present in flue gases. Of these gases perfluorocarbons such as tetrafluoromethane (CF_4), hexafluoroethane (C_2F_6), both of which are greenhouse gases, are most likely to be formed. Other perfluorinated carbons like perfluorocyclobutane (C_4F_8), tetrafluoroethylene (C_2F_4), hexafluoropropene (C_3F_6) and perfluoroisobutene (C_4F_8) are less likely to be present in flue gases.

To be mentioned as a relevant part of the measurement method it is technically possible to sample this subgroup of gaseous PFASs, as well as other forms such as polar, water-soluble, dust-bound and dust-based (aerosols) PFASs in flue gases. It is common practice to use a sampling train of filters, adsorption columns and impinger absorption liquids connected in series. The collected filters, adsorption columns and impinger fluids can be chemically analysed in an accredited laboratory after sampling. GC-MS and HPLC-MS/MS are particularly suitable for this purpose as analytical techniques. GC-MS lends itself well to the measurement of gaseous and non-polar to mildly polar PFAS compounds. HPLC-MS/MS, on the other hand, is suitable for polar, dissociable and water-soluble PFAS compounds. HPLC-MS/MS has been accepted as a valid analytical technique for the determination of the content of PFAS compounds in soil, dredge, sediment, groundwater and surface water.

An alternative for the use of adsorption columns to the sampling and GC-MS analysis of gaseous PFAS compounds is the use of canisters, as they are much easier to use.

Fluoride measurement is an obligation in the Dutch Activities Decree for determining the HF emission concentration in the flue gases of waste incineration plants. The standard prescribed measurement method for HF in flue gas, ISO-NEN 15713:2011, is not considered a suitable method of PFAS measurement or a replacement for measurement by GC-MS or HPLC. Furthermore, fluoride measurement is not selective for the PFAS. The LOQ of the standard fluoride methods is three orders of magnitude higher than the LOQ of the HPLC-ESI-tandem-MS or GC-MS analysis of individual PFAS compounds.

A feasible LOQ for the measurement of the emission concentration of PFAS compounds in flue gases is estimated to be in the range 0.1-0.5 ng.m^{-3}. A sampling volume of approximately 4 m^{3} of flue gases is assumed here.

The TOF measurement is another indicator method for the presence of PFAS concentrations in flue gases. It is selective for the sum of PFAS compounds as part of the TOF. However, the limit of quantitation for the TOF measurement is expected between 50 and 250 ng.m^{-3} flue gas, which is still well above the achievable LOQ of individual PFAS compounds. This means that the TOF measurement is also a less suitable indicator of the detectability of PFAS in flue gases.

In view of the expected gaseous PFAS compounds in flue gases, it is recommended to compile a PFAS target list for chemical analysis that includes the gaseous PFAS compounds. It would also be sensible to measure the non-target PFAS compounds, because of the unfamiliarity of the presence of PFASs in the flue gases. This is easily achieved through the use of MS detection techniques.

PFAS measurements at waste incinerators
Recent scientific studies have shown on the basis of PFAS measurements that PFAS emissions from waste-processing activities take place not only via the flue gases from waste incineration. It appears that PFASs can also be released from the site of a waste incineration plant to the outside air (evaporation and/or emitted flue gases) and can leach into the underlying soil. These emissions also take place in landfills or temporary waste storage sites. Evaporation and leaching of PFASs is also possible from the bottom and fly ashes that arise as residual flows after incineration. In The Netherlands, these residual flows are used as secondary building materials. One of the publications concluded that the emission route via leaching causes significantly higher emission loads than that via ambient air. This applies to total PFASs as well as to the subgroups distinguished therein of neutral and ionic PFAS compounds.

From the measurements of PFASs in flue gases and in air, annual emissions from two waste incineration plants located in the Netherlands, as well as emission factors, could be derived. The emission factors based on the flue gas measurements are about a factor of 5 higher than those based on the concentrations in air. As a first indication, emissions of PFASs are expected to be in the range 10–20 g per 100,000 tonnes of waste incinerated. Measured concentrations in bottom ash from the studies in the Netherlands and in Sweden appear to match reasonably well, and are in the same order of magnitude. The amount of PFAS in bottom and fly ashes is about a factor of 100 higher than the amount emitted via flue gases. These numbers should, however, be considered as indicative, as they are based on a limited number of samples at one or two sites. Additional measurements at other waste incineration sites are needed to obtain a representative picture.

It has been shown that several PFASs that were not included in the available flue gas measurements are present in waste and emitted from waste incineration sites. The list of PFASs could be extended to include these compounds to improve the insights into the presence of PFASs in MSWI flue gases. The PFASs in question are 6:2, 8:2 and 10:2 FTOH, and N-MeFOSA. N-MeFOSE and N-EtFOSA were detected in emissions from landfills and waste storage sites but were not detected in the air samples at the incinerators.

Based on the available information on emission measurements and our analysis of the incinerability of PFASs, the generation of incineration by-products and the removal of PFASs via flue gas cleaning, it is proposed that all the PFASs on the advisory list should be measured and that the list should be extended to include the following substances:

Iodine-containing PFASs, FTOs, PFCs, the whole range of FTOHs and FTACs, N-MeFOSA, N-MeFOSE and N-EtFOSA.

Perfluoroalkyl iodides and fluorotelomer iodides are raw material intermediates used to produce additional building blocks that are further reacted to create a family of ‘fluorotelomer-based’ surfactants and polymer products. Fluorotelomer olefins are also used as raw material intermediates and may be formed as an impurity in the synthesis of fluorotelomer alcohols (Buck et al., 2011). It is not expected that these three PFAS categories will be present in municipal and similar commercial or industrial waste and it is therefore probably less relevant to include these PFASs in an extended advisory list for the measurement of PFASs in flue gas, fly ash and bottom ash.

6 Carbon dioxide recovery from incineration plants

In this chapter the influence of the carbon capture and liquefying process on the composition of the flue gas finally emitted and the liquid CO_2 produced at waste incineration plants will be described. The following sections first describe the carbon recovery process. This is followed by a description of what is likely to happen to the PFASs during the carbon capture and liquefaction processes. All the PFASs that were considered in the previous chapter will be taken into consideration, including those that are likely to be formed as incineration by-products.

Available information on the removal of some well-known flue gas components will also be discussed to provide some quantitative information on expected removal rates. This will be followed by qualitative assessments of the different kinds of PFASs considered. A qualitative indication will be provided both for the expected removal from the flue gas that is finally emitted from the CO_2 capture process and for the final liquid CO_2 produced.

The information provided in this chapter should give an answer to the main research question whether PFASs can be present in CO_2 that is recovered from waste incinerator flue gases.

6.1 CO_2 recovery process

CO_2 in waste incinerator flue gas can be recovered, to be applied, for instance, in greenhouse farming. In the CO_2 recovery plant the flue gases are first cooled and washed and then absorbed in an aqueous solution of monoethanolamine (MEA). In the next stage, the captured CO_2 is desorbed from the MEA solution and finally liquefied in order to be transported by tank truck.

The following description of the CO_2 capture and liquefaction process is largely based on the general description of the process at the waste incineration plant in Duiven, the Netherlands, provided by Houben and Boerleider (2020). Additional information obtained by literature searches is provided, e.g. on auxiliary materials (chemicals) used and the processing temperatures and pH of the scrubber water and absorber solution. A process diagram of the CO_2 capture installation is provided in Figure 5. The various elements of the installation will be described next.

DCC-tower: In a direct contact cooling (DCC) tower, flue gas is simultaneously cooled from about 65 to 45 °C and washed to remove residues of sulphur dioxide by adding caustic soda to the scrubbing water. Cooling improves the absorption of CO_2 in the subsequent stage and minimises solvent loss due to evaporation. For effective removal of sulphur dioxide the pH should be in the same range as for the flue gas desulphurisation (FGD) unit, with pH values in the range 5–7. The optimum pH for the dissolution of SO_2 is about 5 (Houben and Boerleider, 2020).

CO_2 absorber: CO_2 is removed from flue gas by bringing it into contact with an absorption agent, also called a solvent. The solvent is usually a solution of MEA in water. Other amine absorption agents can be used, such as diethanolamine (DEA) or methyldiethanolamine (MDEA). Non-amine based solvents are also available, such as glycol based. In the absorber, CO_2 binds to MEA, removing about 80–85% of the CO_2 from the flue gas. The inlet temperature of the absorber is about 45 °C and the outlet temperature about 60 °C. MEA is a weak base with a pKa of 9.51 (Gangarapu, 2014). The pH of the MEA solution decreases with the CO_2 loading, starting at a pH of about 13 and finally reaching a pH of about 8 (Lv et al., 2015; Zhang et al., 2015). Usually, the absorber is equipped with an integral recirculating water wash stage for the removal of MEA solution droplets and aerosols. A small fraction of the recirculating wash water is going to the absorber in order to balance the water that is lost from the absorber (Khakharia, 2015; Moser et al., 2014; Knudsen et al., 2009; IEAGHG, 2012; IPPC, 2005).

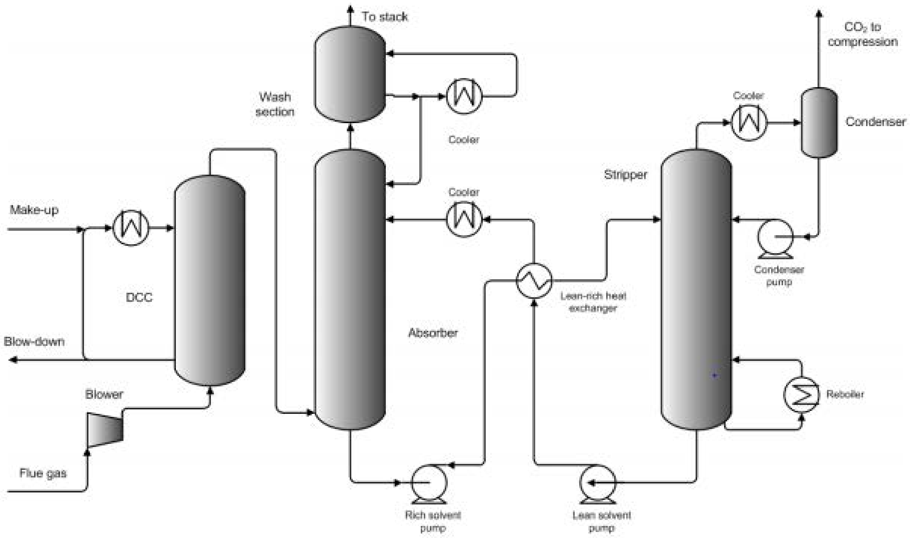

Figure 5 Process diagram of the CO_2 capture unit taken from Fernandez (2013)

In the acid washer, flue gas from the absorber is treated, usually using sulphuric acid, to maintain the pH below a value of 4–5 Knudsen et al. (2013). According to Khakharia (2015) the pH acid wash solution was maintained at a value of 3 in their pilot plant The maximum temperature in the absorber is about 60 °C, which is the outlet temperature of the flue gas leaving the absorber and the temperature of the lean solvent entering at the top of the absorber (Khakharia 2015; Supekar, 2015). At the acid wash stage, water and basic solvent droplets, vapour such as ammonia and decomposition products from the MEA solution are removed from the flue gas (Houben and Boerleider, 2020; Khakharia, 2015; Knudsen et al., 2013).

The absorbed CO_2 in the enriched solvent is removed in the stripper by heating the saturated MEA solution with steam to a temperature of about 120 °C (100–145 °C). Steam/water is recovered in the condenser and fed back to the stripper, while the CO_2 product gas leaves the stripper (IPPC, 2005).

After the absorption and stripping section, the captured CO_2 is liquefied by compression and cooling. In the first step the concentrated CO_2 stream from the CO_2 stripper is cooled from about 120 °C when leaving the stripper to about 35–40 °C before entering the CO_2 compression section (Seo et al., 2015; Supekar, 2015) and washed by direct contact with cold circulating water (Usher and Cerimele, 2012). As the gas stream cools, part of the water that is present is condensed and captured.

In the next stages, the gaseous CO_2 stream is compressed and cooled to finally produce liquid CO_2. The first stage is compressing the CO_2 gas to a pressure of about 16 bar. At compression the temperature rises and the CO_2 gas is then cooled back to about 35 °C (Seo et al., 2015; Supekar, 2015). Again, at the various compression and cooling stages water condenses and is removed from the CO_2 gas stream in knock-out drums. In this way a concentration of about 150 ppm of water in the CO_2 will be established. Remaining water is removed in the drier section using a desiccant such as activated alumina or silica gel (Topham et al., 2014). Triethylene glycol can also be used as a dehumidifier (IEAGHG, 2012). Water removal is essential, as water accelerates corrosion, especially in the presence of CO_2 and other acid substances such as H_2S, NO_2 and SO_2. Furthermore, ice and hydrate formation during gas conditioning can cause damage to or even plugging of process equipment. Therefore, drastic drying is required prior to CO_2 transport (Walspurger and van Dijk, 2012). According to information provided by Houben and Boerleider (2020), a drying section is present at the site in Duiven but no information was provided on the type of desiccant used. An inquiry with the company AVR revealed that in Duiven alumina (Al_2O_3) is used as a drying agent.

After drying, the CO_2 is liquefied by cooling the pressurised gas (16 bar) to a temperature of -16 °C. Condensed water is also removed at this stage. There was no information in the process description provided by Houben and Boerleider (2020) on the presence of an additional AC adsorber. It was therefore assumed that there was no AC bed present for the removal of impurities from the captured CO_2 at the AVR site in Duiven. The planned CO_2 recovery facility at the Twence site in Hengelo/ Enschede will include an AC filter (Acker et al., 2019).

