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Utsläpp av organiska ämnen vid förbränning, inverkan av svaveldosering och svavlets kemiska form på emissionerna

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Abstract

The effect on sulphur additives on the concentration of carbon monoxide and organic substances, *e.g.* PAH, has been determined in the raw gas from combustion of bark in a grate furnace. These concentrations are reduced 75 to 90 % in this furnace when these additives are used. Carbon monoxide and the organics fluctuate in concert and reducing carbon monoxide levels reduces also the level of organics. In practice, there are not any differences in effect, either between the two additives used, ammonium sulphate and elemental sulphur, or between the points of injection, in the combustion chamber for ammonium sulphate and in the fuel for elemental sulphur.

Summary

Reduction of emissions of carbon monoxide and organic substances by injecting either ammonium sulphate or elemental sulphur and the importance of the point of injection has been investigated in full scale in a grate-fired bark boiler. The effect was monitored downstream of the economizer and air preheater, immediately upstream of the electrostatic precipitator.

Concentrations determined in the comprehensive monitoring program include principally carbon monoxide, TOC and several organic substances, including PAH, PCDD/F and polychlorinated benzenes (PCBz). Additionally, the gaseous PAH were determined on-line using a novel mass spectrometer, REMPI-TOF MS, that measures specifically the 2- to 4-ring PAH's.

All concentrations of substances of interest here fluctuate in concert and peak simultaneously. The relationship between the concentrations is not straightforward: there appears to be a threshold in carbon monoxide concentration. Below this threshold, the concentration of organics is low and above it concentrations increase rapidly with increasing carbon monoxide concentration.

It has been confirmed that using sulphur additives not only reduces the concentration of carbon monoxide, but also that of organic substances in the flue gases. These additives do not only reduce the mean level of concentrations, but also dampen the fluctuations in these concentrations. Any measure leading to a reduction in carbon monoxide will also decrease the concentration of most organics, under the conditions prevalent in this boiler.

Both additives tested are equally effective per kg of pure sulphur. The point of injection, in the fuel or above the grate, is not important.

The PCDD/F concentration in the flue gases is very low even without additives, and the effect of sulphur on these emissions is therefore difficult to observe. Here, the effect is masked by the variation of data. The PAH concentration is lowered by an injection of sulphur additives. The variation in data is though rather large, which may be caused by variation in particle content in the gas samples.

Keywords: emissions, carbon monoxide, sulphur additives, organic pollutants, PAH

Kort sammanfattning

Inverkan av formen av svaveladditiv, ammoniumsulfat eller svavelgranuler och av doseringsställe på minskningen av emissionerna av kolmonoxid och organiska ämnen har undersökts genom fullskaleförsök i en barkeldad rosterpanna. Förloppen följdes nedströms från economizern och luftförvärmaren, omedelbart före elfiltret.

De ämnen som bestämdes i det omfattande mätprogrammet är huvudsakligen kolmonoxid, totalt organiskt kol (TOC) och flera organiska ämnen, bland annat polycykliska aromatiska kolväten (PAH), dioxiner och furaner (PCDD/F) och klorerade bensener (PCBz). PAH bestämdes även on-line i gasfasen med en ny typ av masspektrometer, REMPI-TOF MS¹, som mäter specifikt föreningar som PAH med två till fyra aromatiska ringar.

Alla ämnenas koncentrationer samvarierar, med samtidiga toppar i emissionerna. Sambandet mellan koncentrationer är inte enkelt då det förefaller finnas ett tröskelvärde i kolmonoxid. Under tröskelvärdet är koncentrationen av organiska ämnen låg, över det ökar deras koncentration i rökgaserna snabbt med ökande halt kolmonoxid.

Försöken bekräftade att svaveladditiv reducerar inte endast koncentrationen av kolmonoxid utan även de organiska ämnenas koncentration i rökgaserna. Additiven minskar inte endast koncentrationsnivån utan de dämpar också fluktuationerna i koncentrationerna. En åtgärd som leder till en minskning av kolmonoxidhalten kommer också att leda till en minskning av de organiska ämnenas koncentration, under de förhållanden som rådde under fullskaleförsöken.

Båda additiv är lika effektiva räknat per kg rent svavel. Doseringsstället, som tillsats till bränslet eller i gasutrymmet ovanför rosten, har inte någon betydelse.

Koncentrationen av PCDD/F i rökgaserna är mycket låg även utan svavel tillsatser, och additivens inverkan på dessa emissioner är därför svårbestämd. Här maskerades effekten av den statistiska spridningen. Koncentrationen av PAH minskas av svaveladditiven. Spridningen i data är dock betydande, vilket kan ha orsakats av skillnad i partikelhalt mellan olika gasprover.

Nyckelord: utsläpp, kolmonoxid, svavel tillsatser, organiska föroreningar, PAH

¹ REMPI-TOF MS, Resonance Enhanced MultiPhoton Ionisation, Time Of Flight, Mass Spectrometer

Utökad sammanfattning

Bakgrund och målsättning

Idag används ofta en tillsats av svavel, som en svavelförening eller som ett bränsle med högre svavelhalt än huvudbränslet, dels för att minska korrosionsproblem i en panna, dels för att sänka emissioner av kolmonoxid. I det senare fallet är kolmonoxid egentligen inte huvudföremålet, utan gasen är en markör för organiska ämnen som metan, formaldehyd eller polycykliska aromatiska kolväten (PAH) som det är svårare att mäta on-line.

Emellertid är kunskapen om hur svaveltillsatser minskar dessa emissioner, och under vilka förhållanden, inte fullgod. Olika mekanismer har förts fram i litteraturen som en förklaring för effekten. Olika svaveltillsatser har undersökts. Resultat från offentliggjorda undersökningar är ibland inte helt samstämmiga. Vissa resultat tyder på att det finns en gräns för effekten, över vilken en ökad dosering inte ger någon effekt. Andra resultat tyder på att halten av organiska ämnen i rökgaserna uttryckt som totalt organiskt kol (TOC) fortsätter minska efter denna gräns. Ytterligare andra resultat antyder att en minskning av kolmonoxidhalten inte motsvaras av en minskning i halten av organiska ämnen, framför allt PAH.

Det finns två anledningar till att kunskapen inte är fullständig: den komplexa kemin under förbränningen och experimentella svårigheter. Dessutom beror förloppen i en stor volym som en panna inte bara på kemin. Utvärderingen av mätdata tillför också osäkerheter: medelvärdesbildningen under längre perioder gör samband mellan storheter, som inte är linjärt beroende av varandra, otydliga.

Ett praktiskt syfte med det projekt som redovisas i denna rapport är att visa om det finns några skillnader i inverkan mellan olika typer av svaveltillsatser och mellan doseringspunkter som bör tas med i beräkningen när man skall bedöma vilken tillsats som skall användas. Ett mer allmänt syfte är att bidra med dataunderlag från förbränningsförsök i full skala till den fortsatta analysen av svavels och svavelföreningars inverkan.

Särskild uppmärksamhet ägnas åt samplingstiden för mätningar för att locka fram de förlopp som kanske inte skulle märkas i medelvärden över flera timmar eller dygn. Tidsberoendet hos PAH-utsläppen löses därför upp med en nyligen utvecklad masspektrometerteknik, REMPI-MS², som tillåter en selektiv bestämning on-line av dessa med intervaller på ca 1 minut.

² REMPI, Resonance Enhanced Multi-Photon Ionisation

Syftet är inte att utreda mekanismer, vilket svårligen kan göras i storskaliga försök utan lämpligen utförs i laboratorieuppställningar under väl kontrollerade förhållanden. Syftet är inte heller att göra en bäst-i-test jämförelse mellan två tillsatser, därför att förhållandena vid olika pannor varierar. Ekonomin i en dosering är inte heller något mål för utredningen. Svaveltillsatsers inverkan på korrosion berörs inte.

Huvudresultat

Fullskaleförsöken utfördes i en barkpanna med en nominell effekt på 50 ton ånga per timma, motsvarande ca 45 MW bränsle, vid ett massa- och pappersbruk där huvudsakligen bark eldas, men även avverkningsrester, sågspån och slam. Pannan är av rostertyp. Den är inte utrustad med någon SNCR. Skälen till att denna panna valdes är att dess utsläpp av kolmonoxid är jämförelsevis höga och att de fluktuerar ganska mycket.

De två svaveltillsatser, som doserades i separata försöksserier från ca 25 mg/MJ till ca 100 mg/MJ, är:

- Ammoniumsulfat i vattenlösning som injicerades i gasutrymmet ovanför rosten
- Granulerat elementärt svavel som doserades till bränslet i fallet ner till rosten

Koncentrationerna av ämnen i rökgaserna efter economizer och luftförvärmare men före elfiltern följdes genom ett tämligen omfattande mätprogram, se faktarutan nedan för en beskrivning. I huvudsak är resultaten följande:

- Ju mer svavel som doseras, som granuler eller som ammoniumsulfat, desto lägre halter av kolmonoxid, av TOC och av PAH. Effekten av en ökning av dosen på kolmonoxid och TOC avtar dock vid höga doser.
- Båda tillsatser är lika effektiva räknat per kilogram av rent svavel
- Samtidigt som oförbränt i rökgaserna minskar när svavel doseras, ökar kolhalten i flygaskan. Detta är ett nytt resultat men data är få - detta borde bekräftas.
- Halterna av PCDD/F i rökgaserna är låga från början – dosering av svavel ger inte någon effekt som kan skiljas ur databruset
- Det finns tydliga samband mellan kolmonoxid å ena sidan och TOC, metan och PAH å andra sidan – minskar halten av kolmonoxid, minskar också halten av de andra ämnena. Samvariationen mellan koncentrationerna tyder på puffar av ofullständigt utbrända gaser.

Försöken har producerat ett omfattande datamaterial. Detta presenteras mer detaljerat, såväl i denna sammanställning som i huvudrapporten, i två avsnitt:

- Först som medelvärden över provtagningsperioder eller perioder med motsvarande längd - detta tidsperspektiv är det formella miljösystemets, där utsläpp brukar beräknas som timmedelvärden och dygnsmedelvärden
- Därefter som momentana värden, med den tidsupplösning som går att få – i syfte att tydliggöra de eventuellt icke-linjära samband mellan storheter som suddas ut i medelvärden

Faktaruta: utförda mätningar

Samtidigt som mätinstrument användes för att följa koncentrationer av ämnen i rökgaser togs prover dels av rökgaser, dels av bränsle och askor för senare analyser på laboratorier. De koncentrationer som mättes var:

- Kolmonoxid och koldioxid med två IR-instrument i två olika tidsskalor (5 s och 1 min)
- Ammoniak, kväveoxider, svaveldioxid, saltsyra, metan och fukthalt med ett FTIR-instrument
- TOC med ett FID-instrument³ (tidsupplösning på 1 min)
- Enskilda PAH med en masspektrometer (tidsupplösning ca 1 min)
- Och även syre med ett paramagnetiskt instrument

Bränsle- och askproven analyserades med avseende på svavel och klor, kväve samt kol. För flygaskorna bestämdes även TOC. Gasproven analyserades med avseende på mono- till oktaklorerade PCDD/F, på PCBz samt på PAH (EPA 16).

Resultat, medelvärden för flera timmar

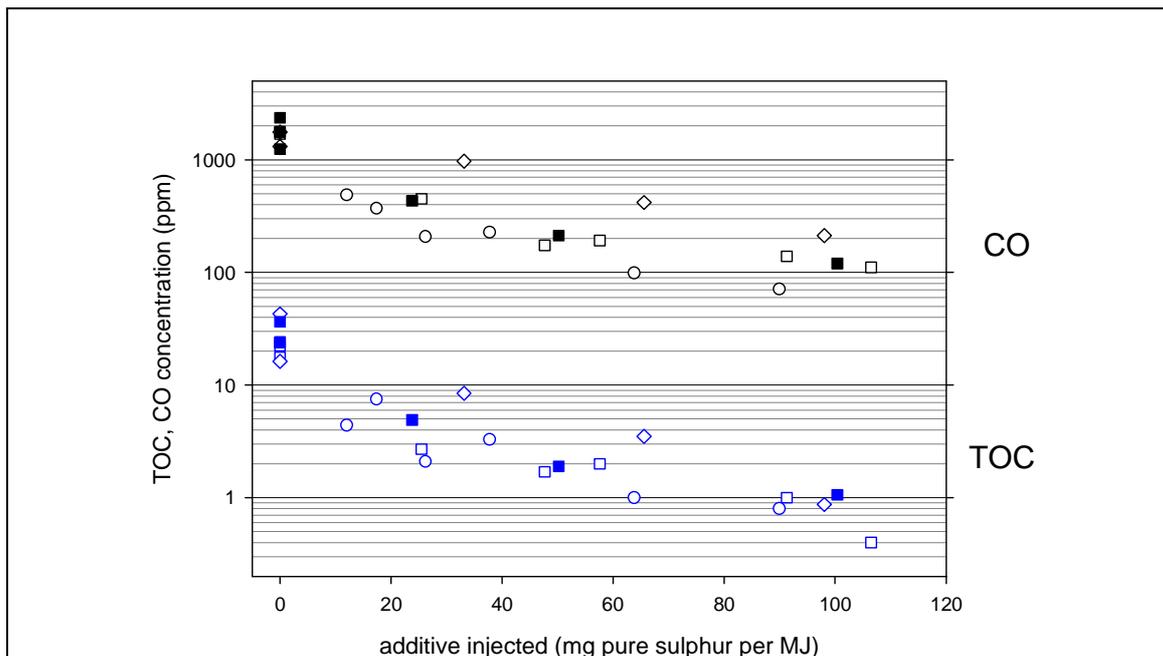
Tidsskalan för resultaten i detta avsnitt är ca sex timmar, d v s den tid under vilken ett gasprov tas för analys av PCDD/F, klorerade bensener samt PAH.

Inverkan av svaveldoseringen på kolmonoxid och på organiska ämnen (här TOC) illustreras med Figur S1. Medelhalten kolmonoxid går ner från något över 1000 ppm när inget svavel doseras till ca 100 ppm när över 100 mg svavel per MJ doseras, oberoende av om tillsatsen är elementärt svavel eller ammoniumsulfat. Minskningen av TOC, de blå punkterna i diagrammet, är något mer markerad: från ca 25 ppm ner till under 1 ppm. I denna logaritmiska skala är det tydligt att ökade doser svavel leder till ännu lägre halter. Övriga halter i rökgaserna, enskilda PAH (bl a naftalen) och metan, följer samma mönster. Slutsatsen är att en tillsats av svavel sänker halten av allt gasformigt oförbränt, från kolmonoxid och metan till PAH.

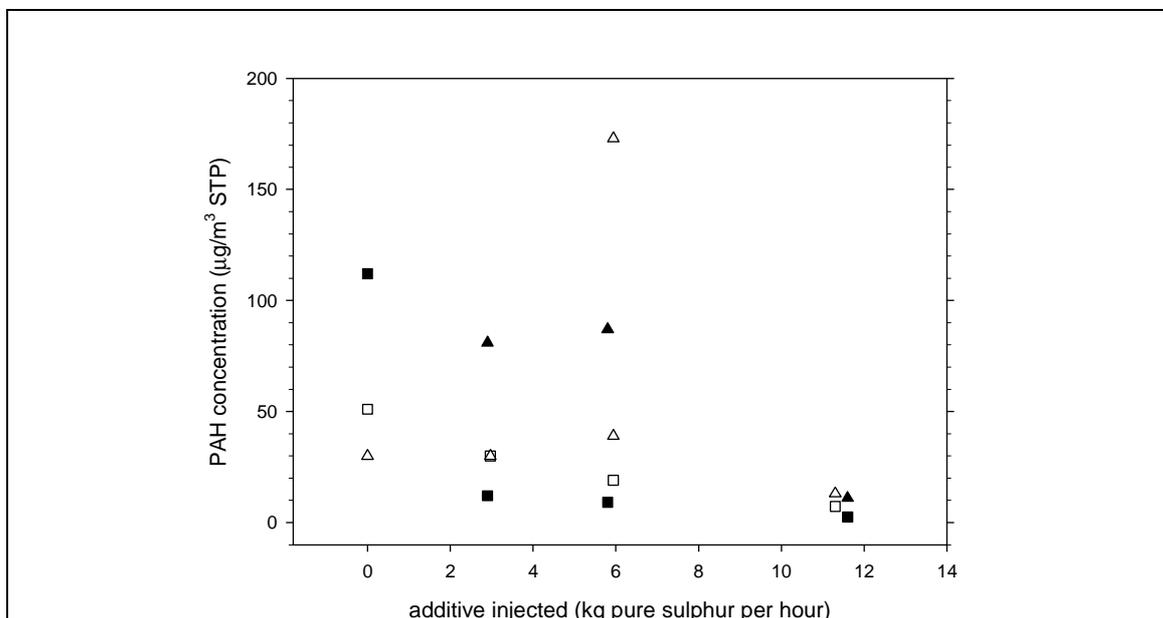
PAH-halten i de uttagna gasproven minskar med ökande svaveldoser men inte alls lika omedelbar, se Figur S2. Spridningen är större, vilket kan bero på att de olika gasproven innehåller en varierande mängd små partiklar.

Halten PCDD/F är redan så låg i referensfallet att man befinner sig på gränsen av det som kan mätas. Spridningen i data, i ett intervall från 0,001 till 0,01 ng TEQ/m³, är så stor att ingen trend kan skönjas.

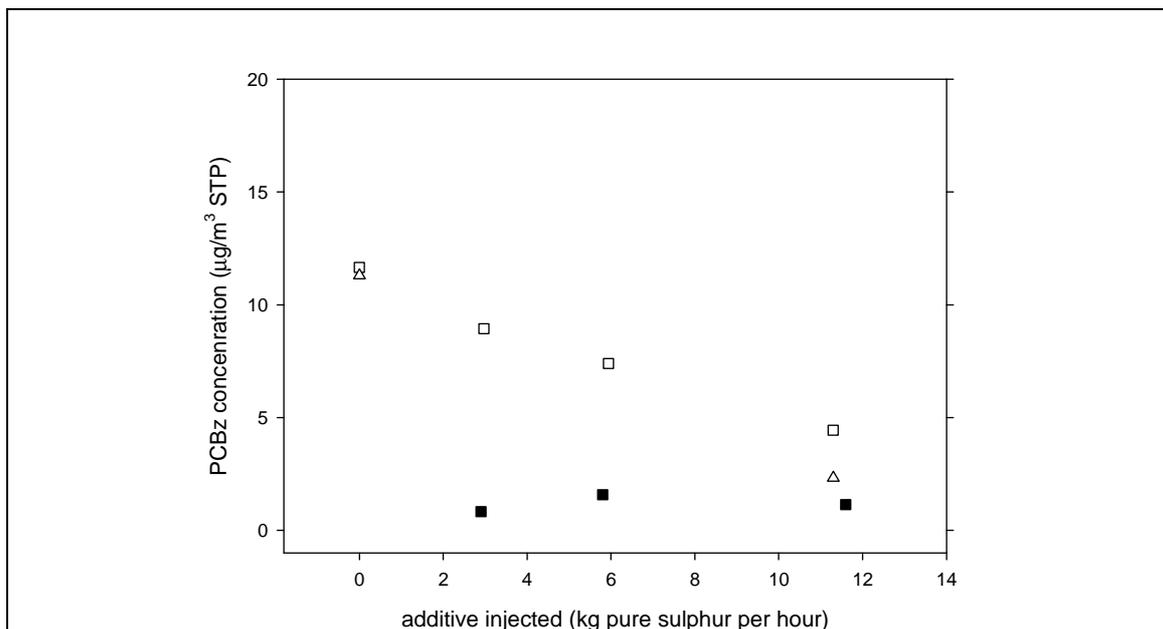
³ Organiska ämnen (formaldehyd, metanol, etan, propan, bensen och fenol) bestämdes med FTIR. Det finns emellertid osannolika samband mellan värdena för deras koncentrationer, varför resultaten är oanvändbara. Bensen kunde dock följas med masspektrometern trots att bensen egentligen kräver en annan reglering av detta instrument.



Figur S1 Koncentrationerna av kolmonoxid (svarta punkter, den övre skaran) och TOC (blå punkter, den lägre skaran) i rågasen som funktion av doserad mängd svaveladditiv. Tomma symboler, ammoniumsulfat: \circ , \square och \diamond , olika försöksserier (se rapporten). Fyllda symboler, elementärt svavel: \blacksquare . Perioder med störningar och låg last har rensats bort.



Figur S2 Koncentrationen av PAH i rökgasproverna som funktion av svaveldosen i kg rent svavel per timma. Skillnaden mellan samtidiga prover tagna vid olika uttag är på gränsen till signifikant, varför uttagen skiljs åt i figuren. Tomma symboler, ammoniumsulfat: \square , stuts B, Δ , stuts A. Fyllda symboler, elementärt svavel: \blacksquare , stuts B, \blacktriangle , stuts A. En dos på ca 3 kg/h motsvarar ca 25 mg/MJ.



Figur S3 Koncentrationen av PCBz i rökgasproverna som funktion av svaveldosen i kg rent svavel per timma. Tomma symboler, ammoniumsulfat: □, stuts B, △, stuts A. Fyllda symboler, elementärt svavel: ■, alla stuts B. En dos på 3 kg/h motsvarar ca 25 mg/MJ.

Däremot syns en tydlig skillnad mellan ammoniumsulfat och elementärt svavel i deras inverkan på halten av klorerade bensener. I ammoniumsulfats fall minskar deras halt linjärt med ökande sulfatdoser. I det elementära svavlets fall har koncentrationen nått lägsta nivå redan efter en liten tillsats av svavel.

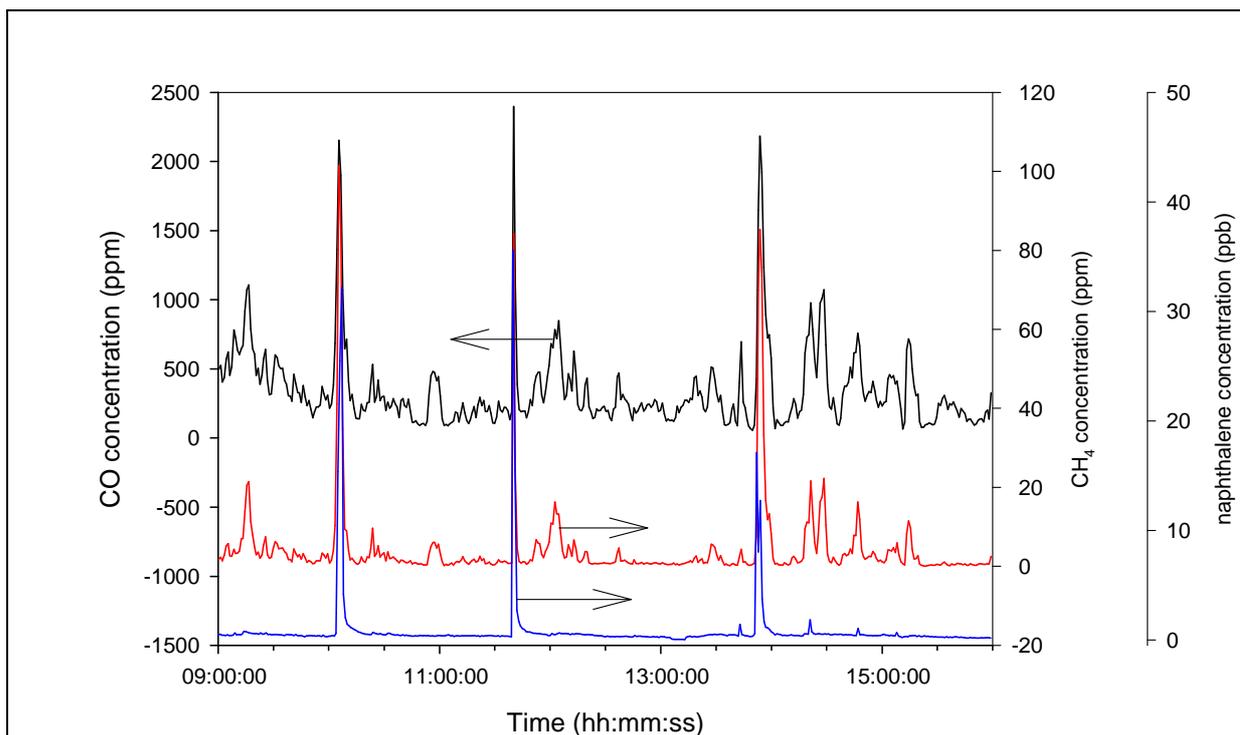
Redan i referensfallet, ingen dosering, tas det mesta svavel ut med rökgaserna och en mindre del med askorna. Svavelhalten i flygaskan ökar något med ökande svaveldosering, vilket är väntat, men huvuddelen av det doserade svavlet går ut genom skorstenen. Vid höga doser (ca 100 mg/MJ) av tillsatserna är halten svaveldioxid i rökgaserna betydligt högre än i referensfallet. Däremot ligger den ökning som iakttagits vid de lägre doserna (20 till 50 mg/MJ) inom de normala variationsgränserna för svavelutsläpp i referensfallet.