CO_2 can be liquefied under various conditions (e.g. pressure and temperature) between the triple point and the critical point. At the site in Duiven low-pressure refrigerated liquid CO_2 is produced. Besides this type of liquefied CO_2, high-pressure liquid CO_2 (at a pressure of about 69 bar and kept at an temperature of around 18 °C in steel cylinders) can be produced. Low-pressure liquid CO_2 is usually transported in insulated road tankers or trailers at a pressure of around 21 bar and a temperature of around -18 °C (Linde, 2021). The Twence CO_2 recovery facility, for instance, will produce liquid CO_2 at a pressure of about 16-18 bar and a temperature of -26 °C (Acker et al., 2019).

6.2 Removal of flue gas components in the carbon capture process

As described in Section 3.3, the flue gas from waste incineration is thoroughly treated to remove different kinds of pollutants such as SO_x,

NO_x, CO, dust, and trace impurities such as mercury, dioxins and PAHs. In the carbon capture and liquefying process various treatment and processing steps are applied that also influence the composition of the flue gas and the liquid CO_2 produced. The following section describes what is likely to happen in the carbon capture and liquefaction process to the PFASs that have survived the waste incineration stage and to those that are likely to be formed as by-products and might not be captured by the various preceding flue gas treatment steps.

As described in Section 5.2, the more volatile PFASs are likely to be only partly captured by the flue gas treatment system of the waste incinerator – especially those that are inert or non-polar or have non-ionising functional groups.

At the various stages in the carbon capture process, PFASs can be removed from the flue gas and the captured CO_2. The carbon capture process scheme presented in Figure 5 shows that CO_2-lean flue gas and a CO_2-rich stream are the two main streams that are separated in the absorber-stripper section. Besides these, aqueous waste streams also result from the process. The focus in this report is on flue gas and recovered CO_2.

Before being emitted to the atmosphere, the flue gas entering the carbon capture and liquefying process is washed three times, i.e. in the DCC tower with a caustic solution, in the absorber tower and in the acid wash section. The CO_2-rich stream is washed twice before going to the compression and cooling section, where the captured CO_2 is liquefied – that is in the wash section of the stripping tower and in the CO_2-wash section. At the stages in the liquefying process where water is condensed and removed into the water knock-out drums and in the drying section, possible residual contaminants can also be removed from the CO_2 stream. Each of these stages of the carbon capture and liquefying process will be discussed in the following paragraphs with a focus on the removal of PFASs.

6.2.1 *Measured data on the removal of flue gas components in the CO_2 recovery process*

As far as is known to date information on the removal of PFASs via the CO_2 capture process is not available. Therefore, a qualitative assessment will be made on the degree to which PFASs, if present in flue gas, might end up in both the captured and liquefied CO_2 and in the flue gas that is emitted from the CO_2 recovery process to the atmosphere. The assessment is based on the applied processes and process conditions such as the acidity of the washing solutions in combination with the physical–chemical properties of the different PFASs that might be present in the flue gas from which the CO_2 is recovered.

There are only a few studies in the scientific literature that address the effects of carbon capture systems on the emissions of air pollutants from combustion facilities. There is some quantitative information on the removal of acid components like HCl and HF and particulate matter at the various wash stages. Koornneef et al. (2010) mentioned that for non-methane volatile organic compounds (NMVOCs) there is a lack of quantitative information on the effect of CO_2 capture and still to date there seems to be little or no information.

The available information on the well-known flue gas components will be discussed first to provide some quantitative information, which will then be used for the qualitative assessment of the removal of the different kinds of PFASs.

The removal and accumulation of dust, SO_x, NO_x, HCl and HF in a CO_2 recovery plant were assessed by Iijima et al. (2007) by measuring these components in both the gas and liquid streams at the inlet and outlet of the different sections in the CO_2 recovery plant. The measurements of dust showed that the capture efficiency of dust is about 40–50% in the combined flue gas cooler and DCC tower and about 40–60% in the CO_2 absorber. The removal of SO_x at the cooler was 98%, while only about 1–3% of the NO_x was removed. The tests performed by Iijima et al. (2007) confirmed that no chlorine or fluorine was detected in the flue gas after the DCC and absorber solvent section, and that chlorine and fluorine were already deeply removed upstream of the CO_2 recovery plant by the preceding flue gas desulphurisation system and other pre-treatment equipment.

Acid gases such as SO_2, NO_2 and HCl react with MEA to form heat-stable salts (Kohl and Nielsen, 1997; Rao and Rubin, 2002; Laribi et al., 2018; Islam et al., 2011). Rao and Rubin (2002) reported the following removal efficiencies by the MEA absorber: for SO_2 >99%, NO_2 20–30% and for HCl 90–95 %. Koornneef (2008) provided an overview of removal efficiencies for various flue gas components based on various publications (see Table 13). According to Koornneef (2008), mercury and other heavy metals may be partially removed in the CO_2 capture process. He reported that mercury is found in the MEA reclaimer bottoms. For indicative purposes he assumed a removal efficiency of 50%.

Table 13 Removal efficiencies for some acid flue gas components (Koornneef, 2008)

Compound	Removal efficiency (%)	Comments
SO_2	90	Depends on type of amine, highest for MEA
NO_x	1.25	In the range 1–3%
HCl	95	Based on Rao and Rubin (2002)
HF	90	Lower than for HCl (own assessment)

High removal rates are obtained for gas components forming highly soluble salts and those that are strong acids with low pKa values and low air–water partition coefficients. The log K_{AW} for HCl and HF is <-2 with pKa’s of -6 and 3, respectively. For non-reactive and non-dissociating gaseous components with high partition coefficients such as nitrogen oxides, the removal rate is low. The log K_{AW} for nitrogen oxides is between 0.5 and 1.5.

6.2.2 *Dissociation of PFASs in scrubber and wash liquids*

To qualitatively assess the removal of PFASs, the same approach as for the flue gas treatment at the waste incineration plant is used here.

Within the group of perfluoralkyl sulphonamides (FASAs)With a pKa values between 6.3–9.7, this means that in the DCC tower FASAs are only slightly dissociated. However, in the MEA scrubber FASAs are completely dissociated at a pH of 8–13. For other perfluoralkyl sulphonamides, such as the methyl- and ethyl-substituted and sulphonamido ethanols, reported pKa values are higher, in the range 8–14. This results in a situation where the degree of dissociation in the MEA absorber is more diverse and uncertain, varying from almost complete to about 10% and not dissociated at all for MeFOSE and EtFOSE with a reported pKa value of 14.4 (Ahrens et al., 2012). Estimated pKa values for the carboxylate groups of sulphonamido acetates (PFASAAs) range from 3.86 to 4.04 (Rayne and Forest, 2009b), resulting in a high degree of ionisation in the DCC tower (pH 5–7) and complete dissociation in the MEA scrubber (pH 8–13).

PFASs can be removed in the acid washer as well as in the DCC tower and MEA scrubber. The acid washer treats the flue gas coming from the MEA scrubber. The pH of the feed of the acid washer is about 3 and it is maintained at a value below 4 to 5 in the washer. For near complete dissociation, the pKa should be lower than 2, only PFASs with sulphonate and phosphate groups being largely dissociated (50–90%).

Based on the above information, for PFASs that are fully dissociated in the DCC tower and the MEA absorber, the removal efficiency is expected to be in the same order as for SO_2, HCl and HF. Thus, near complete removal can be assumed, with a removal efficiency of about the same magnitude (>95%) as for inorganic acid components at each stage. It is, however, important to consider that in the case of absorption, the air–water partition coefficient (K_{AW}) – will determine the extent to which a chemical will dissolve from the gas phase into the acid wash solution. For dissociating substances, the fraction dissociated has to be accounted for by using the effective dimensionless air–water partition coefficient, also known as the air–water distribution coefficient (D_{AW}), as explained in Section 5.2.

6.2.3 *Formation of reaction products with monoethanolamine, heat-stable salts*

Of the potentially reactive gas phase impurities that may enter the absorber such as organic acids (formic or acetic acids), HCl, HCN, SO_2, NH_3 and mercaptans, the acidic compounds form salts with the alkaline amines. If the acids are stronger than CO_2 and H_2S, their amine salts are not efficiently decomposed under the stripping conditions (which are designed to decompose the amine-CO_2 and amine-H_2S salts), and they build up in the solution as heat-stable amine salts (Kohl and Nielsen, 1997). According to Rao and Rubin (2002), besides acid gases such as SO_2, NO_2 may also react with MEA to form heat-stable salts.

Heat-stable salts may also be formed through reaction with MEA degradation products that are formed from the oxidation of MEA due to oxygen. Well-known degradation products are carboxylic acids such as formic acid, acetic acid, glycine, glycolic acid and oxalic acid (Scheiman, 1962; Verma et al., 2009; Supap et al., 2011). Carboxylic acids that react with MEA can form the corresponding amide compound by dehydration (Supap et al., 2011; Penttillä et al., 2014; Dux and Schallert, 2016).

$\text{MEA} + \text{R-COOH} \leftrightarrows \text{MEA}^+ + \text{R-COO}^-$

Hot spots located in the regenerator section of the scrubbing system might provide a suitable environment for dehydration (Scheiman, 1962), forming the following products:

$\text{MEA}^+ + \text{R-COO}^- \leftrightarrows \text{MEA-CO-R} + H_2O$

The formed product is not a heat-stable salt. The relevance of this reaction was not further assessed. In this report we consider only the formation of heat-stable salts.

As with carboxylic acids, other PFASs with an acid group will react with ethanolamine. Thus, for PFASs that are relatively strong acids, that fully dissociate at the prevailing pH in the MEA absorber and that will react with MEA to form heat-stable salts, near complete removal from the CO_2 stream can be assumed.

6.2.4 *Flue gas – MEA liquid partitioning of non-dissociating PFASs*

Some PFASs without an acid functional group also may react with the scrubber or absorption solutions. Scheiman (1962) suggests that MEA can react with aldehydes and ketones in MEA scrubber solutions to form high-boiling-point amino-alcohol products and points to the possible reaction of acids with alcohols to form a positively charged oxonium ion.

Neutral and non-reactive chemicals that are extremely soluble in water and MEA are readily absorbed by amine solutions. They do not, however, react chemically to the amines and are generally expected to be expelled in the stripper, depending on the boiling point of the chemical. On the other hand, neutral non-ionising compounds that are sparingly soluble in water or in MEA remain in the flue gas. Either way, in general the absorption of these compounds is expected to be lower than that of ionising and reactive PFASs, and those that are absorbed are expected to be partially or fully desorbed in the stripper column together with the absorbed CO_2.

6.2.5 *Qualitative assessment of PFAS removal by the wash stages and the MEA absorber*

An indication of the potential removal via the wash stages and the MEA absorber is obtained in the same way as explained in Section 5.2.2 for flue gas treatment. An absorption factor is calculated for each individual stage. The absorption factor is calculated from the volume-based ratio of the flue gas flow rate (G) and the solvent flow rate (L), the G/L ratio, and the air–water distribution coefficient (D_{AW}).

For estimating the absorption in the MEA solution, MEA-based partition coefficients should be used. However, these are available only for those chemicals that are usually removed from gas streams by MEA absorption, such as CO_2 and H_2S. As no MEA-specific partition coefficients are available, the air–water partition coefficient (K_{AW}) is used instead, as this is the only available alternative and thought to provide a good indication. It should be noted that many neutral organic chemicals are known to have higher solubility in MEA solutions than in water (the salting-in effect). Therefore, the removal in the CO_2 absorber based on the K_{AW} is expected to be under estimated. Based on the foregoing, the absorption factors should be considered indicative. They should be seen as a relative measure to compare the removability between substances rather than an absolute measure.

Calculating the absorption factors thus requires G/L flow ratios for the DCC tower, the MEA absorber, the acid wash and the CO_2 wash stages. Knudsen et al. (2009) reported that for a pilot plant at a coal-fired power station, the optimum absorber liquid (solvent) to flue gas ratio (L/G) lies between 2.0 and 3.0 (kg/kg). An L/G ratio of 2.5 (kg/kg) is chosen that corresponds to a volume-based G/L ratio of about 300.

G/L ratios for the DCC tower are calculated from the available data on the flue gas flow rates and DCC water spray flow rates reported in IEAGHG (2012), resulting in an average volume-based ratio of about 650. For the acid wash we used the same G/L ratio as for the DCC tower.

For the flue gas emitted from the CO_2 recovery plant, the indicative removability for the MEA absorber alone and combined with the DCC tower and acid wash, is presented in Table 14. Dissociation is not accounted for in these calculations. The first column gives the removal efficiency for the MEA absorber alone, showing that little to no absorption is expected for PFASs with a log K_{AW} value of zero or higher. High removal efficiencies are expected for PFASs with a log Kaw of -4 or lower. Assuming equal removal efficiencies for the DCC tower and acid washer, this provides an indication of the total PFAS removal from the flue gas. Overall, for the three washing stages the indicative removal efficiencies are 95% or higher for log K_{AW} values of -3 or lower.