Ur analyserna av flygaskorna framgår att deras kolhalt ökar med ökande svaveldosering, från 0,3 % TOC till ca 3 % TOC. En bättre utbränning av gaserna motsvaras alltså av en sämre utbränning av askorna. Det är emellertid för tidigt att dra långtgående slutsatser om svavlets inverkan på kolhalten i askorna då datapunkterna är få.

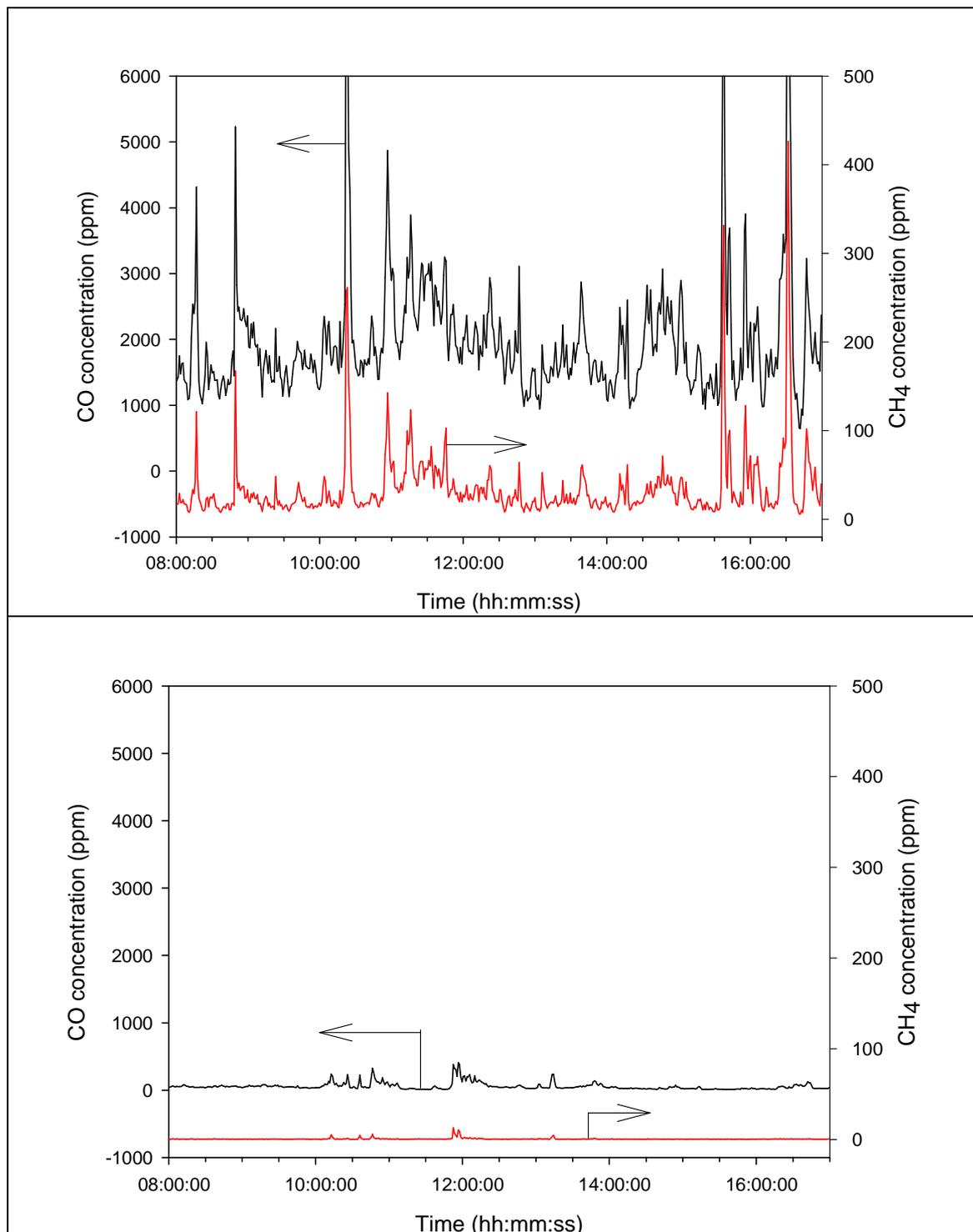
Momentana värden

Syftet med att följa de momentana värdena för koncentrationerna var att, om så behövdes, kunna lösa upp otydliga samband mellan medelvärden: medelvärdesbildningen förvränger nämligen icke-linjära samband och försvårar analysen av orsak och samband. Även om sambanden i föregående avsnitt mellan svavel och kolmonoxid med flera ämnen är rätt tydliga ger en granskning av koncentrationernas momentana värden och deras variation med tiden ytterligare information.

Figur S4 visar att metan samvarierar med kolmonoxid: spikar uppträder i båda storheter samtidigt. I figuren har även halten naftalen, det ämne i PAH-gruppen med högsta koncentration, ritats in. Samtliga ämnen som kunde bestämmas med masspektrometern samvarierar med kolmonoxid. I referensfallet, ingen tillsats, kan samtidiga spikar också ses i ammoniak och svaveldioxid vilka ämnen inte kan ha något annat ursprung än bränslet. Det är alltså frågan om puffar av ofullständigt förbrända gaser som troligen hör ihop med en oregelbunden avgång av brännbara gaser från bränslebädden på rosten. Därmed förtydligas resultatet i förra avsnittet: om en svaveltillsats reducerar koncentrationen av kolmonoxid i rökgaserna reducerar den även organiskt oförbränt.



Figur S4 Samvariationen av naftalen (nedersta blåa linjen) med kolmonoxid (översta svarta linjen) och metan (mellersta röda linjen) under en försöksdag



Figur S5 Inverkan av svaveltillsatser på halterna av kolmonoxid (övre svarta linjen) och metan (nedre röda linjen) i rökgaserna. Övre diagrammet: ingen tillsats, nedre diagrammet: 11,6 kg/h elementärt svavel, d v s högsta dosen.

Effekten av svaveltillsatser är inte bara att nivån för koncentrationerna sjunker (bland annat medelvärdet) utan även att fluktuationerna dämpas, vilket illustreras med Figur S5. Det gäller för samtliga ämnen som kunde mätas med denna tidsupplösning. Tillsatserna bidrar alltså till en bättre utbränning av gaserna i puffarna.

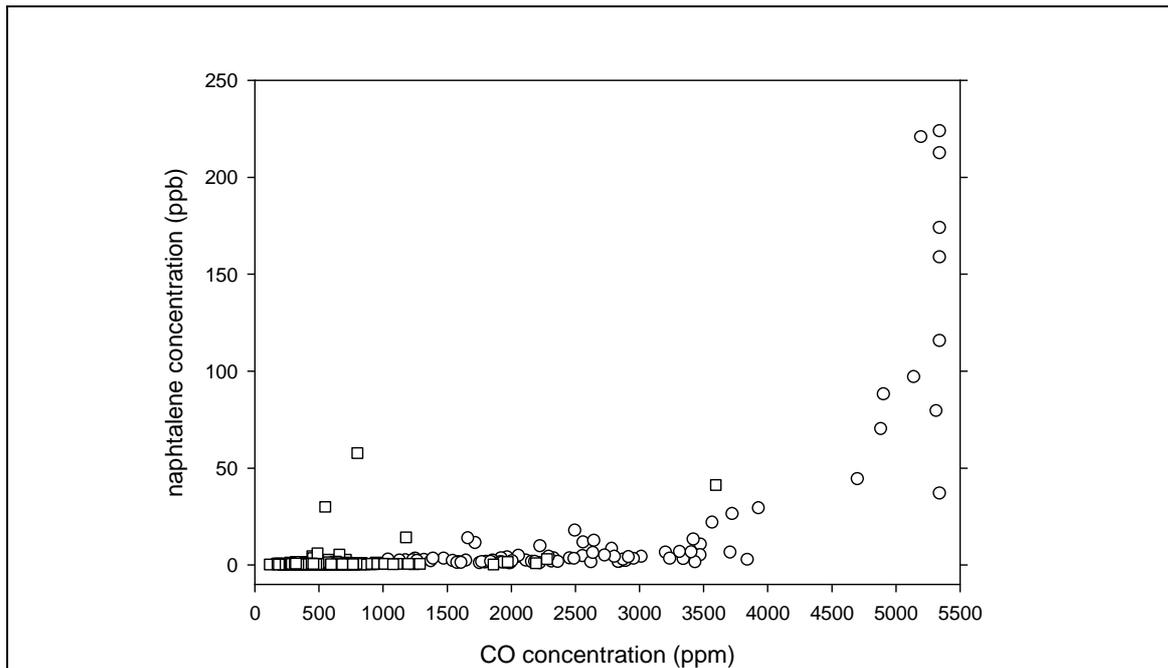
Figur S4 antyder också att fluktuationerna i naftalen är mindre, eller färre än de i kolmonoxid. En riktig spik i naftalen uppträder först när en spik i kolmonoxid överskrider ett tröskelvärde. Dessa pulser av ofullständigt förbrända gaser utgör det största bidraget till det medelvärde för PAH som räknas fram ur momentana mätdata eller erhålles i ett gasprov som analyseras på ett laboratorium. Under ena av de två referensförsöken bestämdes medelvärdet av naftalen till ca 7,4 ppb under de tre timmar som PAH kunde mätas under försöket. Om den enstaka stora spiken upp över 1000 ppb inte räknas med blir medelvärdet ca 1 ppb, nära nollnivån på 0,5 ppb som uppnås under alla försök med svaveldosering.

En närmare granskning av sambandet mellan de organiska ämnena och kolmonoxid bekräftar att det finns ett tröskelvärde i kolmonoxid över vilket koncentrationen av dessa ämnen ökar kraftigt, se Figur S6. För naftalen liksom för TOC som utgör summan av andra organiska ämnen, ligger tröskelvärdet vid ca 4000 ppm kolmonoxid. I verkligheten är stigningen efter tröskeln inte fullt så kraftig som figuren antyder: den övre gränsen för instrumentets mätintervall är ca 5000 ppm.

Alltså kan halten PAH i rökgaser för samma medelkoncentration av kolmonoxid skiljas sig betydligt mellan ett fall där förbränningen är stabil och ett fall där halten fluktuerar mycket, även om medelhalten är den samma.

I dessa försök räckte det med en liten tillsats av svavel för att komma till en betydligt lägre nivå av kolmonoxid och organiska ämnen än i referensfallet. Egentligen skulle kolmonoxidhalten i denna pannas rökgaser, men även TOC och halterna av de organiska ämnena, kunna hållas på en låg nivå även utan svaveltillsatser om fluktuationerna och de stora spikarna kunde begränsas.

I förbigående kan noteras ytterligare en skillnad mellan de två svaveltillsatserna. När elementärt svavel doseras kunde med masspektrometern iakttas ett ämne som troligen är bensotiofen, en heterocykel med svavel.



Figur S6 Koncentrationen av naftalen som funktion av koncentrationen av kolmonoxid vid låga halter av den senare, minutmedelvärden. Symboler: ○, inga additiv och □, medeldosen av ammoniumsulfat. Data har rensats med avseende på störningar och perioder med lägre laster.

Slutsatser

Resultaten i denna undersökning leder till slutsatserna nedan.

Om sambandet mellan kolmonoxid och organiska föreningar:

- Det finns samband mellan halten av kolmonoxid i rökgaserna och halten av organiska ämnen uttryckt som TOC eller halten av enskilda ämnen som metan eller PAH
- Alla ämnen av intresse, kolmonoxid, TOC, metan och de gasformiga PAH i rökgaserna samvarierar, likaså den svaveldioxid som härrör från bränslet, vilket pekar på att toppar i emissioner orsakas av puffar med ofullständigt förbrända gaser.
- Det största bidraget till emissionsnivån, t ex för PAH, kommer från dessa puffar. Att hålla en stadig nivå av kolmonoxid eller tillåta stora fluktuationer ger mycket olika nivåer av emissioner.
- Anledningen till puffarnas betydelse är att det finns trösklar i koncentrationen av kolmonoxid. Under tröskelvärdet är halten organiska ämnen låg och beroendet på halten kolmonoxid litet, men över tröskeln ökar halten av organiska ämnen snabbt och är starkt beroende av halten kolmonoxid.

Om inverkan av svaveladditiv:

- Ju större tillsatsen av svaveladditiv är, desto lägre är koncentrationen i rökgaserna av alla produkter från en ofullständig förbränning, d v s kolmonoxid och organiska ämnen inklusive PAH. Minskningen av koncentrationen avtar dock med ökande doser.
- I denna undersökning kunde ingen större skillnad i effekt mellan ammoniumsulfat och elementärt svavel iakttas vid lika mängder rent svavel, ej heller någon skillnad beroende på var svavlet injiceras.
- För denna panna är kurvan som grafiskt beskriver beroendet av TOC eller något ämnes koncentration på halten kolmonoxid densamma oavsett om ett additiv använts eller inte. Påverkas halten kolmonoxid genom en åtgärd, t ex en dosering av en svavelförening eller genom reglering av pannan, påverkas också halten av de organiska ämnena.
- Minskningen av halten av kolmonoxid och organiska ämnen då additiven injiceras ledsagas av en ökning av halten TOC i flygaskan. Detta bör emellertid bekräftas i en oberoende undersökning.

Om PAH och PCDD/F

- I denna undersökning minskade halten PAH när svaveladditiv injicerades. Den något stora spridningen i resultaten kan bero på varierande partikelhalt mellan gasproven
- Halten av PCDD/F i rökgaserna är redan mycket låg, vid detektionsgränsen, redan innan något svavel tillsatts vilket troligen har samband med den låga klorhalten. Effekten av en svaveltillsats försvinner i variationen i data. Det förefaller vara mindre intressant att fortsätta undersöka PCDD/F-utsläppen från pannor med bark eller rent trä som bränslen.

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Appendices

A	CONDITIONS IN THE BOILER – AT A GLANCE
B	PAH, PCBZ AND PCDD/F RESULTS

Nomenclature

ESP	Electro-Static Precipitator
FID	Flame Ionisation Detector
FTIR	Fourier-Transform Infrared (spectroscopy)
HPLC	High-Pressure Liquid Chromatography
I-TEQ	International TEQ scale
LOQ	Level of Quantification
MS	Mass Spectrometer
m/z	mass to charge ratio
PAH	Polycyclic Aromatic Hydrocarbons
PAS	Photoelectric Aerosol Sensor
PCBz	PolyChlorinated Benzenes
PCDD/F	Polychlorinated Dibenzo-Dioxins and -Furans
REMPI	Resonance Enhanced Multi-Photon Ionization
SCADA	Supervisory Control and Data Acquisition
SCR	Selective Catalytic Reduction (of nitrogen oxides)
SNCR	Selective Non-Catalytic Reduction (of nitrogen oxides)
STP	Standard Temperature and Pressure (0°C and 1013 kPa)
TC	Total Carbon
TEQ	Toxic Equivalents (to 2, 3, 7, 8-Tetrachlorodibenzodioxin)
TIC	Total Inorganic Carbon
TOC	Total Organic Carbon (gases), Total Oxidizable Carbon (ash)
TOF	Time-of.-Flight

1 Introduction

1.1 Background on emissions

An incomplete combustion may be expected to yield larger concentrations in the flue gases of unreacted or partially reacted organic compounds. Some of them, e.g. carbon monoxide and organic compounds such as aromatics are potentially harmful substances. In particular, PAH (polycyclic aromatic hydrocarbons) and PCDD/F (commonly called dioxins and furans) are frequently targets for environmental concern.

Fuel, design of furnace and boiler, design of flue gas system including de-dusting and other flue gas cleaning, operating conditions, all influence the actual performance of the conversion of fuel to energy, residues and exhaust gases as well as emissions.

Monitoring combustion and emissions in order to control them is a complex task: the volume of the system is large, the number of variables is huge and there isn't any on-line measurement technology available for many of the chemical species that may be important. Dust, nitrogen oxides and carbon monoxide are among those that are usually monitored continuously. Carbon monoxide, CO, that can be determined on-line with commercially available instruments is used as markers for the more harmful compounds (PAH, PCDD/F etc) that can't be, at least not at present.

However, while it is true that emissions increase with an increasingly incomplete combustion, the correlation between the concentrations of different species is not necessarily a simple one. It is difficult to reduce complex relationships between reacting species, intermediates and reaction products in a large volume to pair-wise correlations between variables, e.g. concentrations of two chemical species. Such correlations that may be found in some investigations are often disproved in others. Relationships that have been verified in laboratory conditions are not always found in full scale conditions. Relationships that have been found valid for one plant are not valid for another, and if they are, then at best in general terms [1], [2].

One additional cause for the lack of correlation may be the averaging procedure used to assess the overall performance of a plant. If the relationship between two parameters, e.g. instantaneous concentration of two substances in the flue gases, is linear, a series of average values computed at different occasions during a year will also show the same relationship. If the relationship is not linear but more complex it will probably not be recognized in a series of averages for different periods. Rapid fluctuations will also complicate the interdependence of the parameters. Examples of functions that have been observed are [1], [2], [3]:

- A parabolic or exponential dependence of one concentration on carbon monoxide concentration
- A threshold, with e.g. an organic substance being detectable first when the carbon monoxide concentration has risen above a certain value, and then increasing non-linearly.

In the latter case, the average for the concentration of a particular compound during a period will depend on how many times the threshold value of carbon monoxide was exceeded and how much it was exceeded. This yields an additional deviation in the data.

Organics are only one category of pollutants emitted during combustions: nitrogen oxides (NO_x), sulphur oxides (SO_x), hydrochloric acid (HCl) and dust, i.e. small particles, occur in larger concentrations. Several previous investigations have shown the relationship between emissions of NO_x and of carbon monoxide e.g. [1], [2], [4].

In order to lower the concentration of NO_x one reduces the amount of air in the combustion zone, but it is a trade-off: reducing the excess air lowers the NO_x concentration at the cost of increasing carbon monoxide. Normally, SNCR or SCR with ammonia or urea is used to reduce nitrogen oxides, but tests in the bark boilers of the pulp and paper industry have not been very successful [5]. One reason for that could be the large and rapid variations in load, which variations move the temperature zone favourable for NO_x reduction. Another is that pyrolysis of solid biofuels produces an ammonia slip that probably does provide some reduction of nitrogen oxides.

1.2 Sulphur in the combustion process

In plants burning solid biofuels, e.g. wood, the chlorine-rich deposits on heat exchanging surfaces such as super-heaters, can cause severe corrosion. To reduce the problems, it has become common practice in Sweden to use an additional sulphur-rich fuel – peat, or sludge from waste water treatment plants, or waste tires, or even elemental sulphur – which has the effect of reducing the amount of alkali chlorides in the flue gas by forming less corrosive alkali sulphates.

It was also found that injection of sulphur to solve corrosion problems caused a remarkable reduction of the carbon monoxide concentration in the flue gases [6]. Further investigations confirmed the effect and showed that it levels out at a rather low level of sulphur dosage, ca 20 mg sulphur per MJ fuel [7]. If the sulphur content of the fuel is high, additional dosage of a sulphur additive does not produce any noticeable effect, see e.g. [8].

Vattenfall uses a method called ChlorOut where the sulphur is introduced as a sulphate solution into the flue gas. This reduces the alkali chlorides more effectively than adding sulphur to the fuel. The chemical compound most commonly used is ammonium sulphate in a water solution. Ammonium sulphate also acts a SNCR chemical, reducing NO_x . Using ammonium sulphate to reduce simultaneously carbon monoxide and NO_x in grate furnaces is called CleanOx.

Experiments in laboratory rigs suggested that the active form of sulphur is not sulphur dioxide, but another species, as hydrogen sulphide was slightly more efficient than sulphur dioxide [9]. Kassman et al [10] have tested different additives (sulphur dioxide, alkali sulphate, ammonium sulphate) in a full-scale furnace. Skog et al have also tested different additives (hydrogen sulphide, sulphur dioxide, potassium sulphate) in a

laboratory rig [11]. The effect of sulphur on the concentrations of carbon monoxide and organic substances in the flue gases is probably the result of a mixture of homogeneous gas-phase reactions and gas-solid reactions. This is a system of conflicting effects, the results of which may depend very much on the actual conditions in the furnace.

Two reports are particularly relevant to the topic of the present investigation, one by ÅF and one by Umeå University and Vattenfall Research and Development in cooperation.

In a recent investigation [12], the carbon monoxide emissions of three furnaces/boilers were determined and the effect of an injection of elemental sulphur at higher doses than 20 mg/MJ on these was studied. One of the two grate furnaces, plant B, is the furnace where the full-scale experiments in this investigation have been performed. The third was a fluidised bed furnace. The fuel in all three furnaces was bark, with sludge as additional fuel in the fluidised bed. The nominal thermal power of the three furnaces being different, an injection rate of 10 kg/h was chosen for all three in order to provide a sulphur dose sufficiently large for the effect to level out in all of them. In the case of plant B, this would correspond to a sulphur dose of ca 90 mg/MJ.

Emissions were monitored in the flue gas duct in all three plants, upstream of the de-dusting equipment. The instruments used were the same as those in this investigation: IR for CO/CO₂, FID for TOC and FTIR for other species including organic compounds. The EPA 16 PAH's were determined in gas samples. Reference conditions and sulphur injection conditions were maintained for three days each.

In the grate furnaces sulphur injection lowered the carbon monoxide emissions clearly (90 %) and that of TOC slightly less (75 %). It did not have any marked effect on PAH concentrations. In the fluidised bed furnace the effect was the opposite, an increase in all emissions. In this case the dependence of PAH emission on carbon monoxide or TOC concentration is markedly non-linear.

At a finer level of details, the data gathered confirmed the general trend that all emissions of organics increase when the carbon monoxide emission increase. It was though not possible to identify a unique correlation between TOC or methane and carbon monoxide: the relationship varies with time.

The topic of the second investigation was the effect of ammonium sulphate on emissions on PCDD/F [13]. The results were clear (a halving of the concentration of PCDD/F) in the laboratory but inconclusive in full-scale. The latter were performed in a fluidised bed furnace burning waste wood and bark.

1.3 Mass spectrometry, the REMPI-TOF instrument

Some of the knowledge gaps for the combustion process may be filled using novel instrumentation with a time resolution of data of the order of a minute, sometimes even less. Lighter organics may be determined using IR spectroscopy instruments that are commercially available for field use. There hasn't been any readily available technology to determine heavier compounds.

Combustion gases are a complex mixture of gaseous or vaporised substances, as well as suspended particles, and show a pronounced dynamical behaviour with fast changes in concentration. As it is used today in research or analytical laboratories for qualitative and quantitative analysis of gaseous or vaporised substances, mass spectrometry suffers from a few limitations in this context:

- Separation of mixtures, e.g. by gas chromatography, before injection into the instrument implies time delays and does not allow monitoring the rapid changes. Direct injection into the mass spectrometer would be better.
- The conventional ionisation techniques using high-energy electrons at 70 eV are too strong, producing a large number of fragments for one molecule, which makes it nearly impossible to analyse a mixture. Furthermore, as bulk gases such as nitrogen, carbon dioxide or water vapour also are ionised, they swamp the weaker signals from the substances present at low concentrations. A softer ionisation technique better suited to the ionisation potentials required, 7 to 11 eV would produce fewer fragments, ideally only the molecular ion, and would not have any impact on bulk gases at all.
- The charged fragments are often separated in an electro-magnetic field by sweeping over field strengths or scanning over mass to charge ratio. These scans take time, lengthening the response time

The REMPI-TOF mass spectrometer recently developed mainly at Universität Augsburg in cooperation with GSF addresses these two difficulties. The acronym REMPI means Resonance Enhanced Multi-Photon Ionisation. Here, one uses intensive pulses of UV light from a laser. Two or more photons are sequentially absorbed by a molecule, the first photon lifting an electron into an excited state, the following one leading to the shedding of the electron. Normally, the first excited state relaxes rapidly back to the unexcited state, but resonance, i.e. delocalisation of the excited electron in an aromatic structure stabilises this state, making the probability of absorbing a second photon much larger. The two energy inputs correspond to the ionisation potential of the molecule and produce only one species with a positive charge.

The selectivity of this technique is comparable to that of UV spectroscopy, since only those molecules that exhibit appropriate electronic transitions at the wavelength of incoming light may be ionised. Monochromatic REMPI in the region 240 to 300 nm has been proven to be especially efficient for the ionisation of polycyclic aromatic compounds, the PAH's, the by-products from combustion which are of particular interest because of their toxic and carcinogenic properties.

The time-of-flight (TOF) technique for separating ions is better suited to dynamic processes than sweeping periodically over a range or spectrum of mass to charge ratios. It is possible to create a whole mass spectrum from every single ionising laser pulse, increasing the sensitivity of the instrument, which can be used to monitor processes on a shorter time scale.

During the last ten years, several mobile measurement systems have been built at Universität Augsburg. They have been used to monitor aromatics, especially PAH's, in the flue gases of waste incineration plants, for analysis of the roasting process of coffee beans, cigarette smoke etc [14], [15], [16].

At first, fixed frequency lasers used, i.e. a KrF excimer laser ($\lambda = 248$ nm) and a Nd:YAG laser (fourth harmonic, $\lambda = 266$ nm) combined with an effusive molecular beam inlet, ensuring selectivity for PAH, as no other compounds would be ionised under these conditions. The sensitivity of the instrument was down below ppb level. In the first mobile system, a tuneable dye laser was used. To retain selectivity of the ionisation process, a continuous molecular free jet was implemented, allowing cooling of the molecules to 5 K. With this set-up, monochlorobenzene (a surrogate for the PCDD/F) could be monitored selectively. In principle, one could ionize selectively isomers by tuning the dye laser to the appropriate wavelength. The latest addition is an optical parameter oscillator (OPO) system, which provides pulsed light in the interval of wavelengths between 220 and 340 nm. This laser system has also been incorporated in a measurement system with other soft ionisation systems, i.e. single photon ionisation and electron ionisation. Such an instrument has been used for monitoring PAH in the combustion chamber of a waste incineration chamber.

1.4 The purpose of the research assignment and its role within the research area

This research project aims at providing more experimental data on combustion in and emissions from a large-size furnace, in particular on the effect of sulphur additives.

The three topics that this investigation focuses on are:

- The effect of sulphur injection on emissions of carbon monoxide and of volatile organic compounds as well as of PAH and PCDD/F
- The relation between emissions of the widely used marker carbon monoxide and the partially combusted organics, from methane to heavier PAH's, on a short time-scale (of the order of a minute)
- Differences between and equivalences of effects of the two sulphur additives ammonium sulphate and elemental sulphur

This investigation aims at a better understanding of the effect of sulphur additives. It does not aim at developing or confirming theoretical models or mechanisms for the effect of sulphur on emissions of carbon monoxide or organics. However, if evaluation of the results suggests obvious conclusions on models or explanations, these will be noted.

1.5 Audience

The primary audience for this investigation is the members of the Swedish Thermal Engineering Research institute, Värmeforsk, i.e. all the energy conversion plants using solid biomass as a fuel. As the experiments have been performed in a bark boiler belonging to a pulp and paper company, the pulp and paper industry is an especially concerned audience.

As we aim to provide novel experimental data on large-scale combustion we expect the data to be of interest for the scientific and technical community in general, in particular to those concerned with emissions of pollutants and with combustion.

1.6 Project management

This project is performed in cooperation by ÅF-Process, Vattenfall Research and Development and GSF – Forschungszentrum für Umwelt und Gesundheit. ÅF-Process is the lead contractor. The Bayerische Institut für Angewandte Umweltforschung und – technik (BIfA) was contracted for PCDD/F sampling in the flue gases and analysis.

The participants at ÅF-Process were Henrik Bjurström (project director) and Claes Jonsson. Matts Almark and Magnus Berg participated from Vattenfall Research and Development. Besides Professor Ralf Zimmermann and Thorsten Streibel, the following persons at GSF participated: Fabian Mühlberger (modifications of the REMPI-TOF MS and experimental design), Robert Geißler, Mo Saraji and Mathias Bente. At BIfA, the PCDD/F campaign was performed by Hermann Nordsieck.

The project is financed by the group “Plant and Combustion Technology” at the Swedish Thermal Engineering Research Institute (Värmeforsk). The Research Foundation at ÅF (ÅFORSK, Ångpanneföreningens forskningsstiftelse) has financed the modification of the REMPI-TOF mass spectrometer for the present experimental campaign.

The project has been followed on Värmeforsk’s behalf by a reference group consisting of:

- Evalena Wikström-Blomqvist, SP
- Sven Andersson, Götaverken Miljö
- Solvie Herstad Svärd, SEP

2 Experimental

2.1 Furnace for the full-scale measurements

The furnace chosen for this investigation is the grate furnace B in the previous project on sulphur and carbon monoxide emissions [12]. It was first built in 1956 as an oil furnace and retrofitted in 1985 with a moving grate in order to fire bark or hog fuel. The neck between grate and boiler is very wide and the grate is rather steep and short.

The present fuels are bark, sawdust, logging residues, sometimes sludge⁴. They are fed to the grate using three chutes. Fuel oil is used as an auxiliary fuel when the combustion temperature drops below an acceptable level or when additional steam is demanded. The burners are placed above the grate.

The primary air is supplied in six zones. Flue gases are recirculated.

The boiler produces steam at 65 bar (ca 6.5 MPa) and 485°C. When the furnace is fuelled with bark, the boiler has a nominal capacity of 50 tons of steam per hour⁵. The steam demand from the pulp and paper production fluctuates rapidly, which implies an unstable operation of the furnace and boiler.

The furnace is not equipped with SNCR. Results from tests of the ability of SNCR to lower NO_x emissions in the early 1990's were inconclusive [5]. The level of NO_x is relatively low, 40 mg/MJ on a yearly basis and the CO level is high (2000 ppm), which indicates combustion at a low temperature.

The flue gas cleaning equipment consists of an electrostatic precipitator (ESP) and of a flue gas condensing unit in series.

As an experimental object, this furnace offers the following advantages: a high level of CO emissions and a low content of sulphur in the fuel (sludge excepted), which increases the possibilities to observe effects using instruments with a normal sensitivity. Its disadvantages are that it is not representative of modern bark furnaces in the pulp and paper mills and that it is operated with a relatively high excess air, above 10 % oxygen in the flue gases.

⁴ Sludge is mainly fired in another furnace on the site.

⁵ This corresponds to ca 45 MW. When oil is the sole fuel, the capacity is 120 tons of steam per hour.

2.2 Chemicals

Ammonium sulphate was bought from Wibax AB as a solution in water. Its concentration is 40 % by weight. The solution was delivered in plastic containers with a volume of 1 m³.

The solution was injected using mobile injection equipment with a metered pump and injection lances [10]. The lances were placed at ports in the side-walls of the furnace above the grate. The temperature inside the furnace at the available ports was determined in order to find the optimum temperature window for the effect of ammonium sulphate (NO_x and CO reduction). The temperature at the port chosen was ca 850°C. The pump allows injection rates from a few litres per hour to 95 l/h.

Granulated elemental sulphur was obtained from Jacochem, in big bags of 1 ton. The granules were introduced in the middlemost fuel chute using the mobile dosing equipment from the previous investigation [12]. The screw feeding the sulphur granules was calibrated using a bucket and a stop-watch. The time delay between the start of feeding sulphur to the chute until the sulphur reaches the grate is estimated to approximately one hour.

The additives were fed into the furnace at three rates of injection: low, corresponding to the so-called optimum level of 20 mg sulphur per MJ fuel commonly used, middle and high.

Assuming a steam load on the boiler of 35 MW, the quantity of pure sulphur to be injected for a dose of 20 mg/MJ, is of the order of 2.5 kg/h. This corresponds to a flow-rate of ca 25 l/h solution or 3 kg/h elemental sulphur. The injection flow-rates chosen for ammonium sulphate and elemental sulphur are summarised in Table 1. In order to have a reference for these figures, the contribution of the fuel to the sulphur mass flow into the furnace is 25.4 mg/MJ or 3.2 kg/h at 35 MW (2.3 kg/h at 25 MW). Analyses of sulphur content (see section 5) in the fuel were used for this computation.

Table 1. Feed rate of ammonium sulphate or elemental sulphur in the experiments, expressed in kg/h (l/h for the solution) and in mg/MJ at two boiler loads

Dose	Flow-rate of ammonium sulphate solution		Feed-rate of elemental sulphur	Feed-rate of additives	
				at a boiler load of 25 MW	at a boiler load of 35 MW
	<i>l/h</i>	<i>kg S/h</i>	<i>kg S/h</i>	<i>mg S/MJ</i>	<i>mg S/MJ</i>
Low	25	2.97	2.9	32	23
Middle	49.5	5.94	5.8	64	46
High	95	11.3	11.6	129	92

2.3 Location of sampling points

All on-line measurements were performed in the flue gas duct, at some distance from the combustion chamber, after economizer and air preheater, just before the ESP, as shown in the sketch in Figure 1. This investigation is primarily concerned with emissions after combustion has been completed, not with processes in the furnace. Sampling before de-dusting avoids losses of information carried in the fine particles removed first in the ESP and then in the flue gas condensing unit.

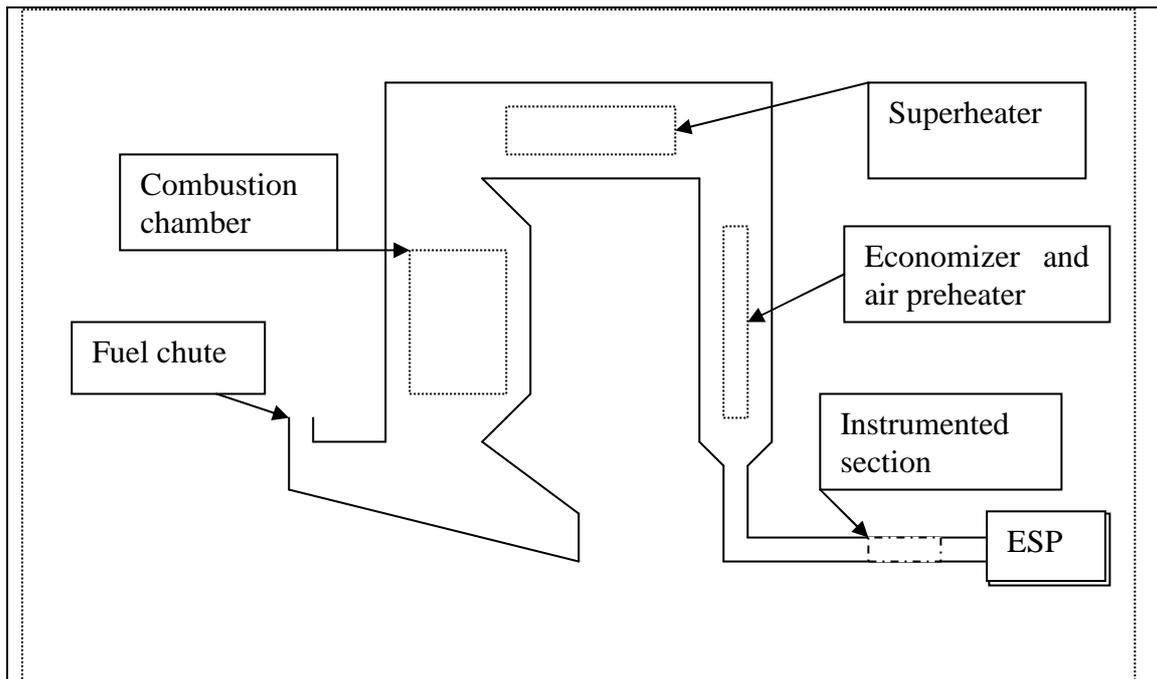


Figure 1. Sketch of the furnace and boiler with flue gas duct showing the position where measurements were performed

The location chosen is a horizontal section of the flue gas duct downstream of the down draft of the boiler, immediately upstream of the ESP. The duct is square with a cross-section of 2×2 m. This part of the duct is already equipped with a sampling cross-section with four ports at ca 0.3 m distance from each others in a vertical line. The temperature of the flue gas is between 125°C and 150°C at that place. The bend at the junction of downdraft, below economizer and air pre-heater, and the horizontal duct is at least 10 m from the sampling cross-section.

These four ports in this ordinary sampling cross-section weren't enough for all the gas samples that must be taken for the conventional measurement equipment, the PCDD/F samples and for the mass spectrometer. Therefore, a port located ca 2.5 m upstream of the sampling cross-section was utilised for the mass spectrometer.

A compromise had to be reached between the wish to take double gas samples for each condition, the length of time during one condition could be maintained, the requirement that sampling take place during at least six hours and a reasonable length of the working day. It was decided to take parallel gas samples and have some overlap of the sampling periods, requiring two gas sampling ports. The second port located ca 1 m up from the floor of the gas duct in the sampling cross-section was used as one port. This is the B port in this report. A new port, the A port, was opened through a blind flange ca 0.5 m downstream of the REMPI-MS port, also 1 m up from the floor of the duct. The position of these sampling points is shown in Figure 2, before any instrument was installed.



Figure 2. A photograph showing the location of sampling points in the flue gas duct. The flow in the duct is from the right to the left and the ESP is to the left outside of the picture. The sampling points are from the left: the ordinary sampling cross-section with four ports in a vertical line, the blind flange where port A was opened and partly hidden behind the pillar, the man-hole where a port for the REMPI-TOF MS was opened.

For the sake of clarity, the injection points for the sulphur additives and the sampling points in the flue gas duct are shown in Figure 3, in the sketch of the furnace, boiler and flue gas duct of Figure 1.

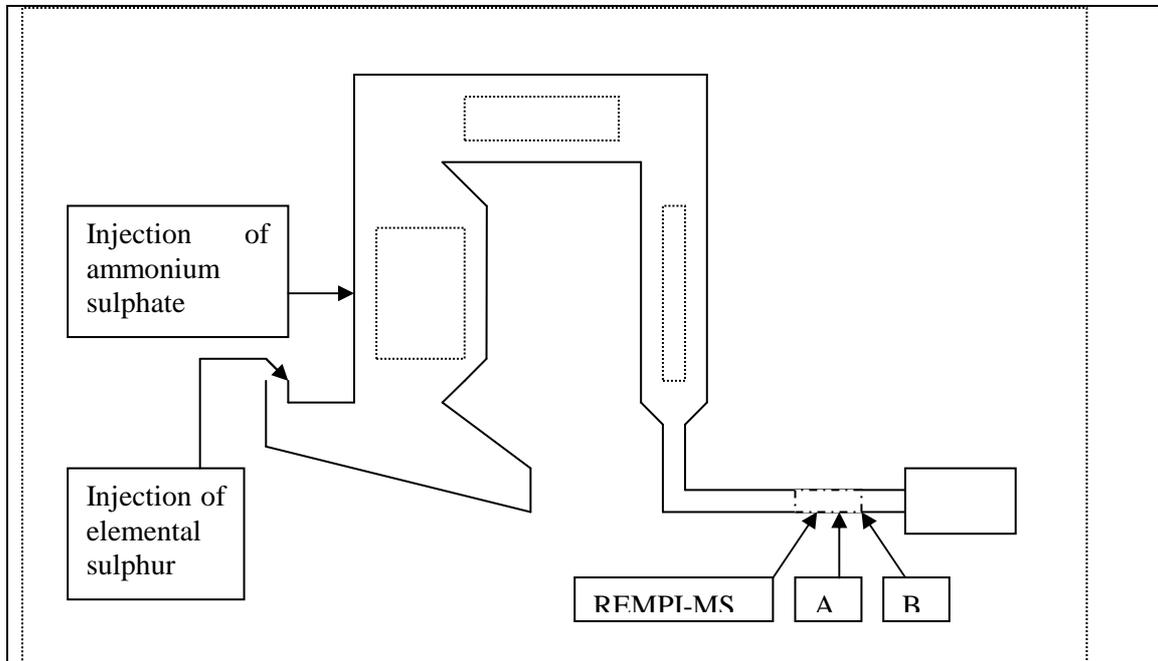


Figure 3. The sketch of furnace, boiler and flue gas duct of Figure 1 with fuel injection points and with sampling points

2.4 Measurements

2.4.1 Conventional measurements

The raw flue gas was sampled using a heated tube. Entrained particles were removed using a filter. The flow in the tube is split into two streams: one (wet) gas stream going to the IR instruments, the other going to the oxygen instrument after being dried. All instruments are equipped with police filters for particles.

A Gaset DX 4000 FTIR instrument has been used to determine the following species on-line: NO, NO₂, N₂O, CO, CO₂, SO₂, HCl, HF, NH₃ and moisture as well as organic compounds. The time resolution chosen for this investigation is one minute. The analyses are performed on wet gas. The instrument has been calibrated using gases with known contents of volatile organic compounds and pure nitrogen as zero level. It has been calibrated down to 10 ppm for benzene (C₆H₆) and down to 4 ppm for methane (CH₄). The next calibration level is 20 ppm for these gases. The uncertainty is 1 ppm to 2 ppm below 10 ppm, 6 % above 10 ppm for nitrogen oxides, sulphur dioxide, ammonia, hydrogen chloride and carbon oxides. The instrument is calibrated yearly in the laboratory. The calibration is quite stable from year to year.

The concentration of oxygen is determined on dry gas using an extractive procedure and a paramagnetic instrument M&C type PMA 10. The range for the measurements is 0 to 20 %. The time resolution is 5 seconds. The instrument has been calibrated using a test gas with a known O₂ content (9.00 %) and nitrogen as zero. The tolerance level for the calibration gas is ± 2 %.

The CO/CO₂ concentration levels are determined using a Fisher Rosemount NGA 2000 IR instrument. The range used for CO₂ is 0 to 30 % and that for CO is 0 to 5000 ppm. The time resolution is 5 seconds. The instrument has been calibrated using a test gas with known carbon dioxide and carbon monoxide contents (14.9 % and 456 ppm respectively) and pure nitrogen gas as zero level. The tolerance level for the calibration gas is ± 2 %.

TOC, Total Organic Carbon, has been determined according to the Swedish standard SS-EN-12619 by continuously supplying the extracted gas to a J.U.M instrument of the type flame ionisation detector (FID). The instrument has five ranges from 0 to 10 ppm to 0 to 100 000 ppm. The time resolution is 5 seconds. The instrument has been calibrated using a gas with known content of propane (C₃H₈), i.e. 79.8 ppm and air as zero. The tolerance level for the calibration gas is ± 2 %. The oxidising gas is a mixture of hydrogen and helium.

The latter two instruments are calibrated yearly. The response, zero and full range, is checked daily.

The data from the measurements are recorded using an INTAB data logger. Each parameter is determined once a second and stored as an average for a period of one minute.

The gas flow has been determined according to SS-ISO 10780 using a Pitot pipe and a micromanometer. The mean flow-rate is determined by traversing the cross-section and performing a measurement at pre-determined points. The flow-rate is then calculated by multiplying the mean flow-rate with the cross-section area. The reference state for the data is 0°C and 101.3 kPa. The gas temperature was determined also according to this standard using a K-type thermoelement and digital reading.

2.4.2 PAH measurements on-line

The requirement on the sampling and inlet system is that the gaseous substances that are analysed are transferred rapidly and without losses to the spectrometer. The flue gas is therefore sampled using a quartz tube and a sampling pump to maintain a flow of gas of 5 litres per minute. Entrained particles are removed using a surface filter (pressed glass fibres). A small portion of the de-dusted gas, ca 10 ml/min, is drawn through a deactivated fused-silica transfer capillary (200 μ m i.d.) to the inlet system of the mass spectrometer. The materials in the inner surfaces of the system are inert. All parts of the sampling train outside the flue gas duct are heated to a temperature of 220°C in order to

avoid condensation of compounds with a high molar mass. The transfer capillary runs in a heated flexible line. At the end of the transfer line, the capillary is embedded in a heated stainless steel needle, the tip of which is located between the electrodes of the ion source. The effusive molecular beam formed is directly hit by the laser pulses from below the tip.

The laser for the mass spectrometer is a compact frequency quadrupled Nd:YAG laser (BigSky Laser) providing intense pulses ($\lambda=266$ nm, 2.5 mJ pulse energy, 10 Hz repetition rate) to the REMPI process. Ions formed in the ionisation source of the reflection time-of-flight mass spectrometer (Stefan Kaesdorf, Munich) are detected using a two-stage multi-channel plate detector (MCP, 40 mm diameter) with extended dynamic range. The folded field free drift region is 380 mm long. The ion source and the flight tube are differentially pumped by two 210 l/s turbo-molecular pumps (TMU 261, Pfeiffer Vacuum, Aslar). The Wiley-McLaren type ion source can be operated with static or pulsed acceleration fields. The repeller electrode and the first extraction electrode are on the same absolute electric potential, but with opposite polarity in order to maintain ground potential at the central ionisation region, thus minimizing the influence of the grounded inlet needle. The TOF mass spectra are recorded using two transient recorder cards (250 MHz, 1 GS, signal resolution 8 bits for 256 points) from Aqcris in Switzerland. One card monitors continuously the low-voltage region of the spectrum (typically below 50 mV) with a resolution of 8 bits and the other cards monitors the whole region up to 5 V. This combination of cards yields a greater dynamic range. In this investigation, the TOF MS spectra from 100 consecutive laser shots have been averaged, yielding a time resolution of 10 seconds. Data processing is done using LabView (National Instruments, USA) and purpose-written software.

Because most PAH have a low vapour pressure at room temperature and as an internal standard could not be used, the results from the mass spectrometer were quantified in the following manner. A standard gas (nitrogen with 100 ppb each of benzene, toluene and p-xylene) was used to calibrate the mass spectrometer with respect to these compounds before and after each measurement cycle. The polycyclic compounds were indirectly calibrated by determining their REMPI cross-sections at 266 nm relative to that of toluene.

The REMPI cross-section was determined by dissolving a known amount of each PAH in methanol, injecting the solution with a constant flow-rate into a stream of nitrogen using a HPLC pump, drawing off a small portion of this gas stream into the ion source of the mass spectrometer and comparing the resulting TOF MS signal with that for 100 ppb toluene. A weight factor is then calculated. Naphthalene (128 m/z), phenanthrene (178 m/z), pyrene (202 m/z), chrysene (228 m/z) and retene (234 m/z) could thus be quantified in the experiments.

Since PAH compounds with a single methyl group exhibit almost identical REMPI cross-sections as the corresponding unmethylated PAH compounds, it was also possible to quantify methylnaphthalene (142 m/z) methylphenanthrene (192 m/z).

The concentration level of anthracene (178 m/z) is of an order of magnitude less than that of its isomer phenanthrene. The REMPI cross-section of fluoranthene (202 m/z) is almost two orders of magnitude lower than that of its isomer pyrene. The error in concentration caused by the inability to separating the contributions of each isomer in the signals is quite small.

Comparison of the two daily REMPI-MS calibrations (before and after each measurement period) showed relatively low deviations: the parameters of the set-up of the instrument such as laser power, TOF performance etc were robust and seemed to be reliable for the whole day. No further adjustments were then needed. In addition to that, a background spectrum was determined for each day and subtracted from the measured spectrum. This is not crucial for naphthalene and phenanthrene, but it has to be done for chrysene and retene. However, the contribution of the latter compounds to the PAH load is negligible.

2.4.3 Gas samples for off-site analysis

Because the access to the flue gas duct was limited and because samples had to be taken during six hours periods, a single gas sample had to be taken for all compounds to be analysed off-line, i.e. PAH, PCBz and PCDD/F.

Isokinetic sampling was done in accordance with EN 1948-1:2006. The high dust load in the gas being sampled clogged the filter, thus making it impossible to sample for more than half an hour using the filter – condenser sampling train. The cooled probe sampling train also tended to become obstructed by large dust particles that adhered to the moist surface of the tube.