Table 14 Indicative absorption factors for the MEA absorber and total PFAS removal including the DCC tower and acid washer

log Kaw	Removal MEA absorber	DCC and MEA absorber	DCC, MEA and acid washer
-4	97%	100%	100%
-3	74%	90%	96%
-2.6	53%	71%	82%
-2	22%	33%	42%
-1	3%	4%	6%
0	0%	0%	1%
1	0%	0%	0%
2	0%	0%	0%
3	0%	0%	0%

For the non-polar substances or monopolar substances with log K_{AW} values of about -1, the overall removal in the washing towers and absorber is expected to be low: less than 10% and for the non-polar PFASs with higher air–water partition coefficients even less.
Taking into account the dissociation of the compound in the absorber liquids, the absorption factors and the overall removal factor for the flue gas emitted from the CO_2 recovery plant is calculated according to the following equations:

The absorption factor:

$$F_{abs} = 1 - \frac{G/L}{G/L + 1/D_{AW}}$$

$$F_{rem-overall} = 1 - (1 - F_{abs-quench}) \cdot (1 - F_{abs-MEA}) \cdot (1 - F_{abs-acid\ wash})$$

In which:

G	gas flow rate (m^3)
L	liquid flow rate (m^3)
D_{AW}	air-to-water distribution constant (-)
$F_{rem-overall}$	overall removal factor for the flue gas from the CO_2 recovery (-)
$F_{abs-DCC}$	absorption factor for the DCC tower (-)
$F_{abs-MEA}$	absorption factor for the MEA absorption stage (-)
$F_{abs-acid\ washi}$	absorption factor for the flue gas acid wash (-).

For the recovered CO_2 the calculation needs to be adapted because we are interested in the fraction of PFASs ending up in the CO_2 steam. The reason for this is that PFASs that are absorbed by the MEA solution will to some degree be released in the stripper column and end up in the recovered CO_2. As a worst-case we assume that the non-dissociated fraction (α, see Section 5.2) in the MEA solution will be released completely and end up in the recovered CO_2 during the regeneration process in the stripper column. In addition, the removal in the DCC tower has to be taken into account as well as the removal in the CO_2 wash. The fraction of PFASs in the recovered CO_2 is calculated according to the following equation:

$$F_{CO_2} = (1 - F_{abs-DCC}) \cdot F_{abs-MEA} \cdot (1 - F_{diss-MEA}) \cdot (1 - F_{abs-CO_2\ wash})$$

In which:

F_{CO2}	fraction of PFASs ending up in the recovered CO_2 (-)
$F_{abs-DCC}$	absorption factor for the DCC tower (-)
$F_{abs-MEA}$	absorption factor for the MEA absorption stage (-)
$F_{diss-MEA}$	fraction of PFASs dissociated in the MEA solution (-)
$F_{abs-CO2\ wash}$	adsorption factor for the CO_2 wash stage (-).

The results of the qualitative assessment of the removal of the different PFASs from the flue gas in the CO_2 recovery process are presented in Appendix VI. The colour coding presented in Section 5.2 is used, red standing for poor removal, orange for average, yellow for good and green for very good.

For the presence of PFASs in the recovered CO_2 before cooling and liquefying, the following qualitative indication is used: green for a very small amount, yellow for a small amount and red for a considerable amount.

Based on the calculations it can be concluded that the substances having the highest tendency to end up in the recovered CO_2 stream, are the non-dissociating substances with a polar character such as fluorotelomer alcohols with a short perfluoro chain of six carbon atoms or smaller (6:2-3:2 FTOH) and the group of substituted perfluoroalkane sulphonamido ethanols (MeFASEs and EtFASEs), and also some of the PFCAs such as PFDA and PFUnDA, 12:2 FTS, DONA, and PFOTSi-hydrates.

Non-dissociating non-polar PFASs are likely not to end up in the recovered CO_2, mainly because according to our assumptions and calculations they are not absorbed by the MEA solution.

6.2.6 *Removal in the CO_2 cooling, compression and drying section*

Vapour–liquid separator drums are needed to prevent liquid entrainment in the CO_2 compressors. Separation by gravity using liquid–vapour separator drums is the simplest and most cost- and energy-effective way to remove the bulk of components with higher density than gaseous CO_2. Components with high solubility in water or components with higher boiling points than CO_2 will be removed, together with the water in the separator drums (Aspelund and Jordal, 2007). Condensable components, having a boiling point in the same range as CO_2, are propane, ethane, H_2S, NO_2 and SO_2, that will condense with CO_2 in the final compression-cooling stage (Walspurger and van Dijk, 2012).

As the gas is compressed and cooled, most of the remaining water condenses and is removed into the separator drums prior to the compressor stage. With proper design the vapour–liquid separator drums can remove water down to approximately 400–500 ppm (Aspelund and Jordal, 2007).

With a CO_2 concentration of about 15 mol% in the flue gas entering the CO_2 capture process and a content of 95 mol% in the captured CO_2 after the regeneration column, the concentration of micro-contaminants, which are in the order of $ng.m^{-3}$ in the flue gas, would be a factor of 6 higher, assuming that all contaminants remain in the captured CO_2 gas stream, but the concentration will still be in the $ng.m^{-3}$ or part per trillion (ppt) range. At such low concentrations, condensation of microcontaminants at the inter-stage cooling is not likely to occur. To what extent components are removed from the CO_2 stream at the interstage cooling steps is difficult to assess. Aspelund and Jordal (2007) indicated that components with a boiling point higher than CO_2 and with high solubility in water might be removed to some extent.

Boiling points for frequently reported PFASs are reported by ITRC (2020) and Concawe (2015). The lowest boiling points of the PFASs considered are in the same range as the boiling point of water, so some removal with the condensed water might be possible for all PFASs that have boiling points higher than that of water. However, due to the anticipated low concentration, removal is expected to be low.

Perfluorinated combustion by-products that are formed from the incineration of PFASs have boiling points comparable to that of CO_2. They will therefore probably condense with the liquefied CO_2. According to the phase change data, perfluorocyclobutane will be in liquid form and condense with the CO_2. CF_4, having a boiling point of -128 °C, which is much lower than the boiling or sublimation point of CO_2 (-78.5 °C), will be in the gaseous phase in the conditions where CO_2 is liquefied. In conclusion, of the fluorinated combustion by-products that are formed, perfluoroethane and perfluorocyclobutane may be present in the liquid CO_2. However, as stated before it is unlikely that these PFCs will end up in the recovered CO_2 as they will not be absorbed by the MEA solution. This is especially true of the volatile PFCs. Our assessment also shows this to be true for the higher molecular weight PFCs (C4–C10).

Additionally, contaminants may be removed in the drying section depending on the process and type of drying medium used. The AVR site in Duiven for instance uses activated alumina as a drying agent.

Activated alumina is a polar adsorbent having a high affinity with polar substances such as water and alcohols and are therefore also called a hydrophilic adsorbent. There are several other polar adsorbents, such as zeolites and silica gel.

As discussed before polar compounds such as organic acids in particular bind strongly to alumina and other polar compounds such as those with a hydroxyl group also adsorb well, as indicated by Filho and Do Carmo (2004), see also Section 5.2.1. Thus, PFASs with an acid en group such as PFCAs and PFSAs and those with a hydroxyl group such as FTOHs are also expected to strongly bind to polar adsorbents like alumina.

Arp et al. (2006) show that FTOHs bind a factor 1000–10,000 better to activated alumina, quartz and calcium carbonate than FTOs. This shows that fluorinated substances, compounds with a polar group, bind better to alumina than non-polar ones. Furthermore, small PFAS molecules bind less well than larger ones (Arp et al., 2006).

Any PFAS with a highly polar functional group (acids and alcohols) still present after compression and cooling will bind to the alumina and will be removed from the CO_2 to some extent before the CO_2 is liquefied. Neutral and non-polar compounds will not bind (or hardly bind) to alumina.

In conclusion, to what extent components are removed from the CO_2 stream is difficult to indicate. On the basis of the available information we assume that microcontaminants are not at all, or only to a very limited extent, removed at the inter stage cooling. Any PFAS with a highly polar functional group (acids and alcohols) still present after compression and cooling but before liquefaction, will bind to the alumina and will be removed from the CO_2 to some extent at the drying stage. Neutral and non-polar compounds, such as perfluorinated products of incomplete combustion, will not bind (or will hardly bind) to alumina. They might be condensed with the liquid CO_2. However, it is unlikely that these compounds will end up in the recovered CO_2 because they will not be absorbed in the MEA solution.

6.3 Conclusions

Compounds with a high air–water partition coefficient are only partially or not at all absorbed in the absorption liquid of the absorption-desorption section and therefore do not end up in the extracted CO_2 stream but are emitted via the flue gas from the recovery process. This applies, for example, to the fluorotelomeric olefins, the iodine-containing compounds and perfluorocarbon compounds. Strong acids (PFCA, PFSA, FTS, mono- and diPAP, PFECAs, etc.) are completely dissociated at the prevailing pH of the MEA absorption solution and form heat-stable salts. They will therefore also not end up in the recovered CO_2 stream. The substances that have the highest tendency to end up in the recovered CO_2 stream are non-ionising substances (or those that ionise only to a limited extent) with a polar character. This mainly applies to fluorotelomer alcohols with a short perfluoro chain of six carbon atoms or smaller (6:2-3:2 FTOH) and the group of substituted perfluoroalkane sulphonamido ethanols (MeFASEs and EtFASEs). Finally, contaminants may be removed in the drying section depending on the process and type of drying medium used. Acid compounds such as PFCA and PFSA can bind to alumina, which is a polar adsorbent that for instance is used in the CO_2 recovery process at the AVR site in Duiven. Compounds containing a polar group such as fluorotelomer alcohols can also bind to alumina through the formation of hydrogen bridges. Because of this it can be expected that members of the above-mentioned three PFAS groups will bind to some extent to the applied alumina.

As an overall conclusion it is expected that most of the PFASs considered will not end up (or will do so only to a very limited extent) in the extracted CO_2 due to the physical and chemical processes in the washing section, in the CO_2 regeneration section and at the liquefaction stage. Of the substances considered, the ones with the highest tendency to end up in the recovered CO_2 stream are substances with a polar character that do not ionise (or do so only to a limited extent). This mainly applies to fluorotelomer alcohols with a short perfluoro chain and the group of substituted perfluoroalkane sulphonamido ethanols (MeFASEs and EtFASEs).

7 Conclusions and recommendations

1. *What is the precise definition of a PFAS and what connection is there between the advisory list of individual PFASs in the Temporary Action Framework and that in the Knowledge Document of the Expertise Centre PFAS?*

In this report we consider all compounds with at least one CF_2 moiety (i.e. C_nF_{2n}–, n ≥ 1) as PFASs. This broad definition is chosen to ensure the inclusion of all past definitions and the definitions that are under consideration in the ongoing work of the OECD and the REACH restriction proposal committee. However, the primary focus is on those PFASs with a perfluoroalkyl moiety with three or more carbons, following the OECD definition. Ozone-depleting substances matching the broader definition such as chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs) and bromine containing Halons that are used as refrigerants, blowing agents, aerosol propellants, degreasing and fire-suppressing agents (and, in principle, the short-chain hydrofluorocarbons that do not have ozone-depleting properties but are known to act as greenhouse gases), are not part of this study.

PFASs are normally divided into two main subgroups: non-polymeric and polymeric PFASs. There are, however, many different groups of PFASs, each with their own physical, chemical and toxicological properties.

The two action frameworks discussed in Chapter 2 aim to facilitate the management of PFASs in soil, sediment and water. The PFASs that are to be measured and monitored according to these frameworks have been selected on the basis of their occurrence in soil sediment and (surface) water in The Netherlands. All the substances mentioned in the two action frameworks are generally regarded as PFASs according to all available definitions.

The listed PFASs are considered relevant to the management of contamination in soil, sediment and surface water. However, their relevance to assessing the safety of incineration gases can be questioned, since the incineration of PFAS-containing waste may produce other PFASs.

2. *Can PFASs be present in the flue gases of a waste incinerator as a result of not breaking down (completely)?*

Yes, despite efficient thermal degradation in the combustion chamber, the presence of PFASs in the flue gases of waste incinerators cannot be ruled out.

To limit the formation of pollutants during waste incineration and their emission into the environment, legal requirements for operating conditions and emission limit values for hazardous pollutants are set for waste incineration facilities.

The minimum requirements for non-hazardous waste are a combustion chamber temperature of at least 850 °C, for at least 2 seconds, in the presence of at least 6% oxygen. For hazardous waste, the minimum temperature of the combustion gases must be 1100 °C.

If these conditions are met, waste incineration is expected to result in a high degree of thermal destruction in the combustion chamber for the groups of PFASs considered, with the exception of PFCs. The short-chain PFCs (C1 and C2) are likely to be formed as products of incomplete combustion from the incineration of PFASs.

PTFE is a fully fluorinated polymer that is the most thermally stable of all known fluorinated polymers. On the basis of experimental data, it is expected that PTFE will thermally degrade completely at the minimum required combustion temperature of 850 °C. However, polymers are solid materials that must evaporate before combustion can occur. Due to their high molecular weight polymers do not evaporate as such but rather first thermally degrade into smaller molecules that evaporate and can be incinerated in the combustion chamber. Key to the combustion of those solid materials are the temperature in the combustion bed, the residence time of the combustion material on the grates of the incinerators and the degree to which the material is mixed. If these factors are insufficient, the material may leave the incinerators incompletely burned via the bottom ashes. The temperature in and at the surface of the bed are well above 1000 °C and thus high enough for the complete pyrolysis of PTFE. Like non-polymeric PFASs, short-chain PFCs are products of incomplete combustion formed on the incineration of polymeric PFASs.

Most important to note is that 100% thermal destruction at waste incineration is unlikely to occur. The central question is to what extent PFASs can thermally be destroyed; and from the studied literature it is concluded that thermal destruction is efficient and a high degree of thermal degradation is usually achieved.

Also critical is the definition of complete combustion. Complete combustion could refer to complete mineralisation to HF and CO_2. It could also mean that the original compounds are destroyed without conversion into end products. In practice, full mineralisation will hardly ever occur, as thermal degradation is always accompanied by the formation of various gaseous organic fluorine-containing products. If the minimum requirements are met, the formation of combustion by-products seems to be limited mainly to the smallest members of perfluorinated carbons, CF_4 and C_2F_6. Both are potent greenhouse gases, resistant to high temperatures and most likely to survive the combustion process. These gaseous PFCs have a much stronger global warming potential compared to CO_2.

Short-chain PFCs are expected to be the main products of the incomplete combustion of PFASs and fluoropolymers. For other combustion products, such as fluorinated dioxins and furans and perfluoro acetic acid, it is judged that formation from PFASs is unlikely. However, the formation of dioxins and furans cannot be completely ruled out because of the potential formation under unfavourable combustion conditions of fluorinated benzenes, which could serve as precursors to fluorinated dioxins and furans. On the other hand, fluorinated dioxins and furans have not been detected in waste incinerator flue gas or fly ash. All things considered, the formation of fluorinated dioxins and furans is not expected.

Our conclusions on the expected thermal destruction of PFASs and fluorinated polymers are based largely on laboratory experiments and qualitative theoretical assessments. Field measurements clearly show that various PFASs have been detected in flue gas and incineration products such as bottom ash and fly ash, leading to the conclusion that, despite efficient thermal degradation in the combustion chamber, the presence of PFASs in the flue gases of waste incinerators cannot be ruled out.

3. *Can PFASs (not broken down or broken down into smaller molecules) be captured from flue gases after one or more cleaning steps?*

This depends very much on the physical and chemical properties of the different groups of PFASs considered. Some types of PFASs may be efficiently removed from flue gas while for others removal is expected to be less efficient.

From the qualitative assessment of the removal efficiencies of the flue gas treatment and the CO_2 recovery processes for the PFASs considered, the types of PFASs with the strongest tendency to pass through the flue gas treatment system are iodine-containing PFASs, fluorotelomer olefins (FTOs), the perfluoroalkanes (PFCs), the fluorotelomer alcohols with a short perfluoro chain of 3 to 5 carbon atoms (3-5:2 FTOH) and the fluorotelomer acrylates (FTACs) – assuming that these compounds survive the combustion process.

4. *Can PFASs (partly depending on the answers to questions 2 and 3 above) be present in the carbon dioxide recovered from waste incinerator flue gases?*

The high degree of thermal degradation in the combustion chamber, the removal of PFASs during flue gas treatment and the subsequent CO_2 recovery process mean that the presence of certain PFASs in the recovered CO_2 is unlikely. However, it cannot be entirely ruled out.

Due to the physical and chemical treatment steps in the CO_2 regeneration process it is expected that most of the PFASs considered will not end up in the extracted CO_2 – or only to a limited extent. Of the substances considered, the ones with the greatest likelihood of ending up in the recovered CO_2 stream are non-dissociating substances with a polar character, which mainly relates to fluorotelomer alcohols with a short perfluoro chain and the group of substituted perfluoroalkane sulphonamido ethanols (MeFASEs and EtFASEs).

Results from field measurements show that various PFASs have been detected in flue gas. The total PFAS concentration found in flue gas was about 20 $ng.m^{-3}$. No measurements of PFASs in recovered CO_2 have been conducted, as far as we know.

As an order of magnitude estimate, 10 ng.m^{-3} could be used for the concentration in recovered CO_2 based on the total PFAS concentration measured in flue gas. However, the concentration is expected to be reduced significantly during the CO_2 recovery process.

5. *Is the chemical analysis of fluoride sufficiently accurate to reveal the presence of PFASs in flue gases and carbon dioxide?*

No. Existing methods such as HF measurement and TOF analysis are not suitable or sufficiently accurate to determine the presence of PFASs.

The literature study shows that no standardised method is yet available to measure the emission concentration of PFAS compounds in the flue gases of waste incineration plants.

It is technically possible to sample gaseous, dust-bound and dust-based (aerosols) PFAS in flue gases. GC-MS and HPLC-MS/MS are suitable analytical techniques to measure PFASs. HPLC-MS/MS has been accepted in available standard requirements for determining the amount of PFASs in soil, dredge, sediment, groundwater and surface water.

The current HF measurement methods (ISO-NEN 15713:2011 and NEN-EN-ISO 10304-1) are not considered a suitable or replacement method for PFAS measurement, as fluoride measurements are not selective for the PFAS. Furthermore, a feasible LOQ for the measurement of the emission concentration of PFAS compounds in flue gases is estimated to be in the range ng.m^{-3}, whereas the LOQ of the fluoride method is an order of magnitude higher by a factor of 1000.

As an alternative, the total organic fluorine (TOF) measurement method can be used to indicate the presence of PFASs in flue gases. It is selective for the sum of PFASs as part of the TOF. However, the LOQ for the TOF measurement is expected be between 50 and 250 ng.m^{-3} flue gas, which is well above the achievable LOQ of individual PFASs. This means that the TOF measurement is not a suitable indicator of the presence of PFASs in flue gases.

In view of the expected presence of gaseous PFAS compounds in flue gases, it is logical to compile a PFAS target list for chemical analysis. It would also be sensible to measure the non-target PFAS compounds, because the nature and extent of PFASs in flue gases is unknown. This can easily be done through the use of MS detection techniques.

6. *Can RIVM advise on the possible presence of PFASs in the carbon dioxide that is recovered from waste incinerator flue gases for applications such as growth improver in greenhouse horticulture?*

The presence of certain PFASs in the recovered CO_2 is unlikely but cannot be entirely ruled out. Concentrations of PFASs in the recovered CO_2 are expected to be low – a maximum of a few nanograms per cubic metre.

As far as we know, no measurements of PFASs in recovered CO_2 have been conducted that could confirm our findings and quantify their presence. In order to confirm whether PFASs are present in recovered CO_2 and to what extent measurements should be conducted, measurements should be conducted simultaneously in the flue gas from the waste incinerator and CO_2 recovery plant and in the recovered CO_2. This could provide some insight into how PFAS might enter and leave the CO2 recovery process via (gaseous) streams.

In addition to the standard sets of PFASs measured in soil and the aquatic environment, it is recommended to measure the PFASs that this study shows to be most likely to survive the combustion process, pass through the flue gas treatment system or end up in the recovered CO_2, if these are not already included in the standard lists. These would include short-chain perfluoro carbons, fluorotelomer alcohols and acrylates and substituted perfluoroalkane sulphonamido ethanols.

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List of abbreviations

General

AOF	adsorbable organic fluorine
ADRT	Avira dioxin reduction technology
BDE	bond dissociation energy
BTX	benzene, toluene and xylenes
CLP	classification, labelling and packaging
DCC	direct contact cooling
EPS	electrostatic precipitator
FGD	flue gas desulphurisation
GAC	granular activated carbon
GC	gas chromatography
HPLC	high-pressure liquid chromatography
LOQ	limit of quantification
MS	mass spectrometry
MSWI	municipal solid waste incinerator
NMVOC	non-methane volatile organic compound
PAC	powdered activated carbon
PCDDs	polychlorinated dibenzo-p-dioxins
PCDFs	polychlorinated dibenzofurans
PFCB	perfluorocyclobutane
PFAS	per- and polyfluorinated alkyl substances
PIGE	particle-induced gamma ray emission
pKa	negative log of the acid dissociation constant
RWS	Rijkswaterstaat, executive agency of the Ministry of Infrastructure and Water Management,
SNCR	selective non-catalytic reduction
SCR	selective catalytic reduction
SVHC	substance of very high concern
TGA	thermogravimetric analysis
TOF	total organic fluorine
TOP	total oxidisable precursor PFAS
VOCs	volatile organic chemicals

PFASs

ADONA	3H-perfluoro-3-[(3-methoxy-propoxy)propanoic acid], ammonium salt
DONA	3H-perfluoro-3-[(3-methoxy-propoxy)propanoic acid]
diPAP	disubstituted polyfluoroalkyl phosphate (see also PAP)
ECTFE	ethylene/chlorotrifluoroethylene copolymer
EtFASA	N-Ethyl perfluoroalkane sulphonamide
EtFASE	N-Ethyl perfluoroalkane sulphonamido ethanol
ETFE	ethylene/tetrafluoroethylene copolymer
FASA	perfluoroalkane sulphonamide
FASAA	perfluoroalkane sulphonamido acetic acid
FEP	fluorinated ethylene propylene polymer, tetrafluoroethylene/hexafluoropropene copolymer
FRD-903	2,3,3,3-tetrafluoro-2-(heptafluoropropoxy)-propanoic acid
FT	fluorotelomer (substance)
FTI	fluorotelomer iodide
FTOH	fluorotelomer alcohol

FTAC	fluorotelomer acrylate
FTMAC	fluorotelomer methacrylate
FTS	fluorotelomer sulphonate
FTUCA	fluorotelomer unsaturated carboxylic acid
GenX	technology used in the production of fluoropolymers
HFE	hexafluoroethane
HFP	hexafluoropropylene
HFPO-DA	hexafluoropropylene oxide dimer acid
MeFASA	N-Methyl perfluoroalkane sulphonamide
MeFASE	N-Methyl perfluoroalkane sulphonamido ethanol
MFA	tetrafluoroethylene/perfluoro(methylvinyl ether) copolymer
PAF	perfluoroalkanoyl fluoride
PAP	per/polyfluoroalkyl phosphoric acid ester, per/polyfluoroalkyl phosphate, fluorotelomer phosphate
PASF	perfluoroalkane sulphonylfluoride
PCTFE	poly(chlorotrifluoroethylene)
PE	polyethylene
PFA	perfluoroalkoxy alkanes or tetrafluoroethylene/perfluoro(propylvinyl ether) copolymer
PFAA	perfluoroalkyl acid
PFAE	per/polyfluoroalkyl ether
PFAI	perfluoroalkyl iodides
PFAL	perfluoroalkyl aldehyde
PFASA	perfluoroalkyl sulphonamide
PFASE	perfluoroalkyl sulphonamido ethanol
PFBA	perfluorobutanoic acid
PFBS	perfluorobutane sulphonic acid
PFC	perfluorocarbon
PFCA	perfluorocarboxylic acid
PFDA	perfluorodecanoic acid
PFDoDA	perfluorododecanoic acid
PFDS	perfluorodecane sulphonic acid
PFECA	per/polyfluoroether carboxylic acid
PFESA	per/polyfluoroether sulphonic acid
PFHpA	perfluoroheptanoic acid
PFHpS	perfluoroheptane sulphonic acid
PFHxA	perfluorohexanoic acid
PFHxDA	perfluorohexadecanoic acid
PFHxS	perfluorohexane sulphonic acid
PFIB	perfluoroisobutylene
PFNA	perfluorononanoic acid
PFOA	perfluorooctanoic acid
PFODA	perfluorooctadecanoic acid
PFOS	perfluorooctane sulphonic acid
PFOSA	perfluorooctane sulphonamide
PFPA	perfluorophosphonic acid
PFPE	perfluoropolyether
PFPeA	perfluoropentanoic acid
PFPeS	perfluoropentane sulphonic acid
PFPIA	perfluorophosphinate / perfluoroalkyl phosphinic acid
PFSA	perfluoroalkyl sulphonic acid
PFSiA	perfluoroalkyl sulphinic acid
PFSIA	perfluoroalkyl sulphinic acid

PFTeDA	perfluorotetradecanoic acid
PFUnDA	perfluoroundecanoic acid
PTFE	polytetrafluoroethylene
PVDF	polyvinylidene fluoride

Annex I. Overview of waste incineration sites in the Netherlands

Province	**Location**	**Company**	**Type of kiln**	**Combustion chamber**	**Type of waste**	**Temperature (°C)**	
						Average	**Max**
Groningen	Delfzijl	EEW Delfzijl BV	Moving grate, 2 lines	-	Non-hazardous	1195	1200
Friesland	Harlingen	REC Harlingen	Moving grate	-	Non-hazardous waste	-	-
Drenthe	Wijster	Attero Noord BV	Moving grate, 3 lines	Parallel	Non-hazadous waste	950	1100
Overijssel	Hengelo	Twence afval en energie, AEC & BEC	Moving grate, 3 lines Moving grate, 1 line	Centre	Non-hazardous waste Biomass	900	1100
Gelderland	Weurt	ARN B.V.	Moving grate, 2 lines	Parallel	Hazardous and non-hazardous waste	980 1050	1100 1100
	Duiven	AVR Afvalverwerking	Moving grate, 3 lines Fluidized bed	Centre	Non-hazardous waste Paper pulp residue	1050	1250
Noord-Holland	Alkmaar	HVCafvalcentrale	Moving grate, 4 lines	Centre	Non-hazardous waste and biomass	900	1150
	Amsterdam	Afval Energie Bedrijf	AEC: Moving grate HRC: Moving grate	Centre	Hazardous and non-hazardous waste	1100	1100
Zuid-Holland	Rotterdam-Botlek	AVR Rozenburg	Moving grate, 7 lines Vortex ovens	3 Counter 4 Parallel	Hazardous and non-hazardous waste and biomass Aqueous hazardous and high caloric petrochemical waste	950	1200
	Dordrecht	HVCafvalcentrale	Moving grate, 5 lines Fluidized bed	Parallel	Non-hazardous waste Sludges (waste water)	890 920 920 890	974 1121 1036 1005
	Dordrecht	ZAVIN CV	Moving concrete floor		Specific (contagious) hospital waste	1200	1300
Noord-Brabant	Moerdijk	Attero AEC Moerdijk	Moving grate, 4 lines	Centre	Non-hazardous	950	1200
	Moerdijk	N.V. Slibverwerking Noord-Brabant (SNB)	Fluidized bed		Sludges (waste water)		
	Roosendaal	SUEZ ReEnergy	Moving grate, 2 lines	Parallel	Non-hazardous	950	1170

Non-hazardous waste refers to household and commercial waste

Annex II. Description of common waste incineration facilities

II.1 Fluidised bed furnaces

Fluidised bed incinerators are widely applied to the incineration of finely divided waste. For heterogeneous waste, fluidised bed combustion requires the selection and pre-treatment of the waste so that it meets size specifications. Pre-treatment usually consists of sorting and crushing larger inert particles, and shredding. Removal of ferrous and non-ferrous materials may also be required (Neuwahl et al., 2019).