Therefore, as a modification to the method according to standard, a heated probe (125°C) was used in combination with an external Liebig condenser, the inner tubes usually used in the cooled probe sampling train on the inside and a glass cooling jacket on the outside. The inner tube could thus be used as part of the sample and made it possible to check for large dust particles that adhered to the walls. If necessary, these large particles could be removed by interrupting the sampling for a few seconds at the time and flushing them with a small amount of purified water into the condensate bottle.

The condensation temperature was kept below 25°C. PCDD/F internal standards were added to the condensate flask before sampling.

2.4.4 Analysis of gas samples

Samples for analysis were treated according to EN 1948-2:2006. The extraction procedure was modified in order to determine PAH and PCBz in the same samples. In order to minimize losses of relatively non-volatile compounds, a first extraction step with dichloromethane was added.

The dust was filtered off from the condensate and digested with HCl during one hour at pH=2. After washing with purified water, the dust was freeze-dried and added to the XAD-2 adsorbent. The combined aqueous phases were extracted first with dichloromethane and then with toluene. The combined dust and adsorbent sample were extracted first with dichloromethane and then with toluene (Soxhlet, 24 h, more than 100 extraction cycles). PCDD/F extraction recovery standards and PAH and PCBz internal standards were added before extraction.

The dried and combined dichloromethane extracts were reduced to 10 ml in a TurboVap concentrator. In the same way, the toluene extracts were concentrated to 10 ml. A small part, 1 ml, of the dichloromethane extract was analysed for PCBz by GC-MS without further clean-up.

The PAH were analysed from 2 ml each of the dichloromethane and the toluene extracts after solvent exchange to cyclohexane and clean-up on silica gel.

The mono- to octachloro-PCDD/F were cleaned up and analysed according to EN 1948-3:2006, combining 6 ml aliquots of the dichloromethane and toluene extracts.

2.4.5 Fuel and ash samples for later analysis

During the course of experiments samples were taken every now and then of the fuel in the middlemost chute and of both bottom ash and ESP ash, making up daily samples.

The elemental analysis of fuel and ashes consists of:

- Total carbon, hydrogen and nitrogen (CEN/TS 15104)
- Sulphur (SS 187177/ASTM D4239 C)
- Chlorine (SS187185 for ashes, ASTM D 4208 for fuel)
- Ash content of the fuel after ashing at 550°C (CEN/TS 14775)
- Moisture (CEN/TS 14774-1,2)
- In addition, the TIC and TOC⁶ of the ESP ashes were determined using the indirect EN 13137 method – Total Carbon and TIC are determined for two sub-samples and TOC is obtained by subtraction

The uncertainty in the analyses is ± 30 % of stated value for nitrogen and ± 10 % for hydrogen and carbon in the EN method. The uncertainty is ± 25 % for chlorine and ± 10 % for sulphur. The uncertainty is ± 3 % for moisture content. That for total inorganic carbon (TIC) is ± 5 % and that for total oxidizable (organic) carbon (TOC) is ± 10 %.

⁶ TIC is Total Inorganic Carbon. TOC is usually taken to be Total Organic Carbon. This is true for gases, but for ashes, one should read TOC as total oxidizable carbon as TOC includes both organic and elemental carbon.

2.4.6 Data gathered from the SCADA system

Operating parameters were collected from the SCADA system at the plant. This includes:

- NO_x, oxygen, carbon monoxide, sulphur dioxide
- Boiler load (MW)
- Flow of fuel oil to the furnace (MW)
- Dust after the ESP
- Temperature

All measurement data are collected every eight minutes. Concentrations in flue gases from this furnace are measured in a time sharing system using one gas analyser for the several boilers at the pulp and paper plant. Taking into account the rotation between furnaces, flushing periods etc, the value recorded represents one to one and a half minutes out of these eight minutes. It was not possible to determine when these one and a half minutes occur during an eight-minute cycle.

The values collected from the SCADA system were used only as a check of operating conditions.

3 Reporting structure

A larger than usual number of variables has been monitored during the experiments. Recording their momentary values has generated a large collection of data. The challenge of presenting them in a concise, easy to read yet exhaustive fashion has been met as follows:

- In this section, the main results are summarised as a list
- An experimental logbook is then given in next section, 4, in order to record how the experimental campaign has proceeded and major events that may have influenced the results
- In section 5, the results are presented as values averaged over several hours, which is a time scale more relevant to environmental permits than the data on a time scale of minutes or seconds
- Last, results on a short time scale are presented in section 6 as a complement with the purpose of providing more information on the actual physical processes that have been investigated

The results are analysed and discussed section by section.

4 Experimental logbook

The experiments at the furnace were run with full instrumentation in March 2007, from 19/3 to 30/3. The working week 19/3 to 23/3 was dedicated to ammonium sulphate and the week 26/3 to 30/3 was dedicated to elemental sulphur.

As the FTIR instrument failed during the first week and the expected effect of ammonium sulphate on NO_x could not be observed, the experiments with ammonium sulphate were repeated on a single day, 24/4, without the REMPI mass spectrometer and without taking gas or ash samples.

4.1 Ammonium sulphate week

In the first week, the additive used was ammonium sulphate. The experimental schedule was as follows:

- Monday 19/3, reference period without any sulphur dosage
- Tuesday 20/3, increasing the feed-rate of ammonium sulphate in seven successive steps in order to map the dose-response behaviour, from 6.2 l/h to 95 l/h
- Wednesday 21/3, injection of 50 l/h ammonium sulphate solution
- Thursday 22/3, injection of 25 l/h ammonium sulphate solution
- Friday 23/3, injection of 95 l/h ammonium sulphate solution

The power output of the boiler was 30 to 35 MW during that week, with a temporary dip at 20 MW for some hours. Fuel oil was used occasionally.

The FTIR instrument broke down on 20/3 and was repaired first at noon on 23/3. Therefore, FTIR data are missing for these experiments with the exception of the tail end of the 11.6 l/h ammonium sulphate period on 23/3.

When the data from the SCADA system were examined on the spot, the expected effect of ammonium sulphate on NO_x emissions could not be observed. Different injection points were tested between 14:00 and 16:00 on 23/3 without yielding any better results regarding NO_x .

The injection of ammonium sulphate was interrupted at 16:00 and the system was left to relax to ordinary conditions. These were reached within one hour for most concentrations, ammonia and NO_x taking slightly more time. The response of the system was also of the order of half an hour to an hour for all variables when the injection rate was changed during the week.

All instruments except the mass spectrometer were left on during the week-end. The temperature sensor malfunctioned and did not yield reasonable values.

It was decided to perform additional measurements with ammonium sulphate at a later date in order to complement for the missing FTIR data.

4.2 Elemental sulphur week

In the second week, elemental sulphur was injected. The experimental schedule was as follows:

- Monday 26/3, a second reference period without any sulphur
- Tuesday 27/3, the lowest sulphur feed-rate, 2.9 kg/h
- Wednesday 28/3, next sulphur feed-rate, 5.8 kg/h
- Thursday 29/3, the highest sulphur feed-rate, 11.6 kg/h

There was a fuel shortage on 26/3, reducing the steam power delivered by the boiler to ca 20 MW or lower for most of the day. The consequence was a large increase in all emissions and several instruments were at times disconnected from the flue gas duct in order to avoid condensation of tars and subsequent contamination. The operation returned to normal during early afternoon.

The injection of sulphur was stopped at 16:00 on 29/3 and the instruments except the mass spectrometer were left on to record the relaxation process to normal conditions until next morning.

The response of the system was slower in this case than in the case of ammonium sulphate: it took an hour for an increase in sulphur injection to reach the grate and cause a change in concentration. When injection was interrupted on 29/3, it took two to three hours for all concentrations to reach their final values. Sulphur dioxide concentration fell after an hour to an hour and a half, after which time the concentration of carbon monoxide and other substances started to react.

All instruments worked as planned that second week except for the CO/CO₂ IR instrument which malfunctioned during the night 28/3 to 29/3, i.e. the highest dose of sulphur. It was back in operation next morning.

On the 28/3, the temperature distribution in the furnace was determined in order to find a more appropriate injection port for the additional experiments with ammonia sulphate.

4.3 Complementary ammonium sulphate experiment

The day (24/4) was started with a renewed search for a suitable injection port for the ammonium sulphate. The temperature distribution in the furnace had changed and it was impossible to observe any effect of ammonium sulphate on NO_x. Therefore, the ambition to obtain a NO_x reduction had to be abandoned and it was decided to inject the ammonium sulphate solution at the same point as in the previous campaign.

Production runs were started in the afternoon. The two lowest concentrations were kept for a couple of hours, and the highest concentration was kept for 8 hours. The injection pump was shut down at 03:00 and the relaxation recorded until shortly before 09:00 next morning.

4.4 Choosing samples for analysis

Fuel, fly ash and bottom ash samples were taken daily. Out of these ten samples for each material, five were chosen for analysis: reference condition (no additive), lowest and highest dosage of an additive (both ammonium sulphate and elemental sulphur).

Every day at least two gas samples were taken for PCDD/F, PCBz and PAH analysis off-site. On the first reference day (19/3) and on the day with maximum ammonium sulphate dose (23/3) both samples were analysed for all three groups. All other days, only one gas sample was analysed for all three groups of substances, the remaining samples being analysed for PAH's only.

5 Results averaged over several hours

5.1 Concentrations in raw gas

The effect of sulphur on the concentration of species in the raw gas is summarised in the following tables and it will be illustrated in diagrams in section 5.3. All data are reported for wet gas and actual oxygen concentration⁷.

The results for the dose-response mapping experiment are collected in Table 2.

Table 2. The effect of ammonium sulphate on carbon monoxide and TOC in the raw gas during the dose-response mapping day (20/3), actual data averaged over the 1½ hours during which a dosage was maintained.

Rate of injection of ammonium sulphate solution			CO	TOC
<i>l/h</i>	<i>kg S/h</i>	<i>mg/MJ</i>	<i>ppm</i>	<i>ppm</i>
0	0	0	2108	25.2
6.2	0.74	7.1	223	1.74
12.4	1.49	13.0	447	4.06
18.7	2.24	19.6	325	7.24
28.2	3.38	27.0	292	3.58
42.6	5.54	41.1	192	2.78
64.4	8.73	74.2	107	0.82
97.2	11.7	93.4	73	0.83

In order to allow a straight comparison between the values of the concentrations of various substances, the time intervals chosen for reporting results from the main series of experiments in Table 3 to Table 6 are the periods during which gas samples were taken. For a summary of samples and times, see Appendix B.1.

In all tables the concentration of the non-detects for PCDD/F is set to the level of quantification (LOQ), in order to provide an upper limit. The blank value over the total procedure, including sample handling and transport is ca 0.0005 ng TEQ/m³, which value has been taken into account in the results reported. Detailed results for PCDD/F, PCBz and PAH are found in Appendix B.

⁷ Because of the malfunctioning FTIR instrument there are no moisture data during the first week of experiments. All data are therefore reported as wet gas. To convert to an approximately dry gas condition, multiply all data with 1.175.

Table 3. The effect of ammonium sulphate on concentrations of substances in the raw gas, data averaged over the periods during which raw gas was sampled for PCDD/F, PCBz and PAH analysis off-site – data for wet gas and actual oxygen concentration

Day		19/3	19/3	22/3	21/3	23/3	23/3
Rate of injection	<i>l/h</i>	0	0	25	49.5	95	95
Dose	<i>mg/MJ</i>	0	0	25.9	51.9	114.2	121.2
O₂	<i>%</i>	13	14	14	14	14	15
CO	<i>ppm</i>	2100	2600	620	240	210	260
TOC	<i>ppm</i>	25	42	4.3	2.2	2.2	0.9
SO₂	<i>ppm</i>	-	-	-	-	-	22 ¹
HCl	<i>ppm</i>	-	-	-	-	-	0.5 ¹
NO_x	<i>ppm</i>	-	-	-	-	-	49 ¹
NH₃	<i>ppm</i>	-	-	-	-	-	0.2 ¹
Methane	<i>ppm</i>	-	-	-	-	-	1.0 ¹
Port		A	B	B	B	A	B
PAH gas samples²	<i>µg/m³</i>	30	51	19	30	13	7.2
PAH on-line³	<i>µg/m³</i>	-	390 ⁶	15	11	-	4.5
PCBz	<i>µg/m³</i>	11 ⁴	12	8.9	7.4 ⁴	2.3	4.4
PCDD/F	<i>ng TEQ/m³</i>	0.0016	0.0008	0.0052	0.0019	0.0097	0.0038
PCDD/F⁵ total	<i>ng total/m³</i>	0.47	0.93	3.7	1.8	2.6	1.8
Benzene	<i>ppb</i>	-	1715	51	26.7	-	34.4

Footnote to Table 3:

¹ Results for the last 1½ hour of the sampling period, starting when the FTIR was back in operation and ending when searches for a more appropriate injection port began

² Results from analysis off-site of gas samples, the EPA 16

³ Results obtained with the REMPI MS, 7 PAH with their isomers

⁴ Monochlorobenzene could not be quantified – actual sum is estimated to be at most 10 % larger

⁵ Total of mono- to octachlorinated PCDD/F

⁶ This value is the average for a period of three hours, the latter half of the six-hour gas sampling period

Table 4. The effect of elemental sulphur on the concentrations of substances in the raw gas, averaged over the periods during which gas samples were taken for later analysis of PCDD/F, PCBz and PAH – data for wet gas and actual oxygen concentration

Day		26/3	27/3	28/3	29/3
Rate of injection	kg/h	0	2.9	5.8	11.6
Dose	mg/MJ	0	24.1	41.1	98.2
O₂	%	13.4	13.1	12.4	13.3
CO	ppm	1800	360	280	130
TOC	ppm	24	3.6	2.8	1.0
SO₂	ppm	3.2	2.5	4.0	17
HCl	ppm	0.10	0.15	0.26	0.05
NO_x	ppm	30	37	44	47
NH₃	ppm	13	5.3	4.2	0.8
Methane	ppm	39	4.4	3.8	0.7
Port		B	B	B	B
PAH gas samples¹	µg/m ³	112	12	9.1	2.5
PAH on-line²	µg/m ³	70	7.7	4.9	1.9
PCBz	µg/m ³	42	0.8	1.6	1.1
PCDD/F	ng TEQ/m ³	0.0037	0.0021	0.0007	0.0006
PCDD/F³ total	ng total/m ³	-	2.130	1.161	0.764
Benzene	ppb	170	24	19	6.1

Footnote to Table 4:

¹ Results from analysis off-site of gas samples, the EPA 16

² Results obtained with the REMPI MS, 7 PAH with their isomers

³ Total of mono- to octachlorinated PCDD/F

Table 5. Concentration of PAH's in raw gas on the additional gas samples not analysed for PCDD/F and PCBz, data for wet gas and actual oxygen concentration

Day	Additive	Dose	Port	PAH (µg/m ³)
21/3	ammonium sulphate	49.5 l/h	A	30
22/3	ammonium sulphate	25 l/h	A	39
22/3	ammonium sulphate	25 l/h	A	170
26/3	none	0	B	7700
26/3	none	0	A	4300
27/3	sulphur	2.9 kg/h	A	81
28/3	sulphur	5.8 kg/h	A	87
29/3	sulphur	11.6 kg/h	A	11

Please note in Table 3 and Table 4 the following:

- Data for PAH's are available from two sources: analysis of the gas samples (the EPA 16) and the REMPI MS, the latter yielding the sum of naphthalene, methylnaphthalene, phenanthrene, methylphenanthrene, pyrene, chrysene and retene
- Data for benzene are from the REMPI MS, not from the FTIR instrument
- PCDD/F data are given both as I-TEQ (17 congeners) and total, i.e. the sum of mono- to octachlorinated PCDD/F

The FTIR instrument delivered also values for the concentrations of organic compounds other than methane. However, there are very improbable cross-relationships between the concentrations of the various organic substances on the basis of one minute that make the value of these data extremely doubtful. The algorithm used for evaluation of the spectra is probably not able to process the data correctly at these low signal intensities. Nothing useful can then be obtained from these data, except that the concentrations of methanol, ethanol, formaldehyde, ethane, propane, benzene and phenol are very low. Therefore, the only data for benzene reported here are those from the REMPI mass spectrometer.

Table 6. *The effect of ammonium sulphate on measured species in the raw gas during the complementary ammonium sulphate experiments on 24/4, data averaged over the last hour of a dosing period of 1½ hours except for the 95 l/h data which are averaged over the last four hours – data for wet gas and actual oxygen concentration*

Day		24/4	24/4	24/4	24/4
Flow-rate of solution	<i>l/h</i>	0	25	49.5	95
Dosage	<i>mg/MJ</i>	0	30.8	68.8	94.3
O₂	<i>%</i>		15.2	15.4	13.8
CO	<i>ppm</i>	1700	730	670	230
TOC	<i>ppm</i>	48	3.2	3.0	0.9
SO₂	<i>ppm</i>	5.0	1.8	8.4	16
HCl	<i>ppm</i>	0.1	0.4	0.1	0.2
NO_x	<i>ppm</i>	29	46	56	61
NH₃	<i>ppm</i>	22	0.83	0.0	0.0
Methane	<i>ppm</i>	88	5.9	4.3	1.0

The effects of the sulphur additives on carbon monoxide are illustrated in Figure 4. As expected, the carbon monoxide concentration in the raw gas decreases considerably with a low rate of injection of sulphur. However, further increases of the injection rate of sulphur additives yield diminishing returns. A similar diagram may be drawn for TOC or for methane.

The concentration of PAH's, from the analysis of gas samples and from the REMPI data, also decrease with increasing doses of sulphur additive. The concentrations of the PCDD/F in the raw gas are quite low, from 0.0008 to 0.0097 ng TEQ/m³, which values should be compared with the emission limit value of 0.1 ng TEQ/m³ for waste incineration. The sum of mono- to octachlorinated PCDD/F (Sum 1-8 PCDD/F) is also quite low, from 0.5 ng/m³ to 3.7 ng/m³. The concentration of PCBz decreases with increasing dosage of ammonium sulphate but is low and almost constant with elemental sulphur.

As expected, the concentration of sulphur dioxide in the raw gas increases with increasing dosage of additives, lower diagram in Figure 4. The effect on hydrogen chloride concentration is not very large and it is not consistent (monotonous increase or decrease), which may be related to the low chlorine concentration in the bark.

Please note that data for reference conditions (19/3) and (24/3 to 26/3), no sulphur additives, are represented in all diagrams using the symbols for the experimental series that follow them.

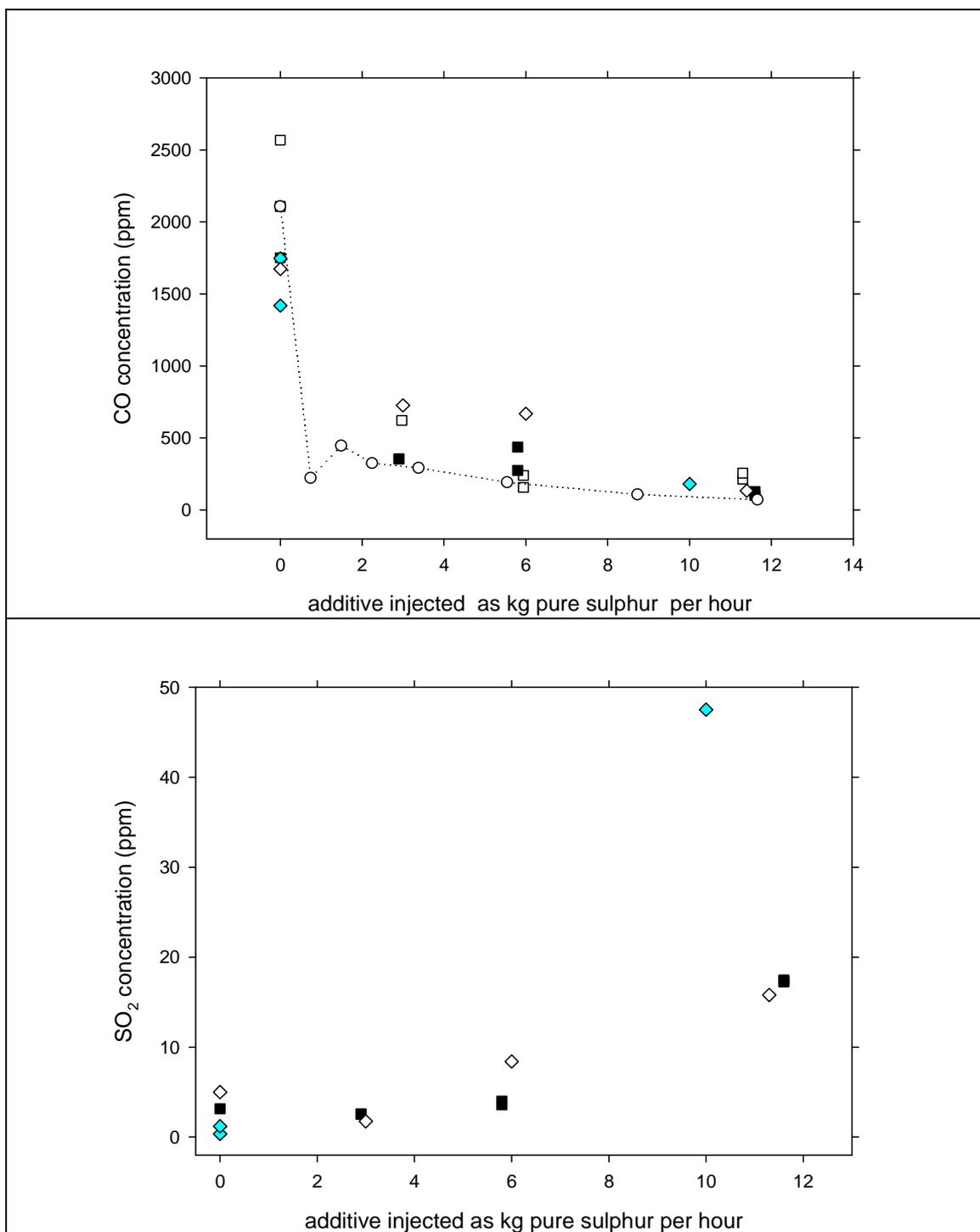


Figure 4. *Upper diagram:* The effect of additive injection in kg pure sulphur on the concentration of carbon monoxide in the raw gas. *Lower diagram:* the concentration of sulphur dioxide as a function of additive injection. Empty symbols, ammonium sulphate series: o, dose-response mapping experiments, □, main series of experiments and ◇, complementary experiments. Filled symbols, elemental sulphur series: ■, main series and ◆, previous investigation with elemental sulphur [12].

5.2 Analyses of fuel and ash samples off-site

Five samples out of the ten daily fuel samples were analysed for ash content, sulphur and chlorine, see Table 7. The corresponding ash samples were also analysed, Table 8 and Table 9. Information on type of additive and dose is also given in the table for ease of reference.

Table 7. Analysis of fuel samples – the dosage of additive is given for indicative purposes (the dose of ammonium sulphate has been converted to a dose of pure sulphur).

	Date	19/3	22/3	23/3	27/3	29/3
Additive		none	ammonium sulphate	ammonium sulphate	sulphur	sulphur
Dose	kg S/h	0	3.0	11.3	2.9	11.6
Carbon	% D.S.	51.7	52.2	51.8	51.5	52.4
Hydrogen	% D.S.	5.4	5.7	5.8	5.8	5.8
Nitrogen	% D.S.	0.37	0.45	0.38	0.36	0.38
Sulphur	% D.S.	0.03	0.04	0.04	0.04	0.06
Chlorine	% D.S.	< 0.01	< 0.01	0.01	< 0.01	< 0.01
Ash	% D.S.	3.2	3.3	-	3.3	-
Moisture	% D.S.	61.3	60.8	61.6	61.7	61.0

Although the physical aspect of the bark fuel was different from day to day its chemical composition is remarkably constant. The sulphur content varies very little if one takes into account the experimental uncertainty. The ash content is stable at ca 3.3 %. These data are within the normal interval for bark fuel as reported by the Swedish Environmental Protection Agency [17]. The chlorine content is low, mostly below the limit of determinability.

The results of analyses of ash are summarised in Table 8 for the ESP ash and Table 9 for the bottom ash. The moisture content of the bottom ash is high because wet extraction is used.

As one can expect, the sulphur content of the fly ash increases somewhat and the chlorine content decreases slightly with increasing doses of additives. There is practically no effect of the additives on sulphur and chlorine content of the bottom ash.

The TOC content of the fly ash increases with increasing doses of sulphur additive. The exact figures themselves must though be interpreted with some caution: the total carbon and the TIC values for the sample on 23/3 depart somewhat from those for the other samples. It is also possible that the total carbon content of the bottom ash on 19/3 is slightly too low.

Table 8. Results from the analysis of the ESP or fly ash – the dosage of additive is given for indicative purposes (the dose of ammonium sulphate has been converted to a dose of pure sulphur).

	Date	19/3	22/3	23/3	27/3	29/3
Additive		none	ammonium sulphate	ammonium sulphate	sulphur	sulphur
Dose	<i>kg S/h</i>	0	3.0	11.3	2.9	11.6
Total carbon	<i>% D.S.</i>	7.2	7.9	9.7	6.4	6.8
TIC	<i>% D.S.</i>	6.9	4.4	2.4	5.2	4.0
TOC	<i>% D.S.</i>	0.3	3.5	7.3	1.2	2.8
Hydrogen	<i>% D.S.</i>	0.1	0.05	0.2	0.2	0.1
Nitrogen	<i>% D.S.</i>	< 0.1	< 0.1	0.16	< 0.1	< 0.1
Sulphur	<i>% D.S.</i>	1.46	3.26	5.8	2.1	6.1
Chlorine	<i>% D.S.</i>	0.57	0.55	0.45	0.60	0.43
Moisture	<i>%</i>	0.5	0.9	1.7	0.5	0.8

Table 9. Results from the analyses of the bottom ash – the dosage of additive is given for indicative purposes (the dose of ammonium sulphate has been converted to a dose of pure sulphur).

	Date	19/3	22/3	23/3	27/3	29/3
Additive		none	ammonium sulphate	ammonium sulphate	sulphur	sulphur
Dose	<i>kg S/h</i>	0	3.0	11.3	2.9	11.6
Total carbon	<i>% D.S.</i>	49.9	67.2	65.7	71.5	65.7
Hydrogen	<i>% D.S.</i>	< 0.1	< 0.1	0.7	1.6	0.7
Nitrogen	<i>% D.S.</i>	0.40	0.51	0.51	0.54	0.49
Sulphur	<i>% D.S.</i>	< 0.12	0.05	0.06	0.06	0.08
Chlorine	<i>% D.S.</i>	0.020	0.018	0.021	0.021	0.018
Moisture	<i>%</i>	77.0	81.3	80.1	80.9	80.4

5.3 Analysis of the results

5.3.1 Carbon monoxide, TOC and gaseous PAH

The diagram in Figure 4 confirms the expected effect of sulphur additives on carbon monoxide. The carbon monoxide continues to decrease when the amount of additive injected increases, which contradicts the observation by Lindau and Skog who presented results that indicate that there is a dose beyond which there is no further effect [7], 20 mg per MJ fuel or 1.8 kg/h for the 30 MW_{th} fluidised bed furnace in Falun.

The data that are reported in Table 2 to Table 4 and Table 6 are averages for a gas sampling period, including all data available. Removing data for intervals within these periods with disturbances, with low boiler load (below 20 MW) as well as periods with malfunctioning control system and computing a sulphur dose per MJ for the sake of comparisons with published data, one obtains the diagram in Figure 5. Using a logarithmic scale instead of the linear scale in Figure 4 makes clearer that there is no limit to the effect of sulphur additive at 20 mg/MJ in this furnace. If limit there is, it may be at larger doses. The appearance of a plot of naphthalene vs injected sulphur is the same as that of the plots for carbon monoxide or TOC in Figure 5.

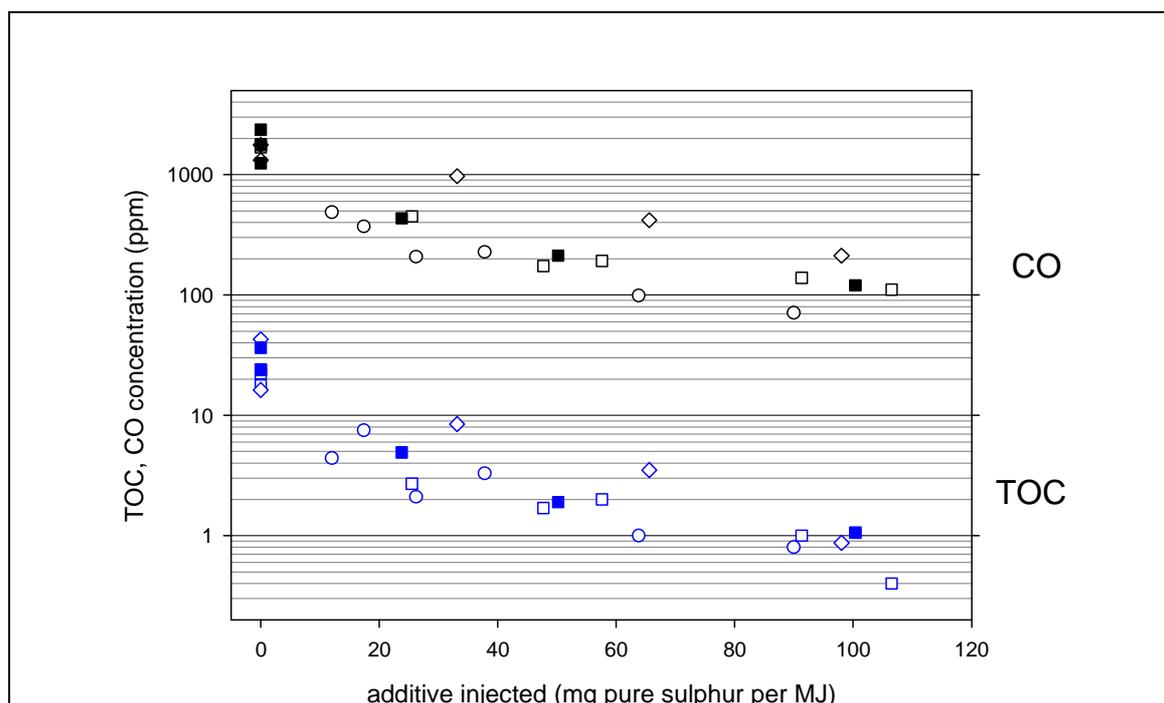


Figure 5. The effect of sulphur additives on concentrations of CO (black symbols, upper cluster of points) obtained with the CO/CO₂ IR and TOC (blue symbols, lower clusters of points) in the raw gas, wet gas and actual oxygen concentration. Periods with disturbances or with low boiler load have been removed. Empty symbols, ammonium sulphate: ○, dose-response mapping experiments, □, main series and ◇, complementary series. Filled symbols: ■, elemental sulphur.

The deviation that may be observed between data points in Figure 5 is not a random variation between points, but more a deviation between series of points. The results from the experiments in March are comparable, although those from the dose-response mapping day are slightly lower, and the complementary series of experiments with ammonium sulphate in April gave points somewhat higher up in the diagram. This reflects differences in operation of the furnace.

Please note that there is already a considerable variation in carbon monoxide or TOC concentration in data for operation without sulphur additives.

There doesn't seem to be any difference between the two additives, ammonium sulphate and elemental sulphur, in the magnitude of the effect: all curves coincide within a reasonable margin for experimental deviations and variations in conditions between different experimental series, Figure 4 and Figure 5.

In Lindau and Skog's experiments [7], as well as in later experiments [11], the reduction of carbon monoxide concentration was ca 50 % at 20 mg/MJ. Similar information is less easy to extract from Kassman et al [10]. In Aurell et al [13] the reduction is larger: 90 % at a dose of 40 mg S/MJ. The reduction observed here is also larger than that in Lindau and Skog, already ca 75 % at a low dose of any of the two additives used. The initial concentration of carbon monoxide is though much higher here.

The TOC reduction was stated by Lindau and Skog to be of the same order although the few figures provided in a diagram yield a reduction of ca 85 % at 30 mg S/MJ without any sign of levelling out [7]. The TOC concentration does not level out here either and the reduction is of the same order of magnitude at 30 mg/MJ.

The relationship between CO and TOC concentrations is plotted in Figure 6, removing periods with disturbances or low load. The correlation between the two concentrations is quite clear, and it is reasonable to fit a straight line to all data, whether they are for conditions with a sulphur additive or for conditions without any dosage of sulphur. The data for sulphur additives are found below a carbon monoxide concentration of ca 500 ppm, data without sulphur additives are found above that concentration. The correlation is approximately the same if data during disturbances and low load periods are not removed but with a larger deviation for individual points on the diagram.

A conclusion is that lowering the carbon monoxide concentration by a better control of the combustion or using sulphur additives yields similar results for the TOC, i.e. the content of organic substances.

However, it should be remembered that the correlation is not always a straight line for all furnaces and that it changes with load and with furnace, see e.g. the data reported by Schuster [1], [2], [3]. Monitoring carbon monoxide instead of TOC may be justified, but the response should be calibrated from case to case.

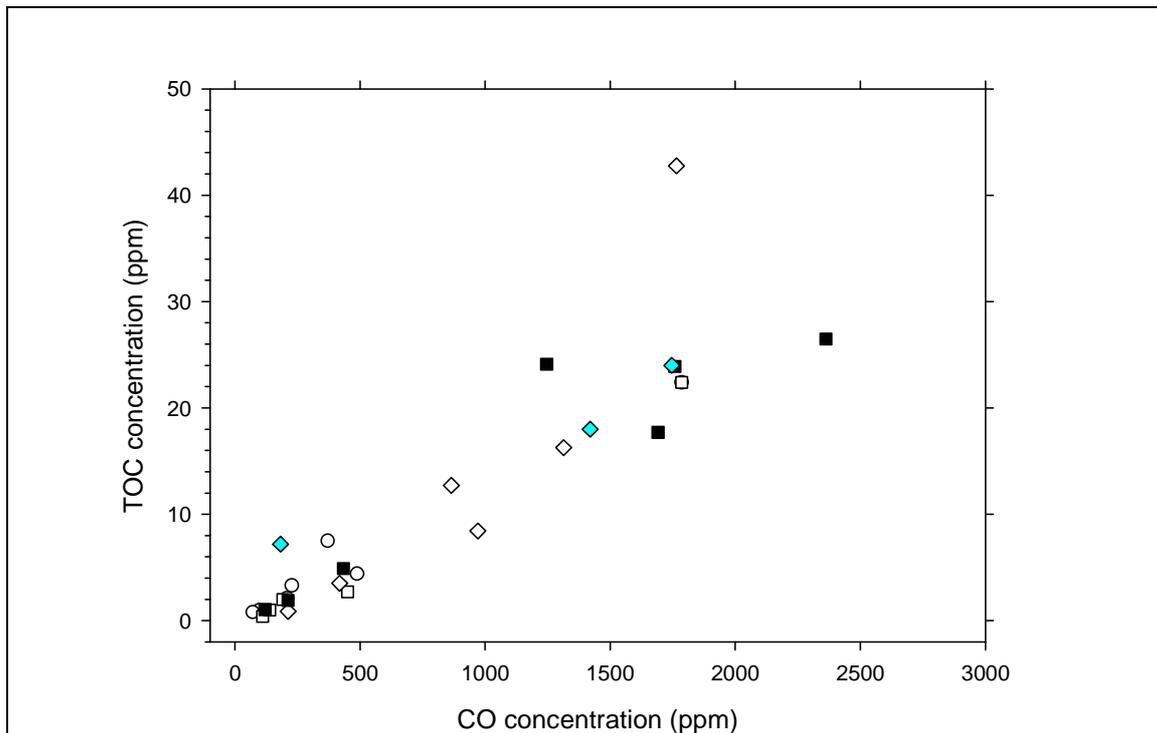


Figure 6. The concentration of Total Organic Carbon (TOC) as a function of carbon monoxide concentration (CO/CO₂ IR instrument) in the raw gas before the ESP. Periods with disturbances or with low boiler load have been removed. Empty symbols, ammonium sulphate: o, dose-response mapping experiments, □, main series and ◇, complementary series. Filled symbols, elemental sulphur: ■, main series, ◆, previous investigation [12].

The next question is whether carbon monoxide, or TOC, correlates in a similarly straightforward fashion with the aromatics, i.e. with naphthalene in the first place and with PAH's in the second place. Averaging data for naphthalene from the REMPI measurements and using the averages of carbon monoxide concentrations from the CO/CO₂ IR instrument (data at 5 s intervals) yields Figure 7. The appearance of the curve is more that of a "hockey stick", small changes in naphthalene concentration at low carbon monoxide concentration and a rapid increase above a threshold value of the latter. There isn't enough information at average carbon monoxide concentrations of ca 1000 ppm to determine where the threshold is.

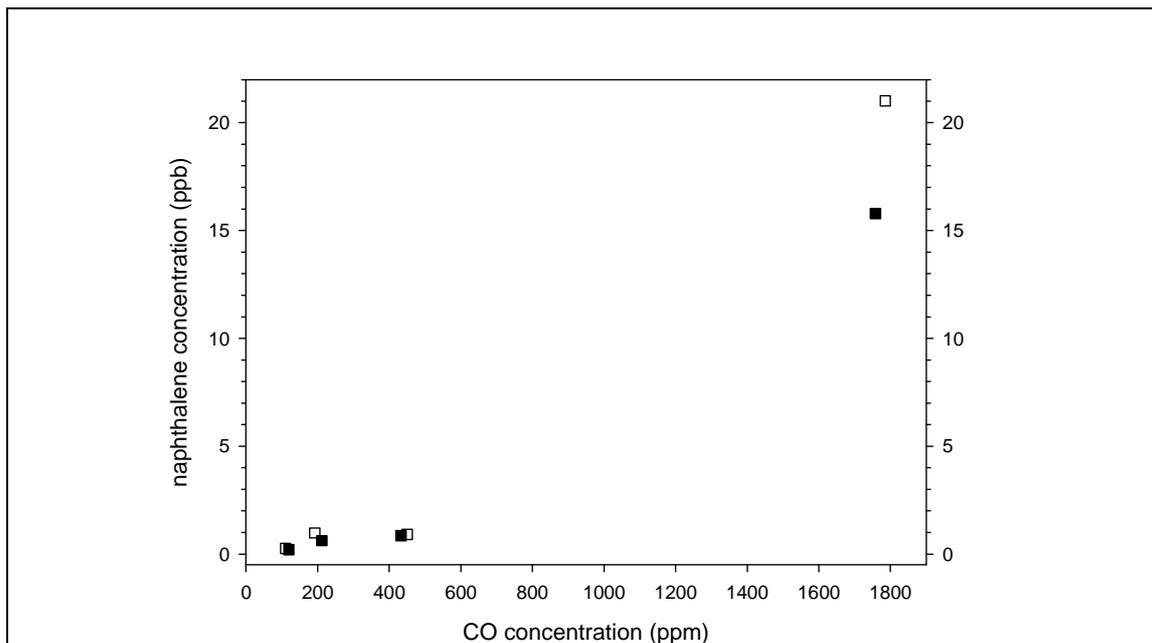


Figure 7. Naphthalene concentration from the REMPI measurements as a function of carbon monoxide concentration for the main experiments; empty symbols, ammonium sulphate series, filled symbols, elemental sulphur series. The points above 500 ppm carbon monoxide are without sulphur additives.

5.3.2 PAH, PCBz and PCDD/F

The concentrations of PAH's, PCBz and PCDD/F in the gas samples taken were reported in section 5.1. The dependence of PAH concentrations on the dose of additive is illustrated in Figure 8. Please note that the two highest values at low load on 26/3 have been omitted as the loads are not really comparable to the loads in the other experimental points. In spite of some variation, the general trend is that PAH concentration becomes lower as more additive is injected. If one disregards the point at $173 \mu\text{g}/\text{m}^3$ on the 22/3 (the uppermost triangle at an ammonium sulphate dose of 25 l/h or 2.9 kg sulphur per hour) and the points from the previous investigation [12], the decrease in PAH with increasing sulphur dosage becomes more convincing.

Part of the variation is caused by an apparent difference between values for samples taken at port B and those for samples taken at port A, which is upstream of port B. Samples from both ports should be equivalent, but the results at port A are usually at a higher level than those at port B for an unknown reason. The two ports are at the same level, without any noticeable differences in gas flow velocities. There is an overlap between sampling periods at ports A and B but an examination of CO and naphthalene concentrations for the periods without overlaps doesn't show any event that would be proportionate to e.g. the difference in PAH values between $9.1 \mu\text{g}/\text{m}^3$ and $87 \mu\text{g}/\text{m}^3$ on the 28/3. One possible reason could be a difference a difference in particle loading of the raw gas between the two locations.

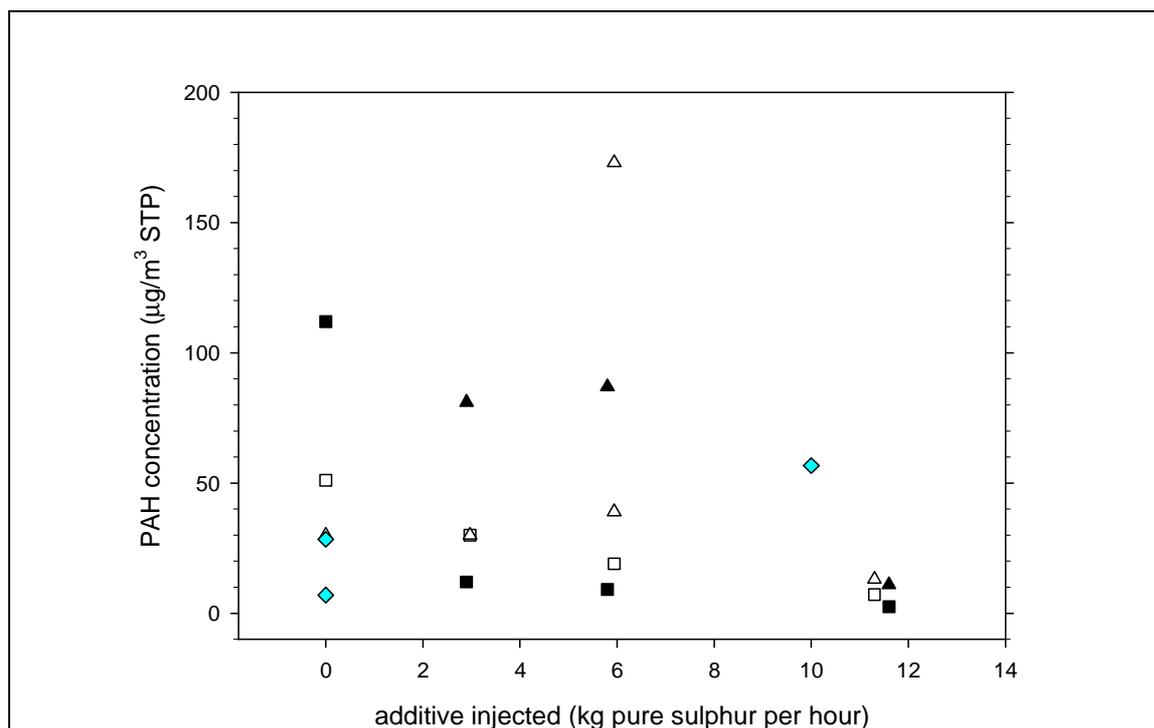


Figure 8. The PAH concentration in the gas samples as a function of sulphur dose, wet gas and actual oxygen concentration. Empty symbols, ammonium sulphate main series: □, sampling port B, △, sampling port A. Filled symbols, elemental sulphur: ■, sampling port B, ▲, sampling port A and ◆, previous investigation with elemental sulphur [12], sampling port B. The two values at unusually low load and without sulphur additive (7710 and 4303 µg/m³) are omitted.

Plots of PAH concentration in the gas samples against carbon monoxide concentrations do not reveal any clear trend. The expected general trend of increasing PAH with increasing carbon monoxide is blurred by the variation in the set of data. The plot of PAH against TOC is slightly better, but still unusable for correlations.

As can be seen in Table 18 and Table 19 of Appendix B.4, the dominating PAH species is naphthalene, with a share between 74 % and 92 % of the EPA 16 sum. The species with the next highest shares are phenanthrene (ca 3 % to 13 %), fluoranthene and acenaphthylene. A similar pattern was observed in the previous investigation [12]. Shares for the different PAH's that can be computed from the REMPI MS measurement results are similar, although the share of naphthalene is a little lower as the MS allows measuring other aromatic compounds that are not included in the EPA 16.

The effect of sulphur on PCDD/F formation is not quite clear. A plot of I-TEQ values against dose of additive did not show any recognizable trend. Therefore, the total PCDD/F concentration was plotted in Figure 9. The gas sample taken on the second reference day (26/3) is not included: its I-TEQ value is quite high compared to I-TEQ values for other samples, but there are no data for mono- to trichlorinated PCDD/F for this sample.

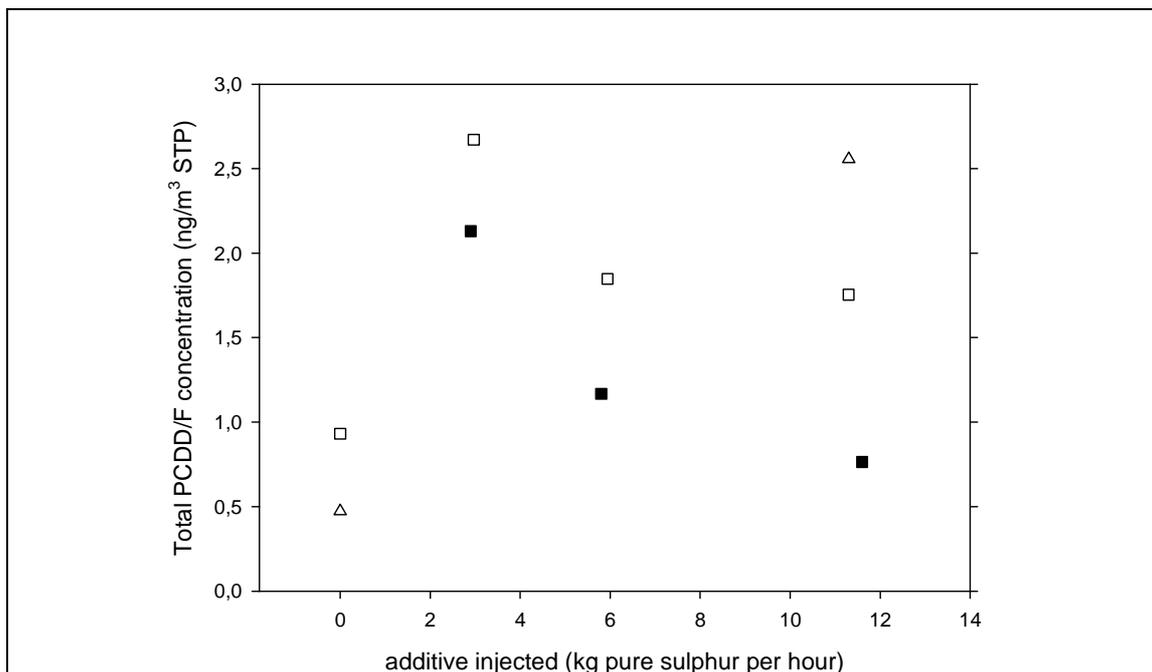


Figure 9. The dependence of total (Cl1-8) PCDD/F concentration in the raw gas on the dose of sulphur additives injected. Empty symbols, ammonium sulphate: □, port B and △, port A. Filled symbols, elemental sulphur: ■, all data from port B.

It seems that the total PCDD/F for the reference day (19/3) without any sulphur additive is lower than any sample for days with dosage of additive. The missing point from the 26/3 would probably have erased this impression if a total PCDD/F could have been calculated. An average chlorination may be computed: it is ca 2.3 in the ammonium sulphate series, and ca 2.2 in the elemental sulphur series. It is ca 2 (average of two values) in the reference no-additive case.

The PCDD/F concentrations are very low, close to not being measurable, and far below the emission limit value for waste incinerators of 0.1 ng I-TEQ/m³. In order to obtain a reliable estimate of the effect of sulphur on PCDD/F concentrations in flue gases, many more samples must be taken over a long period to build up a statistical basis. This is beyond the scope of this investigation.

The dose of ammonium sulphate injected by Aurell et al in a fluidised bed furnace was 40 mg of pure sulphur per MJ fuel for a chlorine content of ca 0.05 % in the fuel [13]. This corresponds to ca 6 kg/h in the diagrams in this report, but here there is less than 0.01 % chlorine in the fuel. Double gas samples yielded 0.01 and 0.02 ng I-TEQ/Nm³ for reference conditions (no additive) and 0.02 and 0.03 ng I-TEQ/Nm³ when ammonium sulphate was injected [13].