A fluidised bed furnace is a lined combustion chamber in the form of a vertical cylinder (Figure 6). In the lower section, a sand bed on a grate or distribution plate is fluidised with air. The waste that is to be incinerated is continuously fed into the fluidised sand bed from the top or side. A schematic overview of a fluidised bed incinerator including the flue gas treatment process is presented in Figure 6.

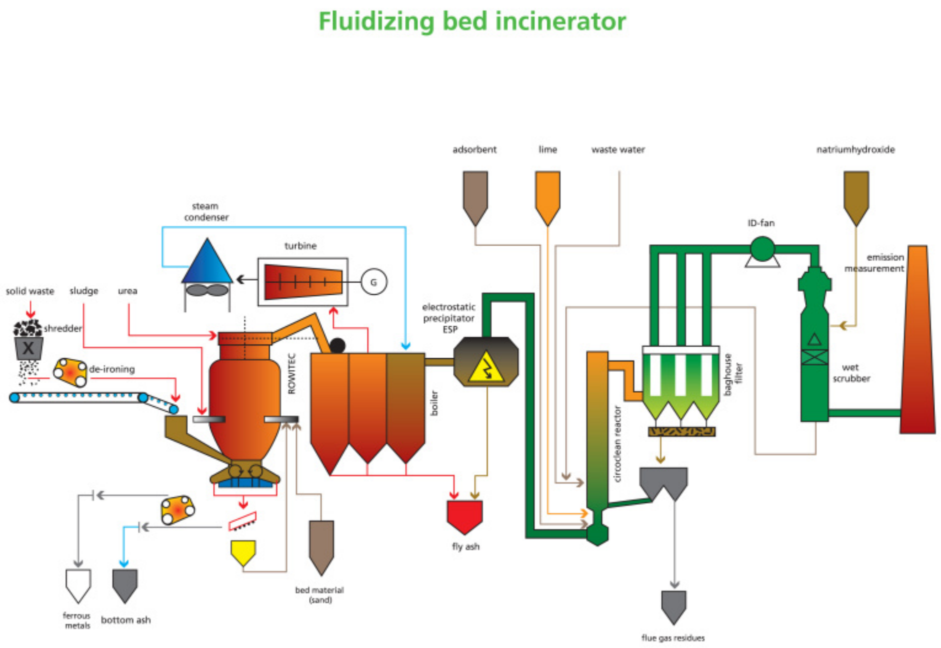

Figure 6 Schematic representation of a fluidised bed incinerator including flue gas treatment system
Source: Indaver (2020a).
Approximate temperature indication by colour: red = 1000–1200 °C; orange = 850–1000 °C; yellow = 700–600 °C; green = 250–100 °C; blue = <80 °C. The colour of the stack does not match; the stack temperature is usually in the range of 80–110 °C.

According to Thomé-Kozminesky et al. (2012), the sand bed has a temperature of about 800–850 °C. Neuwahl et al. (2019) report that the temperature in the space above the bed is generally between 850 °C and 950 °C and that in the bed itself the temperature is lower and may be around 650 °C. In the bottom part of the bed the material first undergoes partial or complete degassing. Actual combustion of the waste happens in the upper part of the bed, where the secondary air is added. The main advantage of fluidised bed furnaces is the complete mixing of waste and combustion air, thus establishing an even temperature distribution and heat transfer within the furnace. Complete mixing allows the whole mass of waste, fuel and sand to be fully circulated through the furnace, resulting favourable incineration conditions and fast combustion. Typical operation temperatures for fluidised bed furnaces are between 850 and 950 °C (SNB, 2019; Indaver, 2020a), with a maximum of 1200 °C (Thomé-Kozminesky et al., 2012).

II.2 Rotary kilns

A rotary kiln consists of a cylinder inclined in the transport direction and lined on the inside with refractory material or a cooled steel shell (Figure 7).

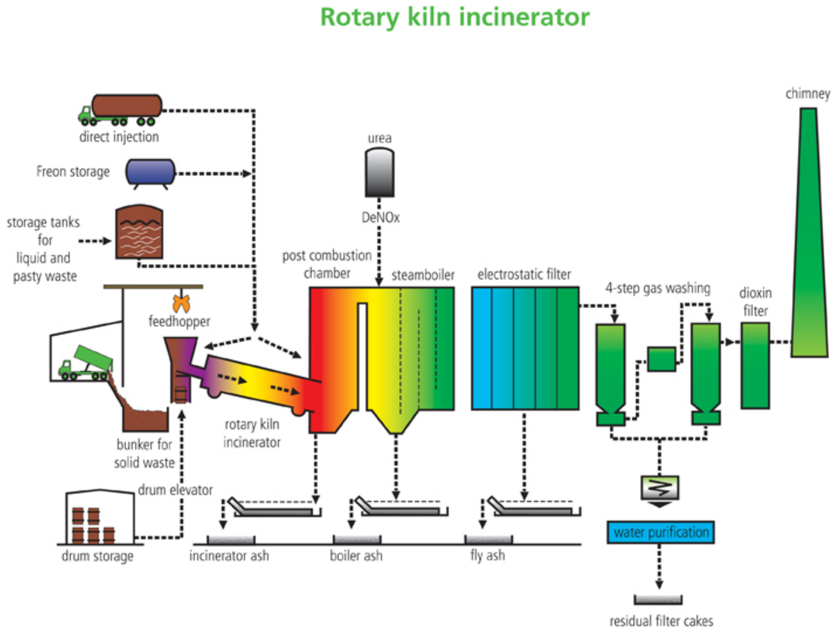

Figure 7 Schematic representation of a rotary kiln incinerator including flue gas treatment system
Source: Indaver (2020b).
Approximate temperature indication by colour: red = 1000–1200 °C; orange = 850–1000 °C; yellow = 700–600 °C; green = 250–100 °C; blue = <80 °C.

The interior of the cylinder can be up to 20% filled with fuel, which forms a moving bed. Rotation of the furnace about its longitudinal axis turns over the contents and, by virtue of the inclination, causes it to move toward the lower end (Thomé-Kozminesky et al., 2012). The rotary kiln is very versatile with respect to the type of waste that can be processed, ranging from solid materials to paste-like and viscous matter to contaminated liquids, which are injected through simple burners in the combustion chamber.

The mean combustion temperature in the furnace is between 800 and 1400 °C, and residence times are c. 60 minutes. As a rule, the residence time of the reaction gases in the furnace is insufficient for complete burning, and afterburning in a post-combustion chamber is carried out to ensure complete burning of the combustion gases. Liquid wastes are injected directly into this chamber through burners (Thomé-Kozminesky et al., 2012). The temperature in the post-combustion chamber typically varies between 900 and 1 200 °C depending on the installation and the waste feed (Neuwahl et al., 2019).

Indaver (2020b) indicates that the combustion temperature is maintained at a minimum of 950 °C. Neuwahl et al. (2019) report that the operating temperatures of rotary kilns range from around 500 °C (when used as a gasifier) to 1450 °C (as a high-temperature ash melting kiln). Higher temperatures are sometimes encountered, but usually in non-waste incineration applications. When the kilns are used for conventional oxidative combustion, the temperature is generally above 850 °C. Kiln temperatures in the range of 900–1200 °C are typical when incinerating hazardous wastes.

II.3 Moving-grate furnaces

The most common incineration plant for municipal solid waste is a moving-grate incinerator. The older and simpler kind of grate incinerator was a brick-lined cell with a fixed metal grate over a lower ash pit. It is the most widely used process for thermal treatment of wastes. In a moving-grate incinerator the grate conveys the waste in a horizontal or inclined direction towards the end of the combustion chamber (Figure 8). Primary air is distributed beneath the grate. Combustion takes place in the combustion chamber above the grate. Only a small amount of waste is burned on and immediately above the grate; most of it is turned into volatiles. Most of these volatiles are burned in the combustion space above the solid waste. Grate firing has the disadvantage that the generation of reaction products is largely uncontrollable. In the boundary zone between the drying and combustion steps, degasification processes generate carbon compounds that cannot be completely destroyed in the combustion space. Secondary air is injected into the combustion space through nozzles to ensure complete burning of the combustion gases, and intensive mixing of combustion gases to prevent residual unburned gases (Thomé-Kozminesky et al., 2012).

The maximum temperature in the fuel bed is reached at the end of the ignition zone. Here, the temperature in the bed as well as that of the flue gas is about 900 °C. At the end of the grate, the temperature of the bed has dropped to about 400 °C. At this stage the temperature of the gas is slightly higher: about 450 °C. After the addition of secondary air to the combustion chamber, the temperature of the flue gas lies in the range 900–1050 °C (Gehrmann et al., 2013). Indaver (2020c) states that combustion temperatures in its moving-grate waste incinerator range from 850 to 1000 °C.

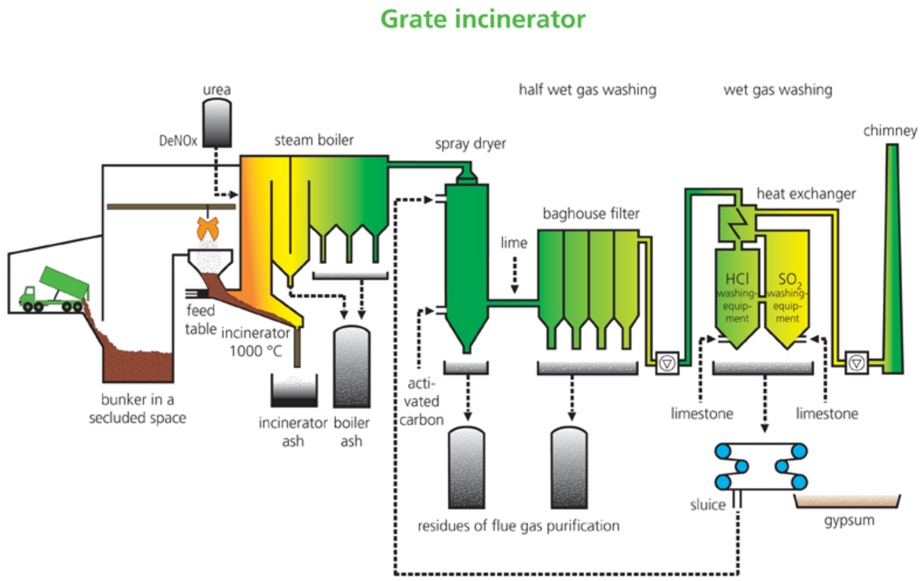

Figure 8 Schematic overview of a grate incinerator including flue gas treatment system
Source: Indaver (2020c).
Approximate temperature indication by colour: red = 1000–1200 °C;
orange = 850–1000 °C; yellow = 700–600 °C; green = 250–100 °C; blue = <80 °C.

Moving-grate incinerators can be subdivided according to the position of the entrance to the afterburn chamber with respect to the grate. The afterburn chamber, or the post-combustion chamber, can be considered as the first duct of the steam boiler. The entrance can be positioned at the beginning, the middle or the end of the moving grate. This determines the direction of the flow of the flue gases over the combustion bed. Therefore, three different types of combustion chambers can be distinguished: parallel flow, counter flow and centre flow kilns (Van der Linden and Briffaerts, 2005).

In order to ensure as complete combustion as possible, secondary air is injected, which also facilitates the mixing of the combustion gases. Typically, secondary air injection takes place in the transition area between the kiln and afterburn chamber. Enhanced burning is achieved by counter flow chambers. The residence time is higher using parallel flow, which also leads to higher temperatures in the post combustion chamber (Van der Linden and Briffaerts, 2005). For the municipal solid waste incinerators in the Netherlands, the type of kiln according to the position of the secondary combustion chamber is provided in Appendix I in this report.

Annex III: Flue gas treatment techniques

III.1 Common treatment steps

Each process unit in the flue gas treatment system is designed to remove specific flue gas components. The most common unit processes are listed below, together with their typical operating conditions.

Dust collection
The separation of solid particles and liquid droplets in an electrostatic precipitator (ESP) is achieved by the action of electrostatic forces in an electric field. Separation efficiency is very good and reaches up to 99% (Achternbosch and Richers, 2002). Typical operating temperatures for electrostatic precipitators are 160–260 °C (Neuwahl et al., 2019). Operation at temperatures of up to 450 °C is possible but this is generally avoided, as it can increase the risk of polychlorinated dibenzo-p-dioxin and dibenzofuran (PCDDs/PCDFs) formation. During the process of NO_x reduction the temperature in the electrostatic filter the temperature should not be lower than 180 °C to prevent the condensation of injected ammonia, which otherwise affects the quality of the fly ash. Operating temperatures of electrostatic precipitators in modern waste incineration plants are around 200 °C (Achternbosch and Richers, 2002).