Sulphur additives produce a significant reduction of PCDD/F emissions in laboratory set-ups, but it is well known that it is difficult to confirm this in full-scale furnaces where many other factors influence the processes. The inability to verify the effect in this project does not mean that there is no effect. Duo et al claim to have confirmed the effect for a bark boiler using waste tires as sulphur source [18].

The PCBz were also determined for the gas samples: the results are shown in Figure 10. Please note that the out-of-range value $42.7 \mu\text{g}/\text{m}^3$ on the 26/3, second reference day immediately after the low load period (disturbed conditions), is not included. The PCBz concentration decreases with increasing ammonium sulphate dose, but it is fairly constant and independent of elemental sulphur dose. In Aurell et al there is rather a small increase of PCBz with ammonium sulphate [13]. However, the operational conditions and the fuel (a mixture of paper, wood and plastics with higher chlorine content) are not fully equivalent.

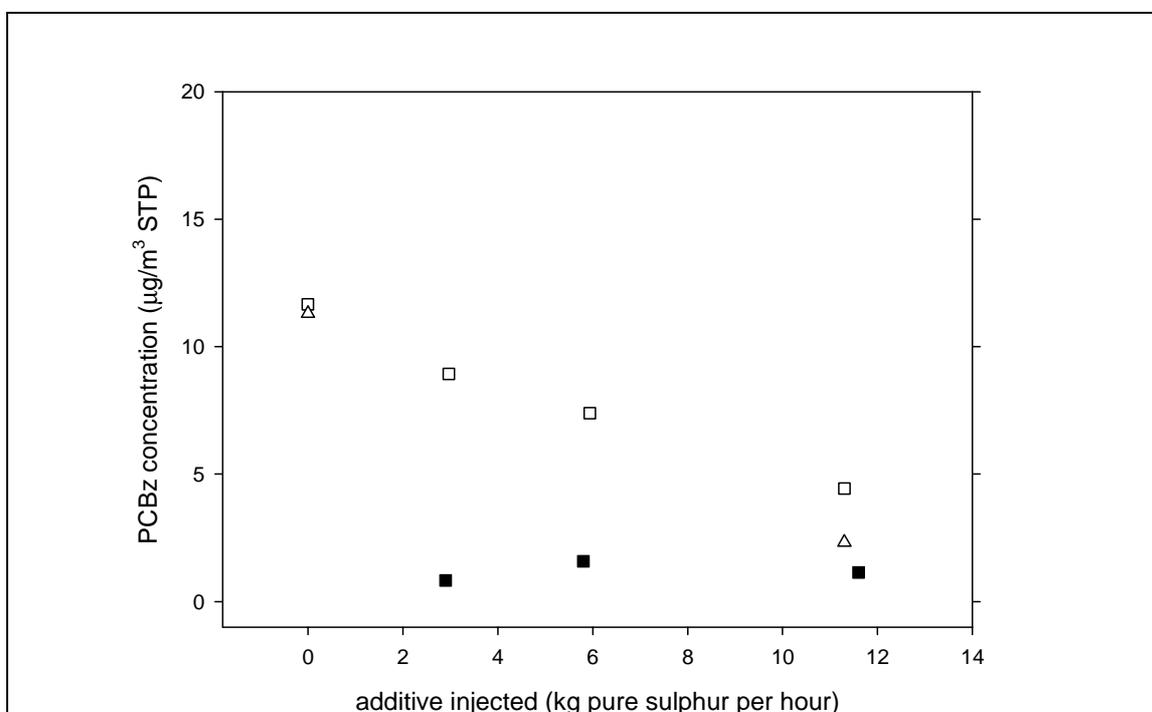


Figure 10. The dependence of the concentration of PCBz on the dose of sulphur additive. The out-of-scale value of $42.7 \mu\text{g}/\text{m}^3$ on 26/3 (very low load and no sulphur dosage) is omitted. Empty symbols, ammonium sulphate main series: □, gas samples taken at port B, △, gas samples taken at port A. Filled symbols, elemental sulphur: ■, all taken at port B.

5.3.3 NO_x and ammonia

The concentration of nitrogen oxides in the raw gas increases slightly with increasing sulphur dose, see Figure 11, as also was found by Lindau and Skog in test runs with SNCR disabled [7]. Kassman et al [10] as well as Lindau and Skog found a reduction with a functioning SNCR system. Aurell et al had an increase in NO_x during gas sampling periods and a decrease during longer periods without sampling [13].

There isn't any SNCR in this plant and it is difficult to find the correct conditions for injection in order to obtain a NO_x reduction [5]. Not only temperature is important but also residence time and composition of the flue gases. In this furnace, there are streaks of hot combustion gases rapidly leaving the furnace and cooler gases coming down the opposite furnace wall. Furthermore, conditions and flow in the furnace fluctuate over time.

The temperature in the furnace at the point of injection chosen was ca 850°C , at the lower end of the SNCR window.

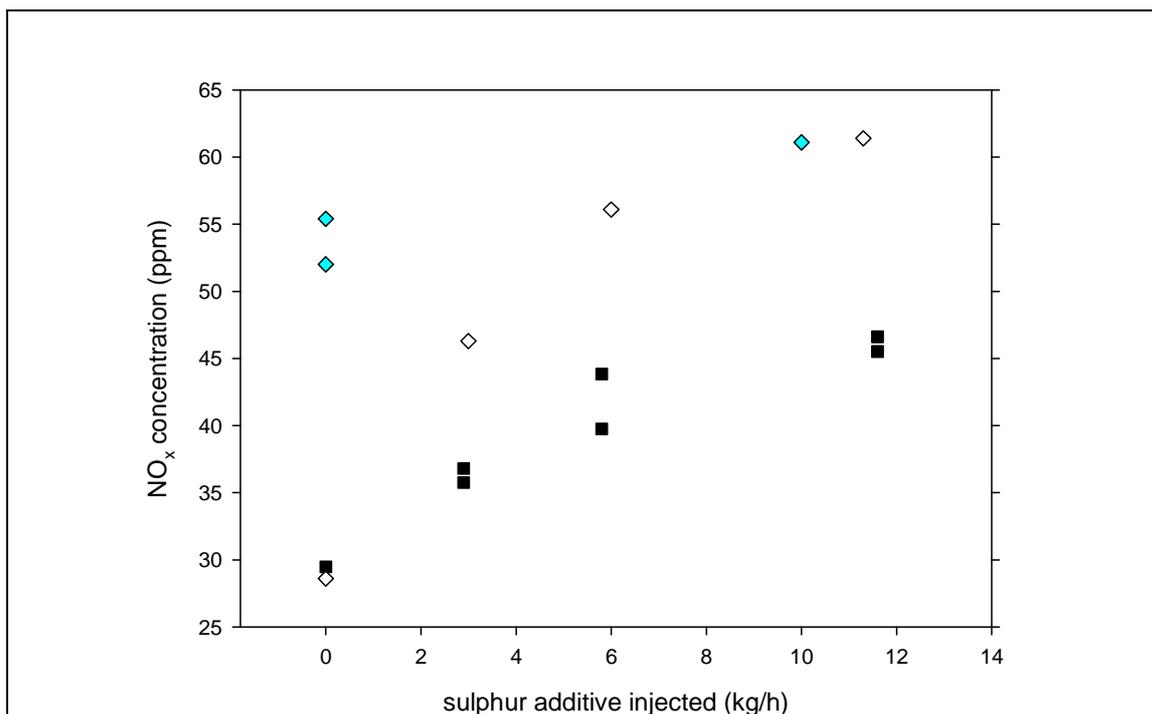


Figure 11. The effect of injection of sulphur additives on the concentration of nitrogen oxides (NO_x counted as NO_2) in the raw gas. Symbols: ■, elemental sulphur series of experiments, ◇, complementary series with ammonium sulphate and ♦, previous investigation with elemental sulphur [12].

It should be noted that there is a natural production of ammonia from a bed of wood fuels in any furnace, caused by the pyrolysis of the fuel. This yields a slip that is generally of the order of 20 to 30 ppm [5], 15 to 25 ppm here. Addition of sulphur, either as elemental sulphur or as ammonium sulphate lowers the ammonia concentration in the raw gas, Figure 12. According to Strömberg, sulphur dioxide is used to lower the ammonia slip from SNCR units [8].

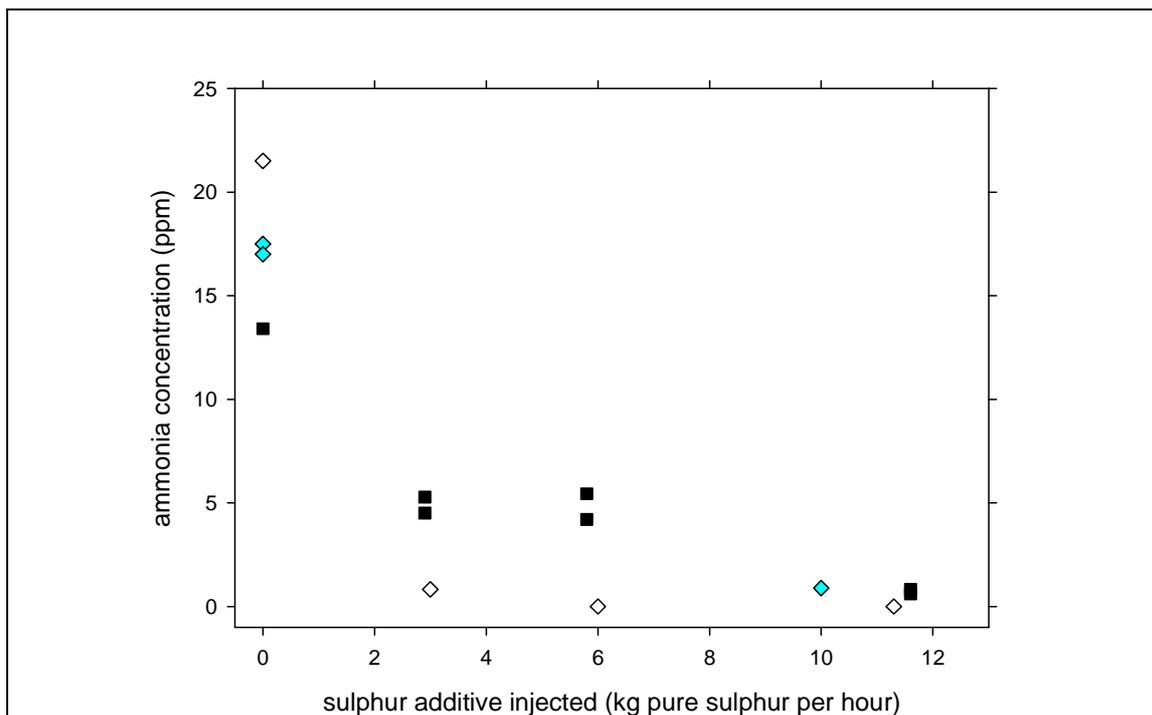


Figure 12. The effect of sulphur injection on the concentration of ammonia in the raw gas. Symbols, ■, elemental sulphur series of experiments, ◇, complementary ammonium sulphate series and ◆, previous investigation with elemental sulphur [12].

6 Time-resolved data

6.1 Fluctuations and peaks

As different instruments are used, with different time resolutions, sets of data are available with different time scales: 5 s (CO/CO₂ IR instrument for carbon monoxide and carbon dioxide, FID for TOC), 10 s (REMPI-MS for aromatic substances) or 1 min (FTIR for nitrogen oxides, ammonia, sulphur dioxide, hydrogen chloride, carbon monoxide, moisture, low-molecular organic substances such as methane). If the time interval is too long one might lose information on processes with a shorter characteristic time. One certainly does with data averaged over several hours if the system investigated is unstable and the relationship between parameters of interest is non-linear. The consequence could be that relationships between variables could no longer be identified.

To check if the difference in time resolution is important at this scale, the carbon monoxide data from two instruments with different sampling intervals are compared in Figure 13.

The general pattern of the carbon monoxide concentration as a function of time is that of small and large peaks. One expects to see a baseline, but it is not easy to separate it from the peaks as these occur frequently. Sampling or averaging over one minute instead of five seconds does not blur the pattern. All larger peaks are found in both curves, and the higher resolution in the five seconds series shows finer detail in the peaks rather than hint at a radically different pattern.

The absolute values of the peaks are, of course, lower in the 1 minute data (FTIR) than in the 5 seconds data because of the averaging implied in a longer measurement interval. Averages of carbon monoxide concentration for the nine hours in the diagrams computed from the 5 seconds series of data and from the 1 minute series of data are practically the same.

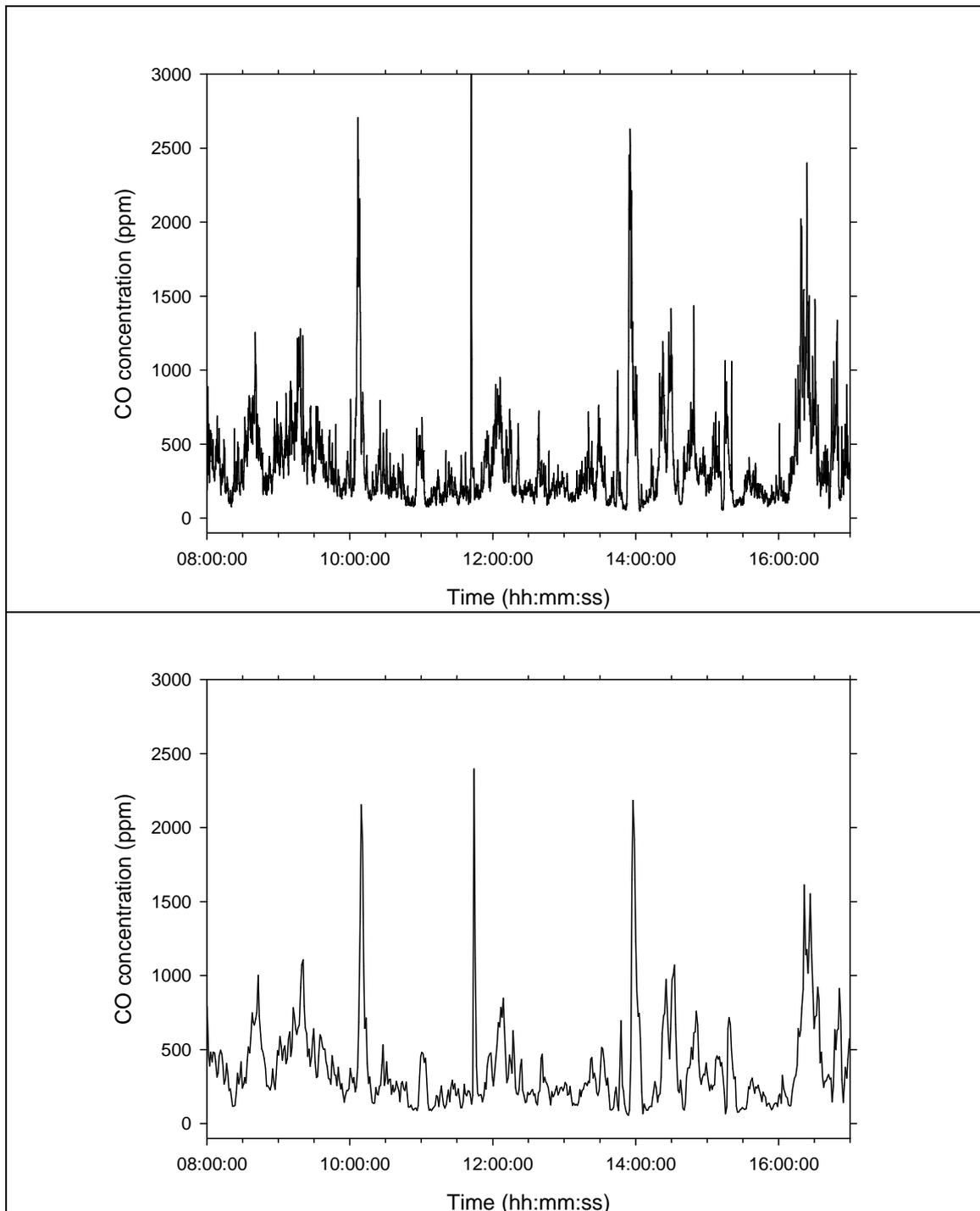


Figure 13. A comparison between the carbon monoxide concentration determined with the CO/CO₂ IR instrument (five seconds intervals, upper diagram) and that determined with the FTIR instrument (one minute intervals, lower diagram) for the 27/3, a dosage of 2.9 kg/h elemental sulphur

The effect of a sulphur additive on the concentration of carbon monoxide and of methane (FTIR data) during a working day is illustrated in Figure 14 and Figure 15 for the elemental sulphur series. As combustion conditions during the first day or reference day of that week (26/3) were influenced by the fuel shortage, results for the previous day with full load (25/3) are shown instead.

When the sulphur concentration is increased, the level of the concentration of carbon monoxide and methane becomes lower. The more sulphur is injected, the lower the concentration level becomes. The peaks become lower but they do not disappear altogether.

The carbon monoxide concentration and the methane concentration peak simultaneously in all the diagrams. Similar diagrams for carbon monoxide (CO/CO₂ IR) and TOC (FID instrument) show that also carbon monoxide and TOC peaks coincide in time.

Diagrams of carbon monoxide (CO/CO₂ IR) and TOC (FID instrument) for the main ammonium sulphate series⁸ show the same pattern as those found for the elemental sulphur series.

A peak in carbon monoxide is almost invariably accompanied by a peak in methane (FTIR data at 1 min intervals) and a peak in TOC (FID at 5 seconds interval). The large peaks are distinct in both carbon monoxide and methane/TOC, but small carbon monoxide peaks from a low concentration level may not always give a peak in methane rising above the noise on the low methane concentration level. Even if one blows up the diagram in the lower half of Figure 15 for the day with maximum dosage of elemental sulphur to a scale showing all the details in peaks, the small accompanying peaks cannot be distinguished.

⁸ FTIR data are not available for the main ammonium sulphate series.

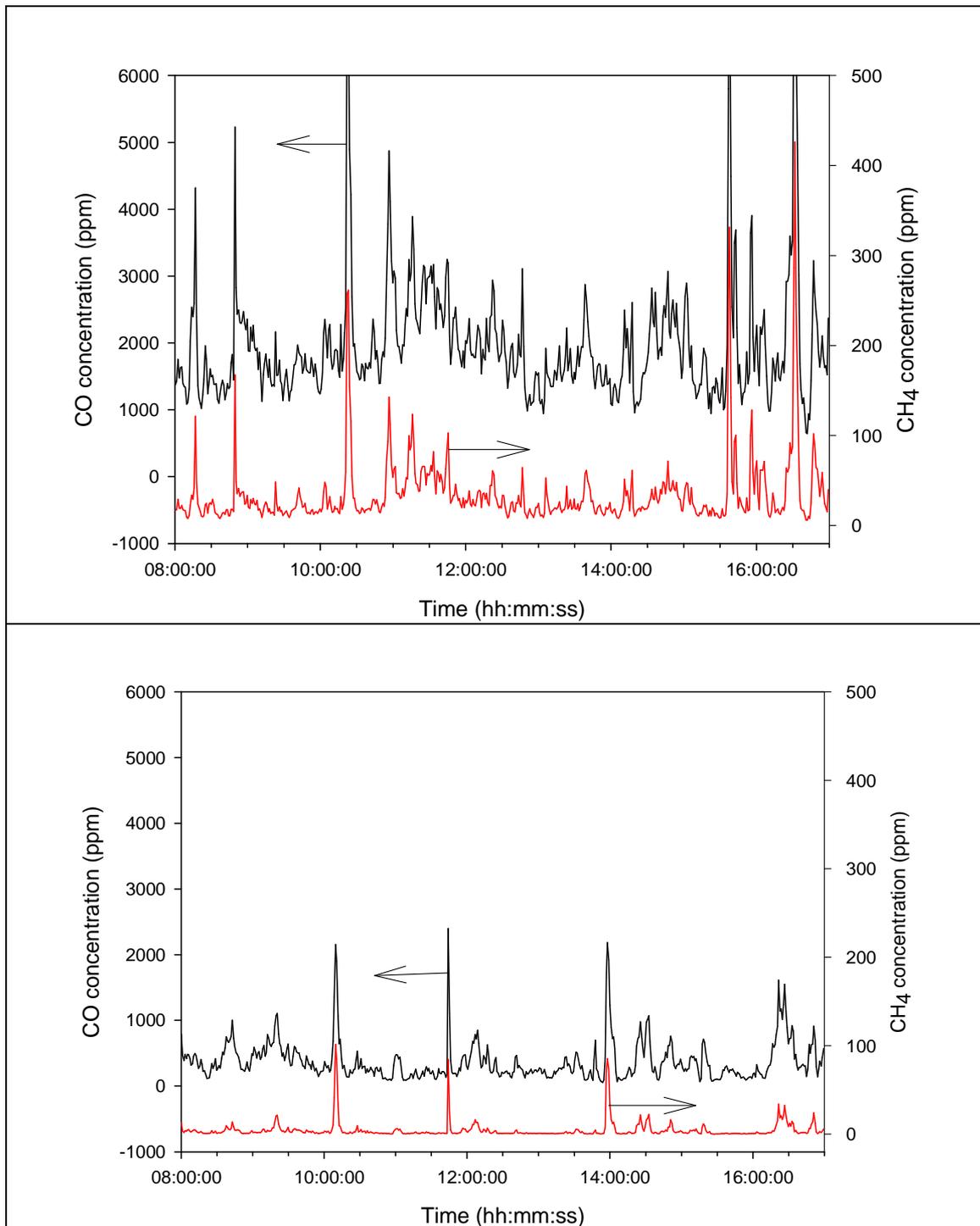


Figure 14. Carbon monoxide and methane concentrations determined using the FTIR instrument during a day without any injection of sulphur additive (upper diagram, 25/3) and the day with a dosage of 2.9 kg/h elemental sulphur (lower diagram, 27/3). Upper black line in diagrams, carbon monoxide and lower red line, methane.

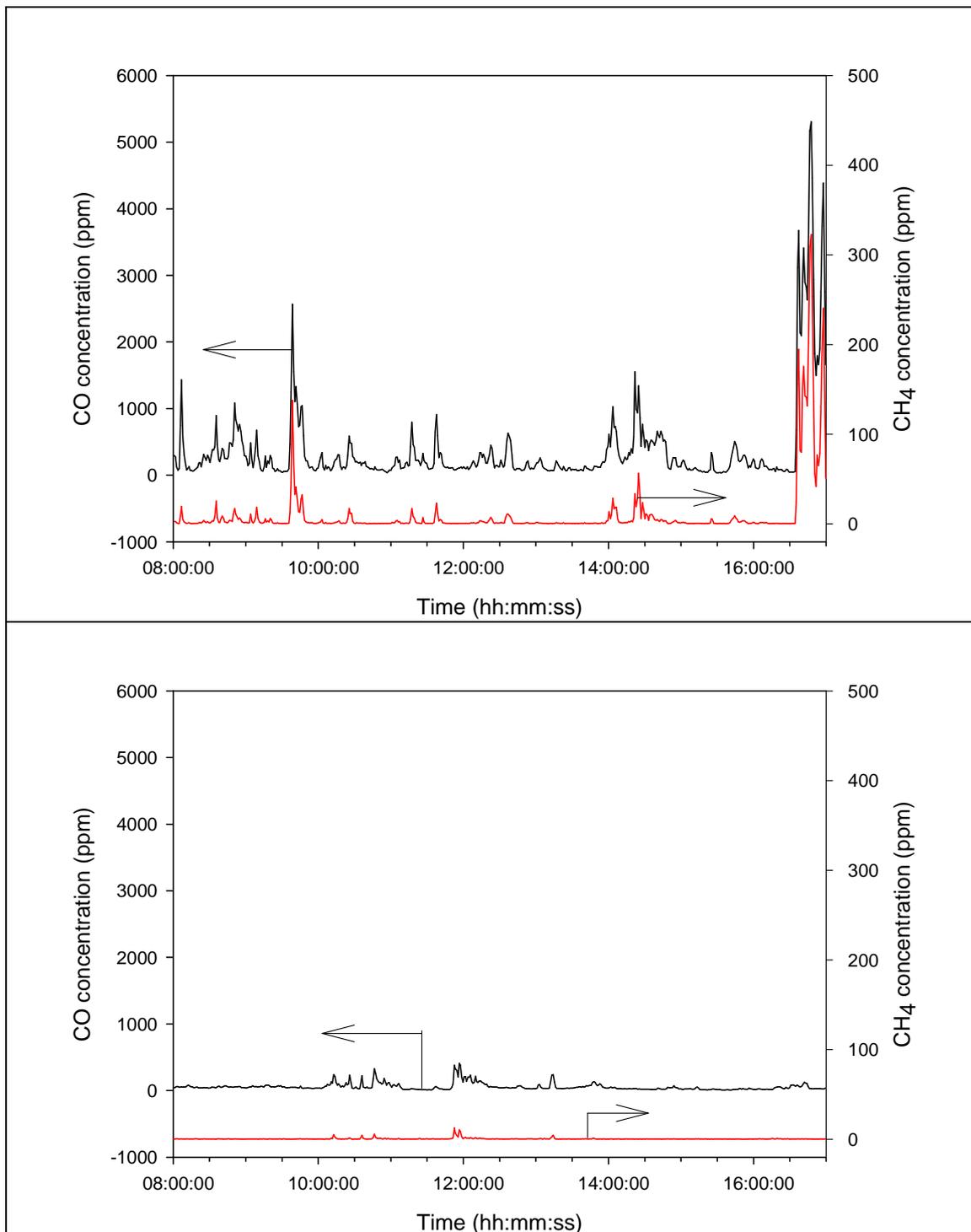


Figure 15. Carbon monoxide and methane concentrations determined using the FTIR during the day with a dosage of 5.8 kg/h elemental sulphur (upper diagram, 28/3) and the day with a dosage of 11.6 kg/h elemental sulphur (lower diagram, 29/3). Upper black line in diagrams, carbon monoxide and lower red line, methane.