Bag filters, also called baghouse filters or fabric filters, are widely used in waste incineration plants. Filtration efficiencies are very high (99%) across a wide range of particle sizes. Bag filters can also be used after an ESP or wet scrubber process. Operating temperatures depend on the bag filter material used and range from 80 °C for cotton up to 260 °C for polyamide and fibreglass. According to Achternbosch and Richers (2002), fabric filters used in large-scale waste incineration plants are operated at temperatures ranging from 170 to 200 °C.

Cyclones and multi-cyclones use centrifugal forces to separate dust from the gas stream. Depending on the particle size, cyclones are generally less efficient than bag and electrostatic filters: about 80% of the dust contained in the flue gas can be removed (Achternbosch and Richers, 2002). A major advantage of cyclones is their wide operational temperature range and robust construction. Cyclones can be used at gas temperatures of up to 1300 °C (Achternbosch and Richers, 2002).

Removal of acid components
Acid gases such as sulphur dioxide and gaseous halogenides such as HF are generally cleaned from flue gases by the injection of alkaline reagents into the flue gas. Depending on the technique, the reaction products are either dissolved or dry salts. Three main types of processes are applied: wet, semi-wet and dry.

1) Wet
The wet process usually consist of two parts. The first stage is aimed at the removal of acids such as HCl and HF by a water quench. The scrubber solution is typically strongly acidic, with a typical pH between 0

and -1. The scrubbing water can be recycled many times without much fresh water addition. Removal of SO_2 at this stage is low. Removal of sulphur dioxide is achieved in a second washing stage, controlled at a pH of 5–7 (Neuwahl et al., 2019).

To maintain scrubbing efficiency and prevent clogging in the wet scrubbing system, a portion of the scrubber liquid must be removed from the circuit as waste water. This waste water must be treated before discharge or re-use.

2) Semi-wet
Water and the absorption agent (hydrated lime) are injected separately or as a suspension or solution into the hot flue gas flow via a spray tower. The heat of the flue gas serves to evaporate the solvent (water). The reaction products generated are solid and need to be deposited from the flue gas as dust in a subsequent stage, e.g. bag filter.

3) Dry
In a dry sorption process, the absorption agent, an alkaline material such as lime is fed into the reactor as a dry powder. If there is no pre-dedusting stage (e.g. electrostatic precipitator or cyclone), particles are removed with the used reagent and reaction products. Solid particles need to be removed from the flue gas as dust in a subsequent stage, normally a bag filter.

Reduction of NO_x
During combustion, part of the nitrogen in the air is oxidised to nitrogen oxides (NO_x). There are two important techniques for reducing emissions of NO_x: selective non-catalytic reduction (SNCR) and selective catalytic reduction (SCR). In the SNCR process, NO_x is removed by injecting ammonia or urea into the hot flue gases. The reactions occur at temperatures of between 850 and 1 000 °C. In the SCR process, an ammonia–air mixture is added to the flue gas and passed over a catalyst, where ammonia reacts with NO_x to give nitrogen and water vapour. To be effective, the catalyst usually requires a temperature of between 150 and 450 °C. The majority of systems used in waste incinerators currently operate in the range 180–250 °C.

Removal of trace organic contaminants and mercury
The flue gas of waste incinerators can contain a variety of trace organic compounds such as polycyclic aromatic compounds, chlorobenzenes and monoaromatic hydrocarbons (BTX). Adsorption on coke, lignite or activated carbon (AC) is often applied for the fine cleaning of flue gas after the removal of acid pollutants. This can be done by leading the flue gas through a fixed bed absorber or by injecting activated carbon powder (PAC) into the gas flow, after which the carbon needs to be filtered using bag filters. Alternatively, the powder can be injected before the scrubber section, where the AC is removed, a so-called ADRT (Avira Dioxin Reduction Technology) system. In this system the AC is collected in the filter cake of the waste water treatment section.

AC shows a high adsorption efficiency for mercury as well as for PCDDs/PCDFs. Different types of activated carbon have different

adsorption efficiencies, which are very much influenced by the manufacturing process.
The adsorptive capacity of the solid carbon for the gas tends to increase with the gas phase concentration, molecular weight, diffusivity, polarity and boiling point. AC can adsorb a wide range of VOCs; however, there are some limitations. First, AC is less effective for compounds that are highly polar or volatile or have small diameters. Typical operating temperatures for activated coal adsorption range from 25 to 40 °C, although adsorption can take place at temperatures as low as 0 °C and even higher than 40 °C (Sorrels, 2018). As volatility plays an important role in adsorption, temperatures should stay within certain limits depending on the type of contaminant to be captured.

At high temperatures thermodesorption will occur. Thermodesorption is a process used, for instance, to regenerate spent AC. The operating temperature for carbon adsorption very much depends on where in the flue gas treatment process it is applied. Injection of the carbon into the flue gas can be done upstream, after dust filtering or at a later stage, downstream of the web scrubbing system. For the effective capturing of dioxins by AC Lu et al. (2012) showed that the temperature should not exceed 150 °C. Vito (2020) indicates that the typical operating temperature is below 50 °C (15–80 °C) except for the dioxin removal stage, where higher temperatures may be employed. As a maximum an operating temperature of 150 °C can be assumed.

In the dry process where injected AC and lime are removed by a bag filter, the temperature is about 80–100 °C, as indicated below (SNB, 1993, 2019). In the (semi-)dry process involving application of the CircoClean reactor, the temperature is about 165 °C according to SLECO (2018). According to Herden et al. (2002), the operating temperature of the CircoClean reactor at a pilot plant was about 140 °C. In the wet process, carbon is injected into the flue gas at a temperature of between 160 and 200 °C. In the scrubber section, where the carbon is removed, the temperature is about 75 °C.

SCR systems used for NO_x reduction can also destroy gaseous or non-particle-bound trace organics such as PCDDs/PCDFs through catalytic oxidation. However, to establish high destruction efficiencies the SCR system must be designed accordingly (Neuwahl et al., 2019).

III.2 Three examples of flue gas cleaning

Three examples of flue gas cleaning configurations for a fluidised bed furnace are described in the following paragraphs. In the first case (SNB, 1993, 2019) the temperature of the flue gas entering the boiler is about 900 °C. In the boiler, the flue gas cools to a temperature of about 200 °C. Before entering the scrubber, the flue gas is further cooled to a temperature of 160 °C. After the washing stages, the temperature is reduced to 75°C and then the gas is reheated to 80–110 °C to prevent the condensation of water vapour. To remove mercury and trace organics like dioxins, the flue gas is treated with an adsorbent (mixture of AC and calcium hydroxide) and led through a bag filter. Entering the stack, the flue gas is at about the same temperature as when entering the bag filter: 80–110 °C. As a final step, heat can be recovered from the cleaned flue gas by condensers before it enters the stack, and the temperature may then be reduced to about 50 °C.

The second case is the flue gas treatment system at the Sleco fluidised bed incinerator at Doel in Belgium (SLECO, 2018). Hot primary air at 600 °C is blown into the sand bed and, above, secondary air is added to ensure complete combustion. Flue gas with a temperature of at least 850 °C exits the incinerator through the flue gas duct, where urea is injected to convert oxides of nitrogen into nitrogen gas. In the boiler, where steam is generated, the gas is cooled from about 900 °C to an average temperature of 230 °C. The first flue gas treatment step is an electrostatic filter for the removal of solid particles (dust). The next step is a semi-wet scrubbing, where lignite and lime are dosed to capture heavy metals, dioxins, chlorine and sulphur. Here, the flue gas is cooled to 165 °C. The lime and lignite added in the previous step are removed in a bag house filtering system. The final step is a caustic scrubbing column for the removal of any remaining chlorine and sulphur. At this stage, the flue gas is cooled to 65 °C.

The third case is the AVR incineration site at Duiven (Houben and Boerleider, 2020). At this site, CO_2 is recovered from the flue gas. The recovered CO_2 will be used as a plant fertiliser for greenhouse farming. Starting at a combustion temperature of 1200 °C, the flue gas decreases to a temperature of about 1000 °C as it moves towards the steam boiler. Before it enters the boiler at a temperature of between 850 and 1000 °C, ammonia is injected to reduce the formation of NO_x by SNCR. In the upper part of the boiler, the temperature is about 650–700 °C and it is gradually reduced to a temperature of 250 or 280 °C depending on the heat recovery system applied in the final stage.

In the electrostatic filter, the temperature should not be lower than 180 °C to prevent the condensation of ammonia, which affects the quality of the fly ash. The electro filter removes up to 99% of the dust (fly ash).

To remove dioxins and other pollutants, AC is injected into the flue gas before it enters the washing stage. The AC is captured during the washing. The washing stage consists of three consecutive sections combined in one system, the ADRT system:

- quench with wash water to remove salts, ammonia and acids (fly ash that passed the electrofilters is also captured by the wash water); the maximum temperature is 77 °C;
- SO_2 trap, where SO_2 is removed through an alkaline solution (NaOH) at an optimal pH of 5;
- Ring-jet (venturi washer) to remove aerosols and mercury.

Annex IV. Measured PFASs at the ARV sites at Duiven and Rozenburg

PFAS	Bottom ash Rozenburg (n=2)	Bottom ash Duiven (n=3)	Fly ash Rozenburg (n=1)	Filter cake Rozenburg (n=1)	Emission to air Rozenburg (average) (n=4)[1]	Emission to water Rozenburg (n=2)[2]
	µg/kg	µg/kg	µg/kg	µg/kg	ng/Nm^{3}o	µg/l
PFPeA	< 0.10	0.29 & < 0.1	< 0.1	< 0.1	nb	< 0.02
PFHxA	< 0.10	1.1 & < 0.1	< 0.1	< 0.1	2	< 0.02
PFHpA	< 0.10	< 0.1 & < 1.0	< 0.1	< 0.1	0.4	< 0.02
PFOA (lineair)	< 0.10	1.3 & < 0.1	< 0.1	< 0.1	8.2	< 0.01
PFOA (branched)	< 0.10	0.16 & < 0.1	< 0.1	< 0.1	0.7	< 0.01
PFNA	< 0.10	0.12 & < 0.1	< 0.1	< 0.1	0.2	< 0.02
PFBA	< 0.10	1.2 & < 0.1	< 0.1	< 0.1	nb	< 0.02
6:2 FTS	9.9	36 & < 0.1	< 0.1	< 0.5	0.3	< 0.05
FRD 903	< 1.0	< 0.1	< 0.1	< 0.1	< 0.01	< 0.02
E1	nb	nb	nb	nb	nb	nb
PTFE	nb	nb	nb	nb	nb	nb
PPVE	nb	nb	nb	nb	nb	nb
PFDA	< 0.10	0.42 & < 0.1	< 0.1	< 0.1	2.9	< 0.02
PFUnDA	< 0.10	0.21 & < 0.1	< 0.1	< 0.1	0.1	< 0.02
PFDoDA	< 0.10	0.17 & < 0.1	< 0.1	< 0.1	1	< 0.02
PFBS	0.59 & < 0.1	3.6 & < 0.1	< 0.1	< 0.1	0.06	< 0.02
PFHpS	< 0.10	< 0.1	< 0.1	< 0.1	< 0.01	< 0.02
PFHxS	< 0.10	< 0.1	< 0.1	< 0.1	< 0.01	< 0.02
PFPeS	< 0.10	< 0.1	< 0.1	< 0.1	< 0.01	< 0.02
PFOS (linear)	0.15 & < 0.1	0.56 & < 0.1	< 0.1	< 0.1	0.1	< 0.001
PFOS (branched)	< 0.10	0.22 & < 0.1	< 0.1	< 0.1	0.05	< 0.001
PFOSA	< 0.10	0.53 & < 0.1	< 0.1	< 0.1	0.03	< 0.02
PFTeDA	< 0.10	< 0.1	< 0.1	< 0.1	0.6	< 0.02
PFTrDA	< 0.10	< 0.1	< 0.1	< 0.1	0.1	< 0.02
PFHxDA	< 0.20	< 0.1	< 0.1	< 0.1	0.24	< 0.02
PFODA	< 2.0	< 0.1	< 0.1	< 0.1	0.08	< 0.02
PFDS	< 0.10	< 0.1	< 0.1	< 0.1	< 0.02	< 0.02
4:2 FTS	< 0.10	< 0.1	< 0.1	< 0.1	< 0.01	< 0.05
8:2 FTS	0.66	2.5 & < 0.1	< 0.1	< 0.1	1.1	< 0.1
10:2 FTS	< 0.10	0.24 & < 0.1	< 0.1	< 0.1	2.1	< 0.05
N-MeFOSA	< 0.10	< 0.1	< 0.1	< 0.1	< 0.04	< 0.02
N-MeFOSAA	< 0.10	0.13 & < 0.1	< 0.1	< 0.1	< 0.05	< 0.02
N-EtFOSAA	< 0.10	< 0.1	< 0.1	< 0.5	< 0.05	< 0.02
8:2 diPAP	< 0.10	< 0.2 & < 0.1	< 0.1	< 0.1	< 0.05	< 0.1

[1] average of single measurements at four stacks; [2] average of two effluents.
Source: Houben and Boerleider (2020; tables 6.4 and 6.5).

Annex V. Indication of PFAS removal at flue gas treatment

PFAS	**Total removal in Quench**	**Total removal in SO_2 trap**	**Total removal in venturi wash**	**Removal by PAC**	**Total removal**
Fluortelomer alcohols					
4:2 FTOH	Poor	Poor	Poor	Average	Average
6:2 FTOH	Poor	Poor	Poor	Good	Good
8:2 FTOH	Poor	Poor	Poor	Good	Good
10:2 FTOH	Poor	Poor	Poor	Very Good	Very Good
Perfluorinated carboxylate acids (PFCAs)					
PFBA	Average	Very Good	Very Good	Very Good	Very Good
PFPeA	Poor	Very Good	Very Good	Very Good	Very Good
PFHxA	Poor	Very Good	Good	Very Good	Very Good
PFHpA	Poor	Good	Poor	Very Good	Very Good
PFOA	Poor	Very Good	Good	Very Good	Very Good
PFNA	Poor	Very Good	Good	Very Good	Very Good
Perfluorinated sulfonic acids (PFSAs)					
PFBS	Very Good	Very Good	Very Good	Very Good	Very Good
PFHxS	Very Good	Very Good	Very Good	Very Good	Very Good
PFOS	Very Good	Very Good	Very Good	Very Good	Very Good
PFDS	Very Good	Very Good	Very Good	Very Good	Very Good
Perfluoroalkyl sulfinic acids (PFSiAs)					
PFBSi	Poor	Very Good	Very Good	Very Good	Very Good
PFHxSi	Poor	Very Good	Good	Very Good	Very Good
PFOSi	Poor	Very Good	Average	Very Good	Very Good
PFDSi	Poor	Good	Poor	Very Good	Very Good
Perfluorinated phosphonic acids (PFPAs)					
PFBPA	Very Good	Very Good	Very Good	Very Good	Very Good
PFHxPA	Very Good	Very Good	Very Good	Very Good	Very Good
PFOPA	Very Good	Very Good	Very Good	Very Good	Very Good
PFDPA	Very Good	Very Good	Very Good	Very Good	Very Good
Perfluoroalkyl phosphinic acids (PFPiAs)					
C6/C6 PFPiA	Poor	Very Good	Average	Very Good	Very Good
C8/C8 PFPiA	Poor	Good	Poor	Very Good	Very Good
C6/C8 PFPiA	Poor	Poor	Poor	Very Good	Very Good

PFAS	**Total removal in Quench**	**Total removal in SO_2 trap**	**Total removal in venturi wash**	**Removal by PAC**	**Total removal**
Fluorotelomer olefins (FTOs)					
4:2 FTO	Poor	Poor	Poor	Poor	Poor
6:2 FTO	Poor	Poor	Poor	Poor	Poor
8:2 FTO	Poor	Poor	Poor	Poor	Poor
10:2 FTO	Poor	Poor	Poor	Poor	Poor
12:2 FTO	Poor	Poor	Poor	Average	Average
Fluorotelomer sulfonate (FTSs)					
4:2 FTS	Very Good	Very Good	Very Good	Very Good	Very Good
6:2 FTS	Very Good	Very Good	Very Good	Very Good	Very Good
8:2 FTS	Good	Very Good	Very Good	Very Good	Very Good
10:2 FTS	Average	Good	Average	Very Good	Very Good
12:2 FTS	Poor	Average	Poor	Very Good	Very Good
Fluorotelomer iodides (FTIs)					
4:2 FTI	Poor	Poor	Poor	Poor	Poor
6:2 FTI	Poor	Poor	Poor	Average	Average
8:2 FTI	Poor	Poor	Poor	Good	Good
10:2 FTI	Poor	Poor	Poor	Very Good	Very Good
12:2 FTI	Poor	Poor	Poor	Very Good	Very Good
Perfluoroalkyl iodides (PFAIs)					
PFBI	Poor	Poor	Poor	Poor	Poor
PFPeI	Poor	Poor	Poor	Poor	Poor
PFHxI	Poor	Poor	Poor	Poor	Poor
PFHpI	Poor	Poor	Poor	Poor	Poor
PFOI	Poor	Poor	Poor	Poor	Poor
PFNI	Poor	Poor	Poor	Poor	Poor
PFDI	Poor	Poor	Poor	Poor	Poor
PFUnI	Poor	Poor	Poor	Average	Average
PFDoI	Poor	Poor	Poor	Average	Average
PFTrI	Poor	Poor	Poor	Good	Good
PFTeI	Poor	Poor	Poor	Good	Good
Perfluoroalkyl sulfonamides (FASAs)					
FBSA	Average	Good	Average	Very Good	Very Good
FPESA	Poor	Average	Poor	Very Good	Very Good
FHXSA	Poor	Average	Poor	Very Good	Very Good
FHpSA	Poor	Poor	Poor	Very Good	Very Good
FOSA	Poor	Poor	Poor	Very Good	Very Good

PFAS	**Total removal in Quench**	**Total removal in SO_2 trap**	**Total removal in venturi wash**	**Removal by PAC**	**Total removal**
N-Methyl perfluoroalkane sulfonamides (MeFASAs)					
MeFBSA	Poor	Poor	Poor	Very Good	Very Good
MeFPeSA	Poor	Poor	Poor	Very Good	Very Good
MeFHxSA	Poor	Poor	Poor	Very Good	Very Good
MeFHpSA	Poor	Poor	Poor	Very Good	Very Good
MeFOSA	Poor	Poor	Poor	Very Good	Very Good
N-Ethyl perfluoroalkane sulfonamides (EtFASAs)					
EtFBSA	Poor	Poor	Poor	Very Good	Very Good
EtFPeSA	Poor	Poor	Poor	Very Good	Very Good
EtFHxSA	Poor	Poor	Poor	Very Good	Very Good
EtFHpSA	Poor	Poor	Poor	Very Good	Very Good
EtFOSA	Poor	Poor	Poor	Very Good	Very Good
Perfluoroalkyl sulfonamido ethanols (FASEs)					
FBSE	Good	Good	Good	Very Good	Very Good
FPeSE	Good	Good	Good	Very Good	Very Good
FHxSE	Average	Good	Average	Very Good	Very Good
FHpSE	Poor	Average	Poor	Very Good	Very Good
FOSE	Poor	Average	Poor	Very Good	Very Good
N-Methyl perfluoroalkane sulfonamido ethanols (MeFASEs)					
MeFBSE	Poor	Average	Poor	Very Good	Very Good
MeFPeSE	Poor	Average	Poor	Very Good	Very Good
MeFHxSE	Poor	Average	Poor	Very Good	Very Good
MeFHpSE	Poor	Poor	Poor	Very Good	Very Good
MeFOSE	Poor	Poor	Poor	Very Good	Very Good
Perfluoroalkane sulfonamido acetic acids (FASAAs)					
FOSAA	Poor	Poor	Poor	Very Good	Very Good
MeFOSAA	Poor	Poor	Poor	Very Good	Very Good
EtFOSAA	Poor	Poor	Poor	Very Good	Very Good
N-Ethyl perfluoroalkane sulfonamido ethanols (EtFASEs)					
EtFBSE	Average	Good	Average	Very Good	Very Good
EtFPeSE	Poor	Average	Poor	Very Good	Very Good
EtFHxSE	Poor	Average	Poor	Very Good	Very Good
EtFHpSE	Poor	Poor	Poor	Very Good	Very Good
EtFOSE	Poor	Poor	Poor	Very Good	Very Good

PFAS	**Total removal in Quench**	**Total removal in SO_2 trap**	**Total removal in venturi wash**	**Removal by PAC**	**Total removal**
Fluorotelomer phosphate monoesters (monoPAPs)					
4:2 monoPAP	Very Good	Very Good	Very Good	Very Good	Very Good
6:2 monoPAP	Very Good	Very Good	Very Good	Very Good	Very Good
8:2 monoPAP	Very Good	Very Good	Very Good	Very Good	Very Good
10:2 monoPAP	Very Good	Very Good	Very Good	Very Good	Very Good
12:2 monoPAP	Very Good	Very Good	Very Good	Very Good	Very Good
Fluorotelomer phosphate diesters (diPAPs)					
4:2 diPAP	Good	Very Good	Very Good	Very Good	Very Good
4:2/6:2 diPAP	Good	Very Good	Very Good	Very Good	Very Good
6:2 diPAP	Good	Very Good	Very Good	Very Good	Very Good
6:2/8:2 diPAP	Poor	Very Good	Good	Very Good	Very Good
8:2 diPAP	Poor	Very Good	Good	Very Good	Very Good
8:2/10:2 diPAP	Poor	Very Good	Average	Very Good	Very Good
10:2 diPAP	Poor	Very Good	Good	Very Good	Very Good
10:2/12:2 diPAP	Poor	Good	Poor	Very Good	Very Good
12:2 diPAP	Poor	Good	Poor	Very Good	Very Good
Perfluoroalkanes (PFFs)					
PFBF	Poor	Poor	Poor	Poor	Poor
PFHxF	Poor	Poor	Poor	Poor	Poor
PFOF	Poor	Poor	Poor	Poor	Poor
PFDF	Poor	Poor	Poor	Poor	Poor
Fluorotelomer carboxylic acids (FTCAs)					
2:2 FTCA	Good	Good	Good	Very Good	Very Good
4:2 FTCA	Poor	Good	Poor	Very Good	Very Good
6:2 FTCA	Poor	Very Good	Good	Very Good	Very Good
8:2 FTCA	Poor	Poor	Poor	Very Good	Very Good
10:2 FTCA	Poor	Poor	Poor	Very Good	Very Good
12:2 FTCA	Poor	Poor	Poor	Very Good	Very Good
Fluorotelomer unsaturated carboxylic acids (FTUCAs)					
2:2 FTUCA	Average	Good	Average	Good	Very Good
4:2 FTUCA	Poor	Poor	Poor	Very Good	Very Good
6:2 FTUCA	Poor	Poor	Poor	Very Good	Very Good
8:2 FTUCA	Poor	Poor	Poor	Very Good	Very Good
10:2 FTUCA	Poor	Poor	Poor	Very Good	Very Good
12:2 FTUCA	Poor	Poor	Poor	Very Good	Very Good

PFAS	**Total removal in Quench**	**Total removal in SO_2 trap**	**Total removal in venturi wash**	**Removal by PAC**	**Total removal**
Fluorotelomer aldehyde (FTALs)					
2:2 FTAL	Poor	Poor	Poor	Poor	Poor
4:2 FTAL	Poor	Poor	Poor	Poor	Poor
6:2 FTAL	Poor	Poor	Poor	Poor	Poor
8:2 FTAL	Poor	Poor	Poor	Average	Average
10:2 FTAL	Poor	Poor	Poor	Good	Good
12:2 FTAL	Poor	Poor	Poor	Good	Good
Fluorotelomer unsaturated aldehyde (FTUALs)					
4:2 FTUAL	Poor	Poor	Poor	Poor	Poor
6:2 FTUAL	Poor	Poor	Poor	Poor	Poor
8:2 FTUAL	Poor	Poor	Poor	Poor	Poor
10:2 FTUAL	Poor	Poor	Poor	Good	Good
12:2 FTUAL	Poor	Poor	Poor	Good	Good
Perfluorinated aldehyde (PFALs)					
PFBAL	Poor	Poor	Poor	Poor	Poor
PFPAL	Poor	Poor	Poor	Poor	Poor
PFHxAL	Poor	Poor	Poor	Poor	Poor
PFHpAL	Poor	Poor	Poor	Poor	Poor
PFOAL	Poor	Poor	Poor	Poor	Poor
PFNAL	Poor	Poor	Poor	Poor	Poor
PFDAL	Poor	Poor	Poor	Poor	Poor
PFUnAL	Poor	Poor	Poor	Poor	Poor
PFDoAL	Poor	Poor	Poor	Poor	Poor
PFTrAL	Poor	Poor	Poor	Average	Average
PFTeAL	Poor	Poor	Poor	Average	Average
PFOA replacements					
Adona	Poor	Very Good	Very Good	Very Good	Very Good
GenX	Poor	Very Good	Very Good	Very Good	Very Good
PFTECA1	Poor	Very Good	Good	Very Good	Very Good
PFTECA2	Poor	Very Good	Good	Very Good	Very Good
EEA	Poor	Very Good	Very Good	Very Good	Very Good
6:2 FTCA	Poor	Very Good	Average	Very Good	Very Good
PFOS replancements					
F-53	Poor	Very Good	Good	Very Good	Very Good
F-53B	Poor	Very Good	Very Good	Very Good	Very Good
PFBSaPA	Very Good	Very Good	Very Good	Very Good	Very Good

PFAS	**Total removal in Quench**	**Total removal in SO_2 trap**	**Total removal in venturi wash**	**Removal by PAC**	**Total removal**
8:2 FTOH replacements					
3:1 FTOH	Poor	Poor	Poor	Poor	Average
5:1 FTOH	Poor	Poor	Poor	Average	Average
Other alternatives					
EF-N441S-30	Very Good	Very Good	Very Good	Good	Very Good
Novec 1230	Poor	Poor	Poor	Poor	Poor
Forafac 1183	Very Good	Very Good	Very Good	Very Good	Very Good
PFOTSi	Poor	Poor	Poor	Good	Good
PFOTSi -(OH)	Poor	Poor	Poor	Very Good	Very Good
PFOTSi -(OH)2	Poor	Good	Poor	Very Good	Very Good
PFOTSi -(OH)3	Very Good	Very Good	Very Good	Very Good	Very Good
RM720	Poor	Average	Poor	Very Good	Very Good
RM720-(OH)	Very Good	Very Good	Very Good	Very Good	Very Good
RM720-(OH)2	Very Good	Very Good	Very Good	Very Good	Very Good
RM720-(OH)3	Very Good	Very Good	Very Good	Very Good	Very Good
Fluorotelomer metacrylates					
6:2 FTMAC	Poor	Poor	Poor	Poor	Poor
Fluorotelomer acrylates					
6:2 FTAC	Poor	Poor	Poor	Poor	Poor
Fluorinated products of incomplete combustion					
PFM	Poor	Poor	Poor	Poor	Poor
PFE	Poor	Poor	Poor	Poor	Poor
PFCB	Poor	Poor	Poor	Poor	Poor
TFE	Poor	Poor	Poor	Poor	Poor
HFP	Poor	Poor	Poor	Poor	Poor
PFIB	Poor	Poor	Poor	Poor	Poor

The colours indicate the degree of removal as follows: red = poor, orange = average, yellow = good and green = very good. For a more quantitative interpretation, indicative removal efficiencies are provided here for the different classes: green = >99%; yellow = 90–99%; orange= 90–75% and red = <75%. For the qualitative assessment the calculations are described in Sections 5.2.2-5.2.4.