The sulphur dioxide concentration in the raw gas also fluctuates and peaks simultaneously with carbon monoxide concentration for the reference case in Figure 16, i.e. no sulphur dosage. The origin of this sulphur dioxide is the sulphur in the fuel.

The relationship is more complex on the days with the highest dosages of sulphur, Figure 17. In the case of elemental sulphur the sulphur dioxide fluctuates widely, which may be caused by the uneven blending of sulphur with fuel in the chute. As ammonium sulphate solution is pumped into the furnace, there are fewer causes for rapid changes in sulphur dioxide and the fluctuations are smaller. However, the average of sulphur dioxide concentration during the period is the same for both cases as is shown in the lower diagram in Figure 4.

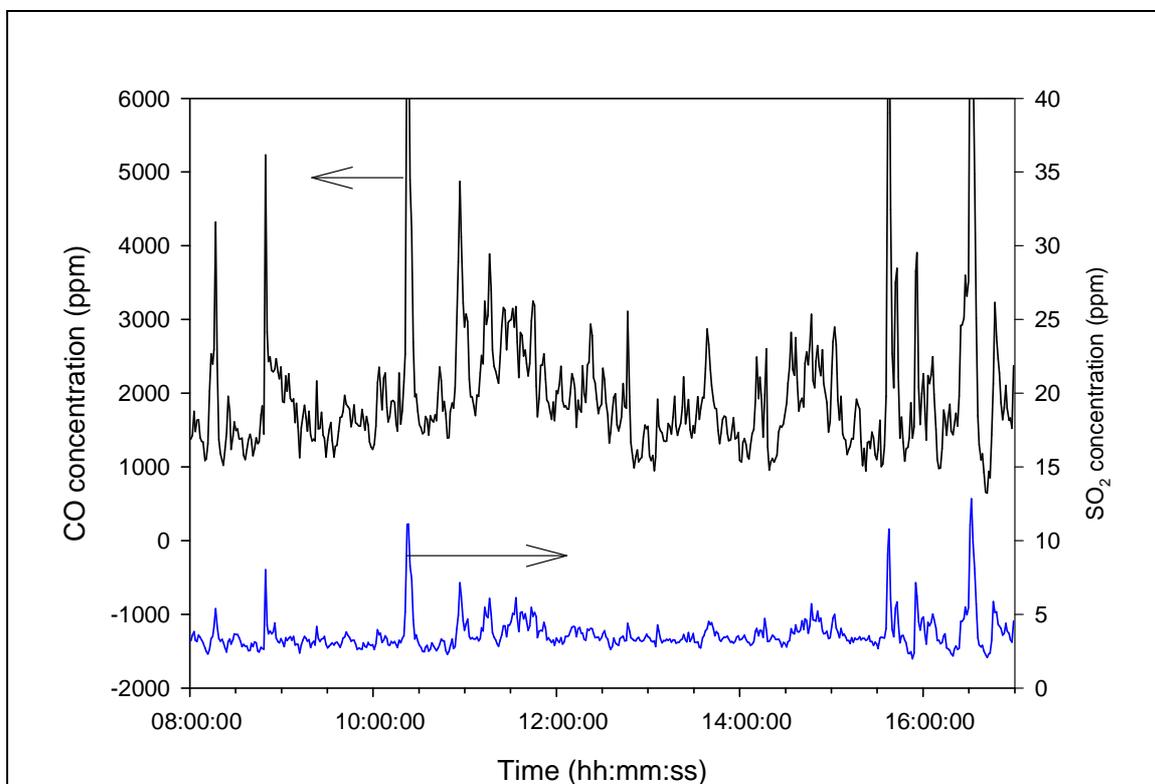


Figure 16. Concentration of carbon monoxide (upper black line) and sulphur dioxide (lower blue line) in the raw gas during a day without any sulphur dosage (25/3).

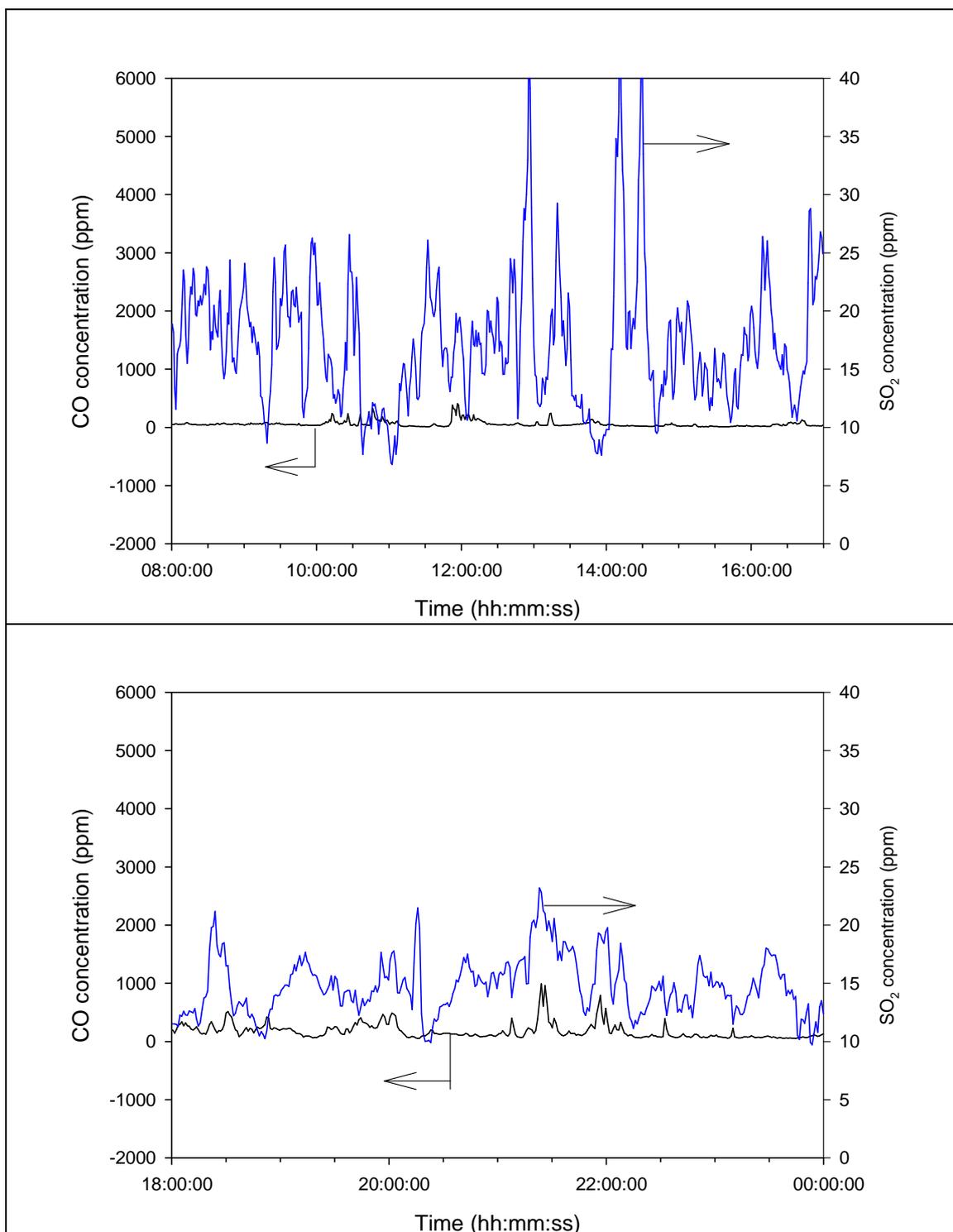


Figure 17. Concentration of carbon monoxide (lower black line) and sulphur dioxide (upper blue line) in the raw gas during periods with maximum sulphur dosage. Both concentrations are determined using the FTIR instrument with 1 minute resolution. Upper diagram: 11.6 kg/h of elemental sulphur (29/3). Lower diagram: 95 l/h or 11.3 kg/h, of ammonium sulphate solution (24/4)

6.2 Data from the REMPI-TOF MS

A number of aromatic compounds could be identified in the spectra delivered by the REMPI mass spectrometer, some of them being the PAH targeted in this investigation. Figure 18 shows an average mass spectrum for the first reference day, before any additive was injected. The substances identified range from monocyclic aromatics to aromatics with four rings:

- Monocyclic aromatics such as benzene (m/z ratio of 78), toluene and phenol,
- Aromatics with two rings such as indane, naphthalene, methylnaphthalene and compounds derived from the decomposition of lignin, such as vanillic acid
- Three-ring systems such as phenanthrene and alkylated homologues
- Four-ring systems such as pyrene and chrysene
- Retene at $m/z = 234$, a characteristic compound from combustion of wood, e.g. in forest fires

All PAH show the same behaviour with time, i.e. they peak simultaneously, see Figure 19. Therefore, naphthalene only will be used from Figure 20 to illustrate the variation of PAH concentrations with time.

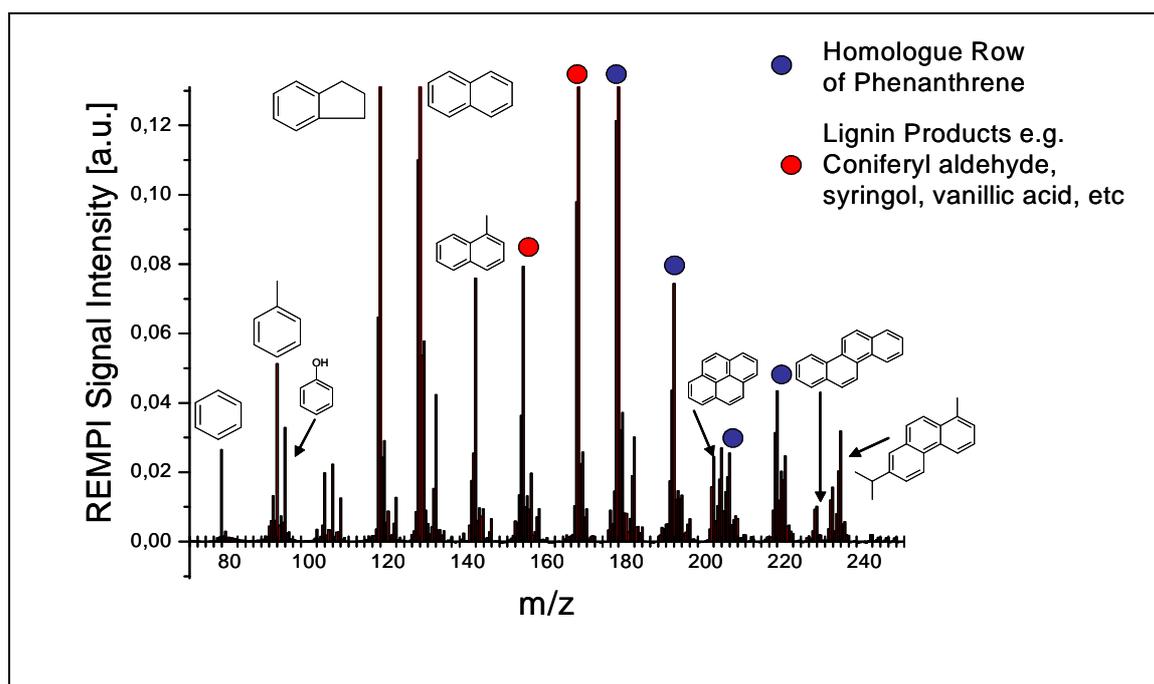


Figure 18. Averaged mass spectrum recorded by the REMPI-TOF MS on the reference day (19/3) without any dosage of sulphur additive. The peaks at $m/z=118$ (indane), 128 (naphthalene) and 178 (phenanthrene) have been cut down so that smaller peaks for other substances may be seen.

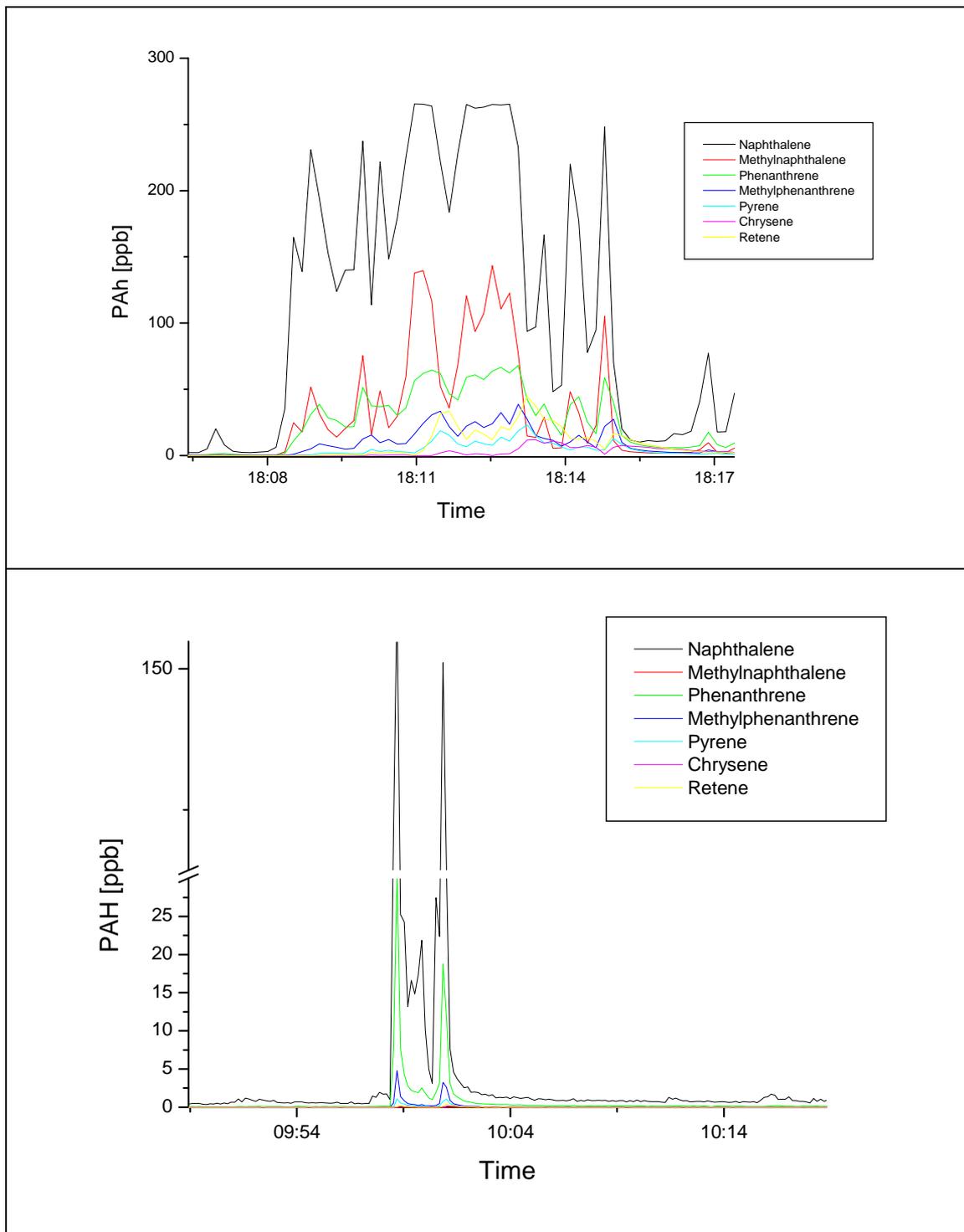


Figure 19. The time dependence of the PAH's that could be detected using the REMPI MS for two peaks in carbon monoxide. Upper diagram, the packet of peaks between 18:08 and 18:15 on the reference day (19/3) without any additive. Lower diagram, the double carbon monoxide peak at ca 09:30 on 22/3 (dosage of 25 l/h ammonium sulphate solution). Please note that anthracene is included in phenanthrene and fluoranthene is included in pyrene.

A further reason for choosing naphthalene is that it makes up at least ca 75 % of the total of the PAH's that could be determined using the REMPI MS. The alkylated PAH methyl-naphthalene and methylphenanthrene as well as retene are not included in the EPA 16 reported in Appendix B.4. Please observe that phenanthrene in the diagrams includes anthracene and pyrene includes fluoranthene.

It has been shown in section 6.1 that carbon monoxide and other organics (methane or TOC) vary in concert. When there is a carbon monoxide peak, there is also a peak in the others. Naphthalene (and other PAH) also peak simultaneously; see Figure 20 for FTIR data (1 minute interval) and Figure 21 for data from the CO/CO₂ IR and the FID for the TOC (5 seconds interval). When there is a large peak in carbon monoxide, there is also one in methane and one in naphthalene. However, not all the peaks in carbon monoxide are accompanied by a peak in naphthalene. One reason is that there seems to be a threshold, slightly above 1000 ppm for carbon monoxide or ca 20 ppm for methane for single peaks in naphthalene in Figure 20. The same behaviour is found for other days, and the same values are found when elemental sulphur is injected. It is more difficult to compute values of thresholds for data series at 5 s intervals.

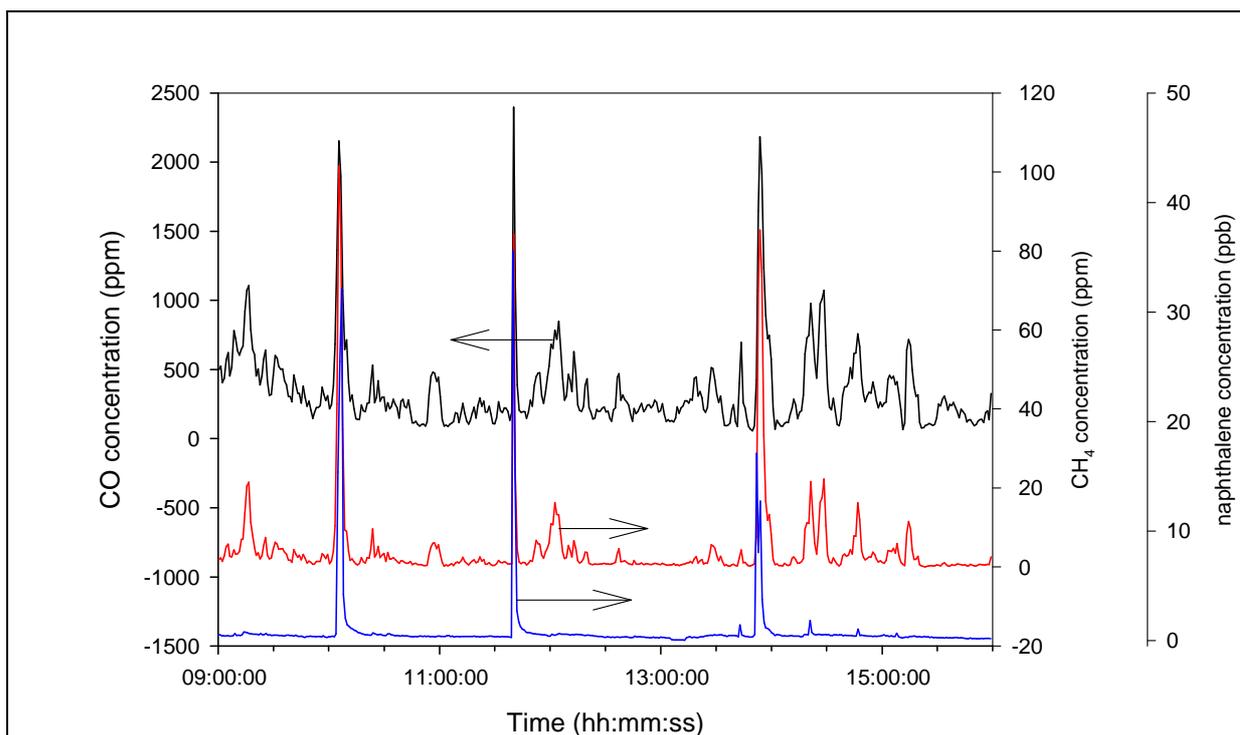


Figure 20. The concentration of carbon monoxide (upper black line), methane (middlemost red line), both from the FTIR measurements at 1 min intervals and naphthalene (lower blue line) from the REMPI MS on 27/3, dosage of 2.9 kg/h elemental sulphur.

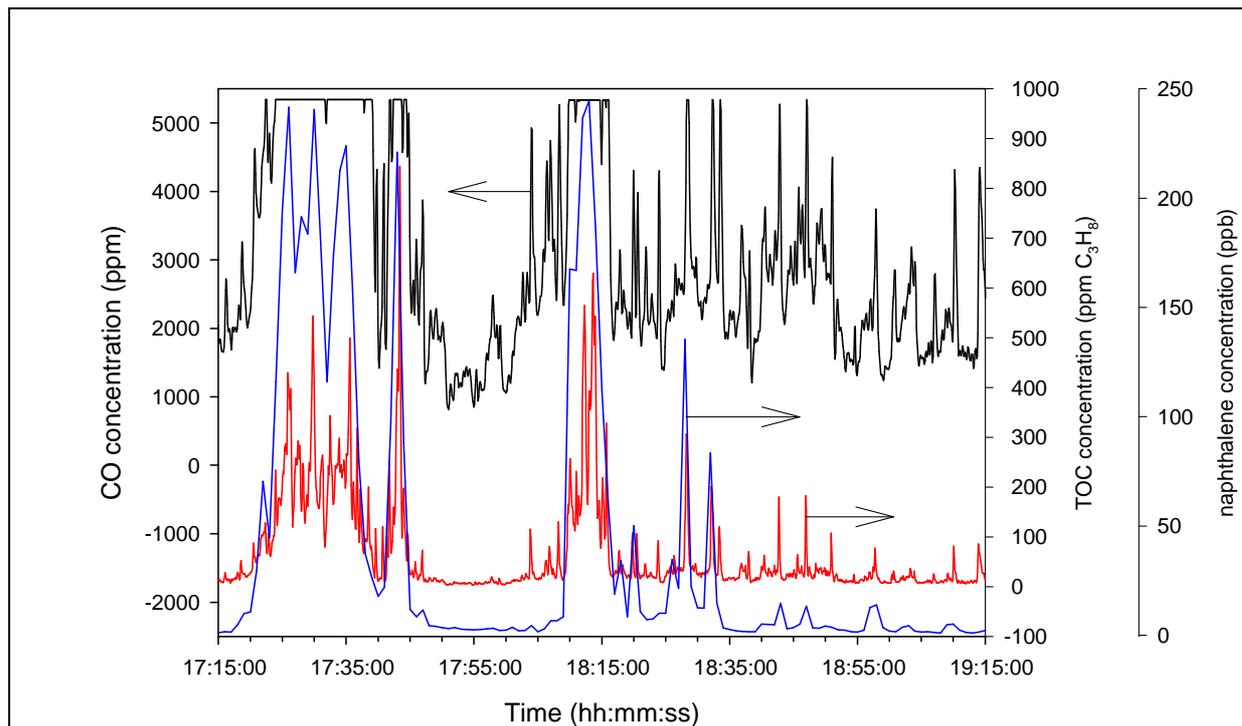


Figure 21. The concentration of carbon monoxide from the CO/CO₂ IR instrument (top black line), TOC from the FID (middlemost red line), both at 5 s intervals and naphthalene (lowest, blue line) from the REMPI MS at 1 minute intervals on the reference day 19/3, without any additive.