Annex VI. PFASs removed and remaining at CO_2 recovery

PFAS	**Removal from flue gas**	**Fraction from flue gas in CO_2**	**Removal in CO_2 washer**	**Fraction left in CO_2 before liquefaction**
Fluortelomer alcohols				
4:2 FTOH	Poor	Considerable	Poor	Considerable
6:2 FTOH	Poor	Small	Poor	Small
8:2 FTOH	Poor	Very small	Poor	Very small
10:2 FTOH	Poor	Very small	Poor	Very small
Perfluorinated carboxylate acids (PFCAs)				
PFBA	Very Good	Very small	Very Good	Very small
PFPeA	Very Good	Very small	Very Good	Very small
PFHxA	Very Good	Very small	Very Good	Very small
PFHpA	Very Good	Very small	Average	Very small
PFOA	Very Good	Very small	Very Good	Very small
PFNA	Very Good	Very small	Very Good	Very small
Perfluorinated sulfonic acids (PFSAs)				
PFBS	Very Good	Very small	Very Good	Very small
PFHxS	Very Good	Very small	Very Good	Very small
PFOS	Very Good	Very small	Very Good	Very small
PFDS	Very Good	Very small	Very Good	Very small
Perfluoroalkyl sulfinic acids (PFSiAs)				
PFBSi	Very Good	Very small	Very Good	Very small
PFHxSi	Very Good	Very small	Very Good	Very small
PFOSi	Very Good	Very small	Good	Very small
PFDSi	Very Good	Very small	Average	Very small
Perfluorinated phosphonic acids (PFPAs)				
PFBPA	Very Good	Very small	Very Good	Very small
PFHxPA	Very Good	Very small	Very Good	Very small
PFOPA	Very Good	Very small	Very Good	Very small
PFDPA	Very Good	Very small	Very Good	Very small
Perfluoroalkyl phosphinic acids (PFPiAs)				
C6/C6 PFPiA	Very Good	Very small	Good	Very small
C8/C8 PFPiA	Very Good	Very small	Average	Very small
C6/C8 PFPiA	Very Good	Very small	Poor	Very small

PFAS	Removal from flue gas	Fraction from flue gas in CO_2	Removal in CO_2 washer	Fraction left in CO_2 before liquefaction
Fluorotelomer olefins (FTOs)				
4:2 FTO	Poor	Very small	Poor	Very small
6:2 FTO	Poor	Very small	Poor	Very small
8:2 FTO	Poor	Very small	Poor	Very small
10:2 FTO	Poor	Very small	Poor	Very small
12:2 FTO	Poor	Very small	Poor	Very small
Fluorotelomer sulfonate (FTSs)				
4:2 FTS	Very Good	Very small	Very Good	Very small
6:2 FTS	Very Good	Very small	Very Good	Very small
8:2 FTS	Very Good	Very small	Very Good	Very small
10:2 FTS	Very Good	Small	Good	Very small
12:2 FTS	Good	Considerable	Poor	Considerable
Fluorotelomer iodides (FTIs)				
4:2 FTI	Poor	Very small	Poor	Very small
6:2 FTI	Poor	Very small	Poor	Very small
8:2 FTI	Poor	Very small	Poor	Very small
10:2 FTI	Poor	Very small	Poor	Very small
12:2 FTI	Poor	Very small	Poor	Very small
Perfluoroalkyl iodides (PFAIs)				
PFBI	Poor	Very small	Poor	Very small
PFPeI	Poor	Very small	Poor	Very small
PFHxI	Poor	Very small	Poor	Very small
PFHpI	Poor	Very small	Poor	Very small
PFOI	Poor	Very small	Poor	Very small
PFNI	Poor	Very small	Poor	Very small
PFDI	Poor	Very small	Poor	Very small
PFUnI	Poor	Very small	Poor	Very small
PFDoI	Poor	Very small	Poor	Very small
PFTrI	Poor	Very small	Poor	Very small
PFTeI	Poor	Very small	Poor	Very small
Perfluoroalkyl sulfonamides (FASAs)				
FBSA	Very Good	Very small	Average	Very small
FPESA	Very Good	Very small	Poor	Very small
FHXSA	Very Good	Very small	Poor	Very small
FHpSA	Very Good	Very small	Poor	Very small
FOSA	Very Good	Very small	Poor	Very small

PFAS	**Removal from flue gas**	**Fraction from flue gas in CO_2**	**Removal in CO_2 washer**	**Fraction left in CO_2 before liquefaction**
N-Methyl perfluoroalkane sulfonamides (MeFASAs)				
MeFBSA	Good	Very small	Poor	Very small
MeFPeSA	Good	Very small	Poor	Very small
MeFHxSA	Good	Very small	Poor	Very small
MeFHpSA	Average	Very small	Poor	Very small
MeFOSA	Poor	Very small	Poor	Very small
N-Ethyl perfluoroalkane sulfonamides (EtFASAs)				
EtFBSA	Good	Very small	Poor	Very small
EtFPeSA	Average	Very small	Poor	Very small
EtFHxSA	Average	Very small	Poor	Very small
EtFHpSA	Poor	Very small	Poor	Very small
EtFOSA	Poor	Very small	Poor	Very small
Perfluoroalkyl sulfonamido ethanols (FASEs)				
FBSE	Very Good	Very small	Good	Very small
FPeSE	Very Good	Very small	Good	Very small
FHxSE	Very Good	Very small	Average	Very small
FHpSE	Very Good	Very small	Average	Very small
FOSE	Very Good	Very small	Poor	Very small
N-Methyl perfluoroalkane sulfonamido ethanols (MeFASEs)				
MeFBSE	Very Good	Considerable	Average	Small
MeFPeSE	Good	Considerable	Poor	Small
MeFHxSE	Good	Considerable	Poor	Considerable
MeFHpSE	Average	Considerable	Poor	Considerable
MeFOSE	Poor	Considerable	Poor	Considerable
Perfluoroalkane sulfonamido acetic acids (FASAAs)				
FOSAA	Very Good	Very small	Poor	Very small
MeFOSAA	Very Good	Very small	Poor	Very small
EtFOSAA	Very Good	Very small	Poor	Very small
N-Ethyl perfluoroalkane sulfonamido ethanols (EtFASEs)				
EtFBSE	Very Good	Considerable	Average	Small
EtFPeSE	Good	Considerable	Poor	Small
EtFHxSE	Good	Considerable	Poor	Considerable
EtFHpSE	Average	Considerable	Poor	Considerable

PFAS	**Removal from flue gas**	**Fraction from flue gas in CO_2**	**Removal in CO_2 washer**	**Fraction left in CO_2 before liquefaction**
EtFOSE	Poor	Considerable	Poor	Considerable
Fluorotelomer phosphate monoesters (monoPAPs)				
4:2 monoPAP	Very Good	Very small	Very Good	Very small
6:2 monoPAP	Very Good	Very small	Very Good	Very small
8:2 monoPAP	Very Good	Very small	Very Good	Very small
10:2 monoPAP	Very Good	Very small	Very Good	Very small
12:2 monoPAP	Very Good	Very small	Very Good	Very small
Fluorotelomer phosphate diesters (diPAPs)				
4:2 diPAP	Very Good	Small	Good	Very small
4:2/6:2 diPAP	Very Good	Very small	Very Good	Very small
6:2 diPAP	Very Good	Very small	Very Good	Very small
6:2/8:2 diPAP	Very Good	Very small	Very Good	Very small
8:2 diPAP	Very Good	Very small	Very Good	Very small
8:2/10:2 diPAP	Very Good	Very small	Good	Very small
10:2 diPAP	Very Good	Very small	Very Good	Very small
10:2/12:2 diPAP	Very Good	Very small	Average	Very small
12:2 diPAP	Very Good	Very small	Good	Very small
Perfluoroalkanes (PFFs)				
PFBF	Poor	Very small	Poor	Very small
PFHxF	Poor	Very small	Poor	Very small
PFOF	Poor	Very small	Poor	Very small
PFDF	Poor	Very small	Poor	Very small
Fluorotelomer carboxylic acids (FTCAs)				
2:2 FTCA				
4:2 FTCA				
6:2 FTCA	Very Good	Very small	Very Good	Very small
8:2 FTCA				
10:2 FTCA				
12:2 FTCA				
Fluorotelomer unsaturated carboxylic acids (FTUCAs)				
2:2 FTUCA	Very Good	Considerable	Average	Small
4:2 FTUCA	Average	Considerable	Poor	Considerable
6:2 FTUCA	Poor	Considerable	Poor	Considerable
8:2 FTUCA	Poor	Small	Poor	Small
10:2 FTUCA	Poor	Small	Poor	Small
12:2 FTUCA	Poor	Very small	Poor	Very small

PFAS	Removal from flue gas	Fraction from flue gas in CO_2	Removal in CO_2 washer	Fraction left in CO_2 before liquefaction
Fluorotelomer aldehyde (FTALs)				
2:2 FTAL	Poor	Small	Poor	Small
4:2 FTAL	Poor	Very small	Poor	Very small
6:2 FTAL	Poor	Very small	Poor	Very small
8:2 FTAL	Poor	Very small	Poor	Very small
10:2 FTAL	Poor	Very small	Poor	Very small
12:2 FTAL	Poor	Very small	Poor	Very small
Fluorotelomer unsaturated aldehyde (FTUALs)				
4:2 FTUAL	Poor	Very small	Poor	Very small
6:2 FTUAL	Poor	Very small	Poor	Very small
8:2 FTUAL	Poor	Very small	Poor	Very small
10:2 FTUAL	Poor	Very small	Poor	Very small
12:2 FTUAL	Poor	Very small	Poor	Very small
Perfluorinated aldehyde (PFALs)				
PFBAL	Poor	Very small	Poor	Very small
PFPAL	Poor	Very small	Poor	Very small
PFHxAL	Poor	Very small	Poor	Very small
PFHpAL	Poor	Very small	Poor	Very small
PFOAL	Poor	Very small	Poor	Very small
PFNAL	Poor	Very small	Poor	Very small
PFDAL	Poor	Very small	Poor	Very small
PFUnAL	Poor	Very small	Poor	Very small
PFDoAL	Poor	Very small	Poor	Very small
PFTrAL	Poor	Very small	Poor	Very small
PFTeAL	Poor	Very small	Poor	Very small
PFOA replacements				
Adona	Very Good	Very small	Very Good	Very small
GenX	Very Good	Very small	Very Good	Very small
PFTECA1	Very Good	Very small	Very Good	Very small
PFTECA2	Very Good	Very small	Very Good	Very small
EEA	Very Good	Very small	Very Good	Very small
6:2 FTCA	Very Good	Very small	Good	Very small
PFOS replacements				
F-53	Very Good	Very small	Very Good	Very small
F-53B	Very Good	Very small	Very Good	Very small
PFBSaPA	Very Good	Very small	Very Good	Very small

PFAS	**Removal from flue gas**	**Fraction from flue gas in CO_2**	**Removal in CO_2 washer**	**Fraction left in CO_2 before liquefaction**
8:2 FTOH replacement				
3:1 FTOH	Poor	Considerable	Poor	Considerable
5:1 FTOH	Poor	Small	Poor	Small
Other alternatives				
EF-N441S-30	Very Good	Very small	Very Good	Very small
Novec 1230	Poor	Very small	Poor	Very small
Forafac 1183	Very Good	Very small	Very Good	Very small
PFOTSi	Poor	Very small	Poor	Very small
PFOTSi -(OH)	Poor	Small	Poor	Small
PFOTSi -(OH)2	Very Good	Considerable	Average	Small
PFOTSi -(OH)3	Very Good	Very small	Very Good	Very small
RM720	Very Good	Very small	Poor	Very small
RM720-(OH)	Very Good	Very small	Very Good	Very small
RM720-(OH)2	Very Good	Very small	Very Good	Very small
RM720-(OH)3	Very Good	Very small	Very Good	Very small
Fluorotelomer metacrylates				
6:2 FTMAC	Poor	Very small	Poor	Very small
Fluorotelomer acrylates				
6:2 FTAC	Poor	Very small	Poor	Very small
Fluorinated products of incomplete combustion				
PFM	Poor	Very small	Poor	Very small
PFE	Poor	Very small	Poor	Very small
PFCB	Poor	Very small	Poor	Very small
TFE	Poor	Very small	Poor	Very small
HFP	Poor	Very small	Poor	Very small
PFIB	Poor	Very small	Poor	Very small

With respect to the colour coding for removal from flue gas and removal in the CO_2 washer: red = poor, orange = average, yellow = good and green = very good. For the fraction from flue gas in CO_2 and the presence of PFASs in the recovered CO_2, before cooling and liquefying, the following qualitative indication is used: Green = very small amount, yellow = small amount and red = considerable amount. The calculations for the qualitative assessment are described in Section 6.2.5.

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