Methylated PAH in significant concentrations are found only on the days without any sulphur additive. As soon as sulphur in any form is injected, their concentrations decrease to close to the detection limit. However, the methylated PAH also peak at the same time as carbon monoxide during severe disturbances on these days. Their concentration is 20 to 25 % only of the concentration of their unmethylated parent compound, see lower diagram in Figure 19, which is a much lower ratio than on days without any additive.

Additional PAH's other than the EPA 16 could be monitored: their trends are the generally the same as these. Possible decomposition products of lignin are e.g. vanillic acid (coniferyl aldehyde) with m/z ratio of 168. In Figure 22 it is shown together with indane, another PAH. The peak shortly before 18:14 is the same as that in the upper diagram in Figure 19 and in Figure 21. The signal intensities have not been converted to concentrations.

On the days when elemental sulphur was injected a unique behaviour was observed for the peak with m/z ratio of 134. This is illustrated in Figure 23: this substance does not follow the same trend as other PAH's. When the phenanthrene signal is low, close to baseline, the signal for this substance may be significant. The signal for this substance does not always peak at the same time as that of phenanthrene or other PAH's. The peaks in phenanthrene coincide with peaks in carbon monoxide and in sulphur dioxide.

This substance with m/z 134 is not seen on the days when ammonium sulphate was injected.

This substance could be:

- A C_4 -derivative of benzene, but then it should follow the same trend as benzene and PAH's and furthermore, xylene and mesitylene should be seen in larger concentrations
- Benzodioxin, but then it should follow the same pattern as the other aromatics
- Benzothiophene, which identification is tentatively given in Figure 23

Thiophene is an aromatic heterocycle, the sulphur analogue of furan.

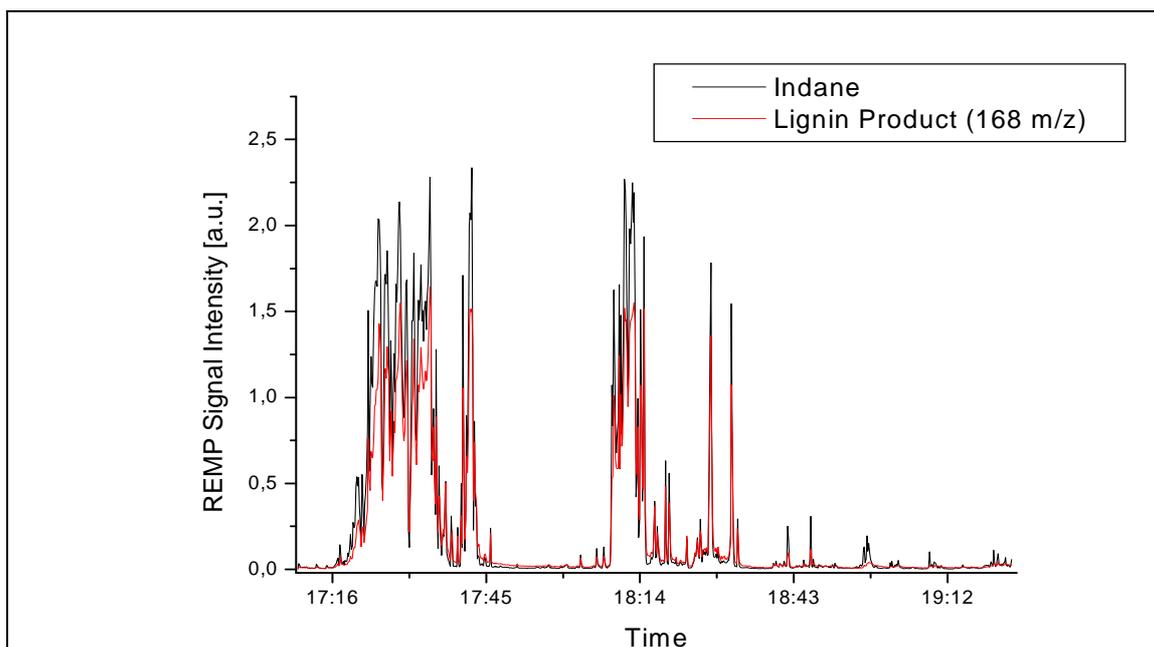


Figure 22. The REMPI mass spectrometer signals for indane and vanillic acid for a period on the reference day (19/3), no additives injected – signals for both substances peak simultaneously with the naphthalene signal

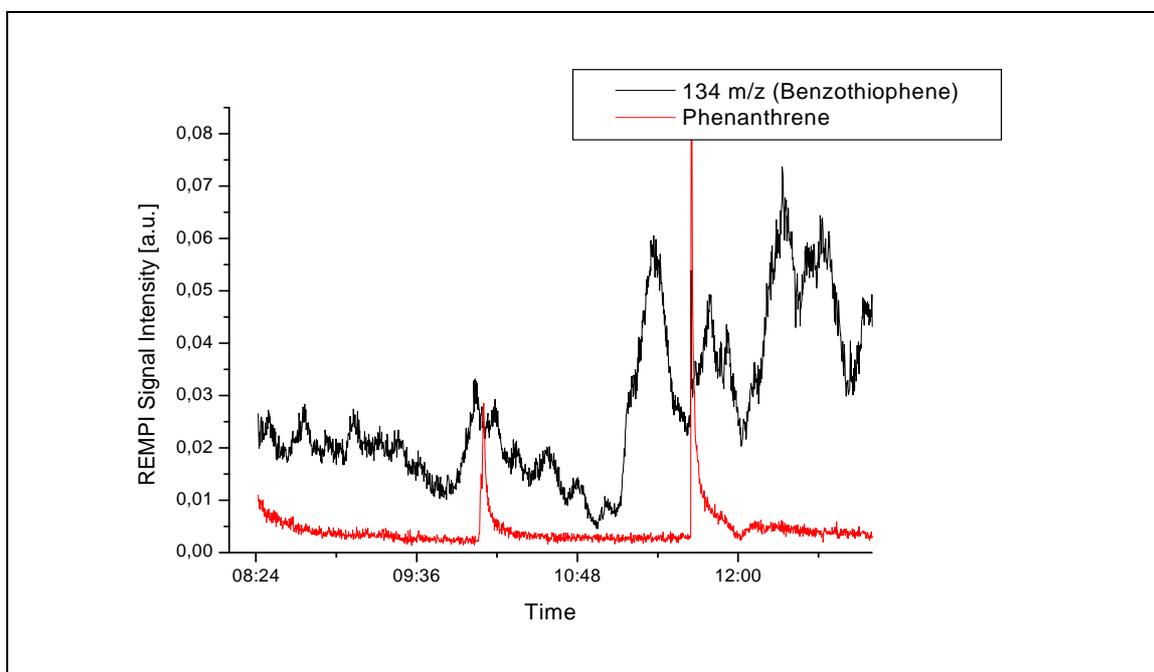


Figure 23. The signal intensity of the substance with m/z ratio of 134, tentatively benzo[*b*]thiophene, during a short period on the 27/3. The peaks in phenanthrene (red line) coincide with peaks in carbon monoxide and sulphur dioxide.

6.3 Analysis of time-resolved data

The correlation between carbon monoxide and all organic substances is obvious. The concentration of carbon monoxide, methane, TOC and aromatics such as the PAH's (e.g. the representative compound naphthalene) peak at the same time. Whenever combustion is incomplete, a burst of partially combusted gases containing the majority of the substances of interest here travels through the system.

As the simultaneous variation is so clear at the 5 seconds to 1 minute scale the concentration of carbon monoxide, of TOC and of naphthalene have been plotted against each other in Figure 24 and Figure 25 for the largest interval of values possible. The concentrations of carbon monoxide and TOC values are averages for 1 minute of the 5 seconds data.

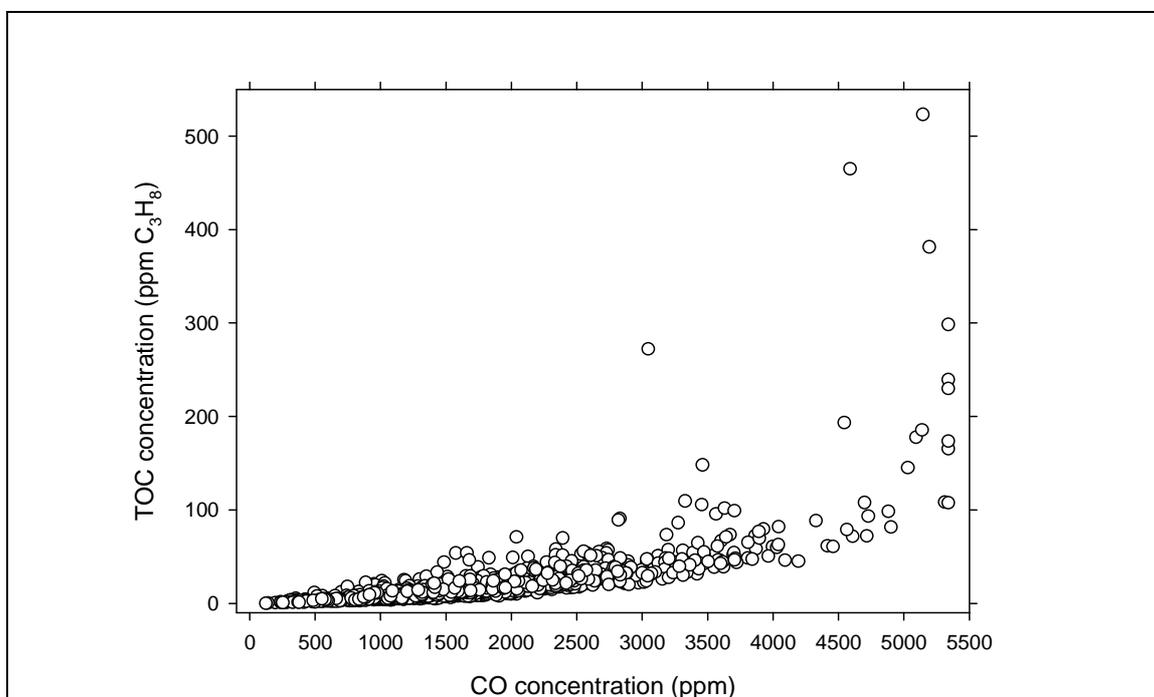


Figure 24. The TOC concentration, 1 minute averages, as a function of carbon monoxide concentration on the reference day (19/3) without any additive. The range of the CO/CO₂ IR instrument is 0 to 5000 ppm: carbon monoxide values close to 5000 ppm and beyond do not indicate the true concentration as they exceed the range of the instrument. TOC data are from the FID instrument.

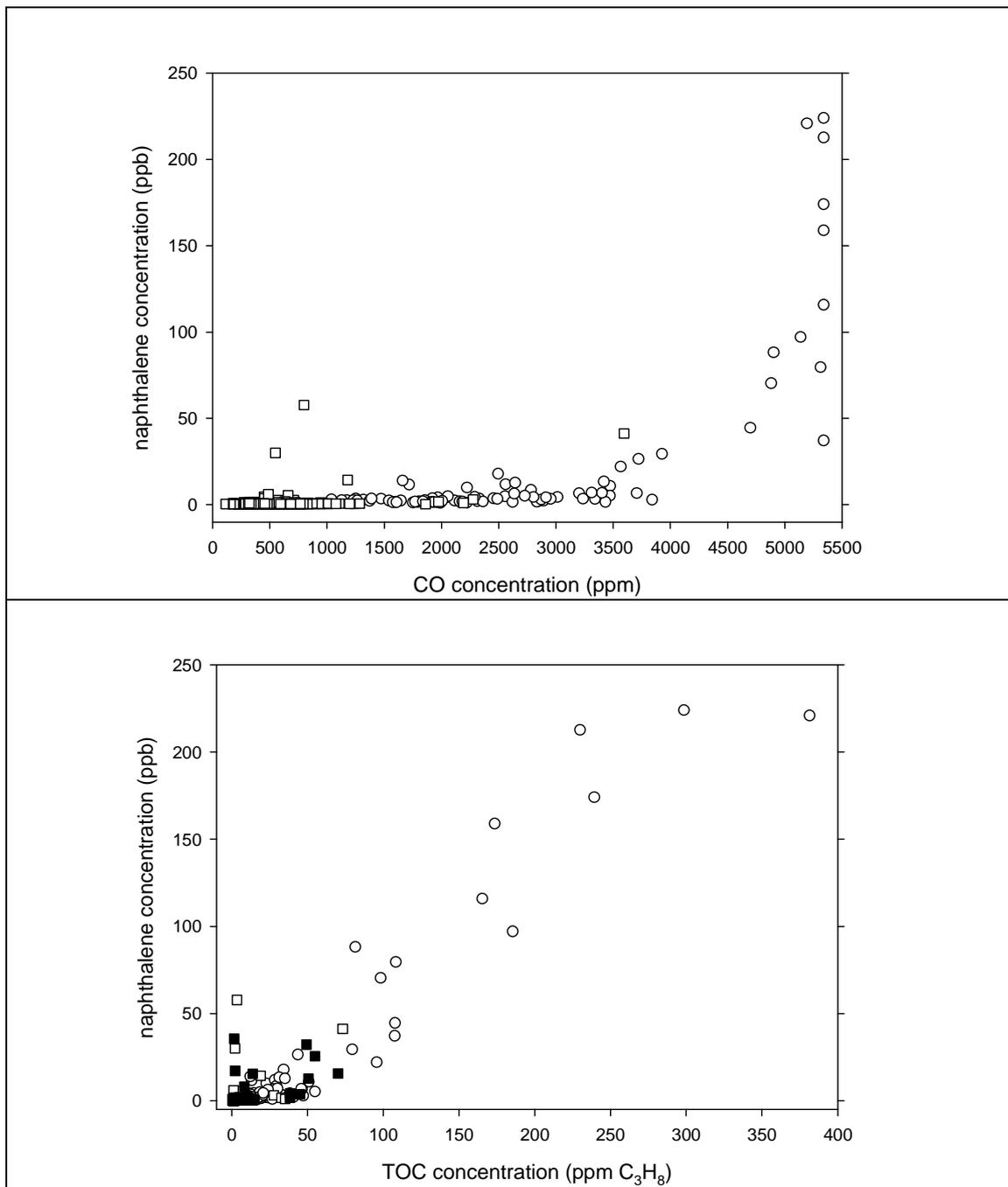


Figure 25. Cross-plots of naphthalene and carbon monoxide (upper diagram) and of naphthalene and TOC (lower diagram), 1 minute averages. Carbon monoxide data are from the CO/CO₂ IR instrument, the TOC from data from the FID and naphthalene from the REMPI MS. Symbols: o, night of the 19/3 to 20/3, no additive, □, medium dose of ammonium sulphate, ca 6 kg pure sulphur per hour, on 21/3 and (lower diagram only) ■, lowest dose of elemental sulphur, 2.9 kg/h

All plots with carbon monoxide concentrations are to some extent distorted at average concentrations of carbon monoxide close to or above 5000 ppm: the range of the CO/CO₂ IR instrument is 0 to 5000 ppm. This “hockey-stick” appearance of the curves for TOC or naphthalene concentrations as function of carbon monoxide concentration may not be the true one at these high carbon monoxide values. Data recorded at 1 minute intervals for carbon monoxide by the FTIR, which does not have that upper limit to its range, are not available for the first reference day, 19/3, so that a direct correction of the diagrams is not possible.

An upper limit for a correction may still be estimated indirectly using data for the fuel shortage period on the 26/3. That day too, the data for carbon monoxide exceed from time to time the range of the CO/CO₂ IR instrument. Peaks in carbon monoxide on 19/3 reaching the upper range of the instrument do so during shorter intervals of time than peaks on the 26/3, i.e. the true carbon monoxide peak values on 19/3 are probably lower than those on 26/3. Selecting those with corresponding TOC peak reaching 500 to 600 ppm on a 5 s basis in the series for both days, the carbon monoxide peak values for data at 1 minute intervals on 26/3 is between 8 000 and 11 000 ppm. The points in both figures here with carbon monoxide close to 5000 ppm and a TOC of ca 500 ppm would then be shifted to the right at most up to these values. The bend in the hockey stick shape is less sharp, but it is still there.

The TOC is more or less linearly dependent on carbon monoxide concentration at low concentrations in this time scale of 1 minute, as it is when an average is computed for several hours, see Figure 6. The correlation seems to curve upwards at high carbon monoxide concentrations, somewhere at ca 4000 ppm.

Plots of naphthalene as a function of carbon monoxide concentration show the same characteristic “hockey-stick” appearance as that in plots for averages over several hours, Figure 7. Although carbon monoxide values are not too reliable close to 5000 ppm, the threshold for significant emissions of naphthalene, and consequently of PAH's seem to be 3500 to 4000 ppm of carbon monoxide, as for TOC. Above this threshold, the naphthalene emissions increase rapidly with increasing carbon monoxide concentrations.

Plotting naphthalene concentration as a function of TOC concentration, lower diagram in Figure 25, yields a more or less straight line, i.e. a linear dependence of naphthalene on TOC. The TOC value corresponding to the break in the curve in Figure 24, TOC and carbon monoxide, is ca 50 ppm. There could also be a threshold TOC concentration of 25 to 50 ppm in the naphthalene and TOC curve, but it is less distinct than that in carbon monoxide.

Below the threshold, the naphthalene concentration is nearly independent on carbon monoxide (or on TOC), as is illustrated in Figure 26. It is almost constant at 0.5 ppb naphthalene. There is more deviation in the TOC plot than in the carbon monoxide plot.

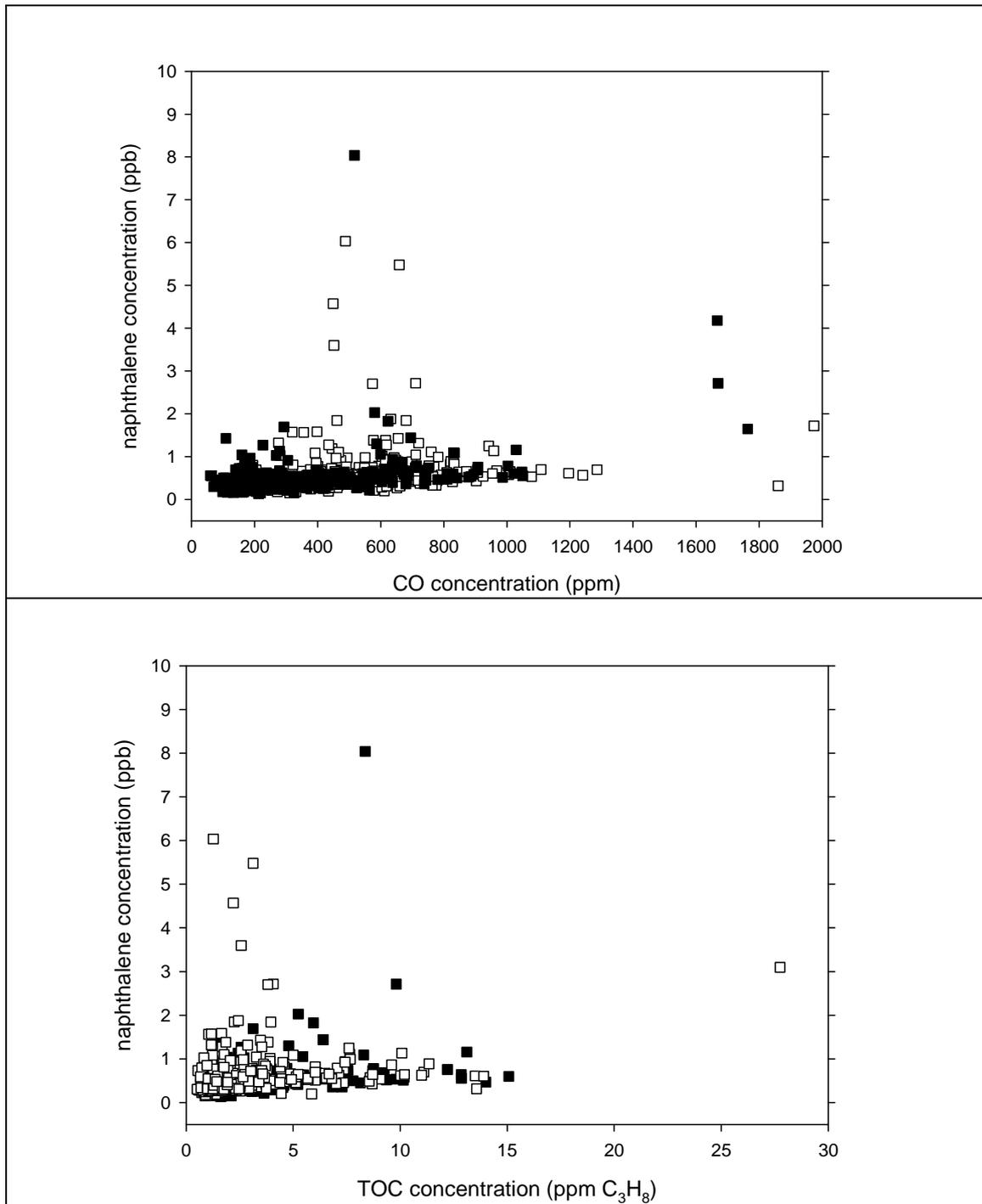


Figure 26. The dependence of naphthalene concentration on carbon monoxide concentration (upper diagram) and on TOC concentration (lower diagram) below the threshold values of carbon monoxide concentration in the raw gas. Symbols: □, 49.5 l/h ammonium sulphate solution (21/3) and ■, 2.9 kg/h elemental sulphur

Cross-plots using the data for TOC and carbon monoxide at 5 seconds intervals are not as easy to interpret as the plots with 1 minute averages. The deviation around a general trend is much larger, producing clouds of data rather than easily identifiable correlations. All one can say with certainty is that TOC concentration increases with increasing carbon monoxide concentrations in a general way.

This threshold value of 3500 to 4000 ppm carbon monoxide translates into a threshold value for data averaged over several hours of somewhere between 1000 ppm and 1500 ppm carbon monoxide, Figure 20.

The dominating influence of the peaks on the average values may be illustrated with the results for the second reference period on 26/3 (no additive). When the conditions had returned to normal after a longer period of low power and increased emissions, the REMPI-MS was put back on-line at 18:12. The first 15 minutes are shown in Figure 27. One observes the following:

- Although the means for carbon monoxide and TOC for this period on 26/3 and for the reference period on 19/3 are comparable, Table 3 and Table 4, the means for naphthalene differ. The value is 38.4 ppb on 19/3 and 7.4 on 26/3. The main difference between the two REMPI-MS monitoring periods on 19/3 and 26/3 is the number of peaks in carbon monoxide, and consequently in naphthalene. Many more are out of range (above ca 5 000 ppm) on 19/3 than on 26/3.
- The single large event on 26/3 after 18:12, Figure 27, is the peak with values out of range for carbon monoxide and ca 1000 ppb naphthalene. If one removes the first three minutes, i.e. the peak at ca 18:13, the mean of naphthalene drops from 7.4 ppb to 1.2 ppb. The median is unchanged: 0.5 ppb, which is almost the same as on days when sulphur additives are used and peaks are suppressed.

In summary, keeping a steady carbon monoxide concentration of 1000 ppm and having an average of 1000 ppm for a widely fluctuating carbon monoxide concentration may yield totally different PAH emissions. The largest part of the naphthalene emissions, taken as a representative substance for PAH in this investigation, as well as of emissions of other organic compounds is caused by peaks or bursts of partially combusted gases. These become large when the instantaneous or 1 minute average carbon monoxide concentration exceeds a threshold value.

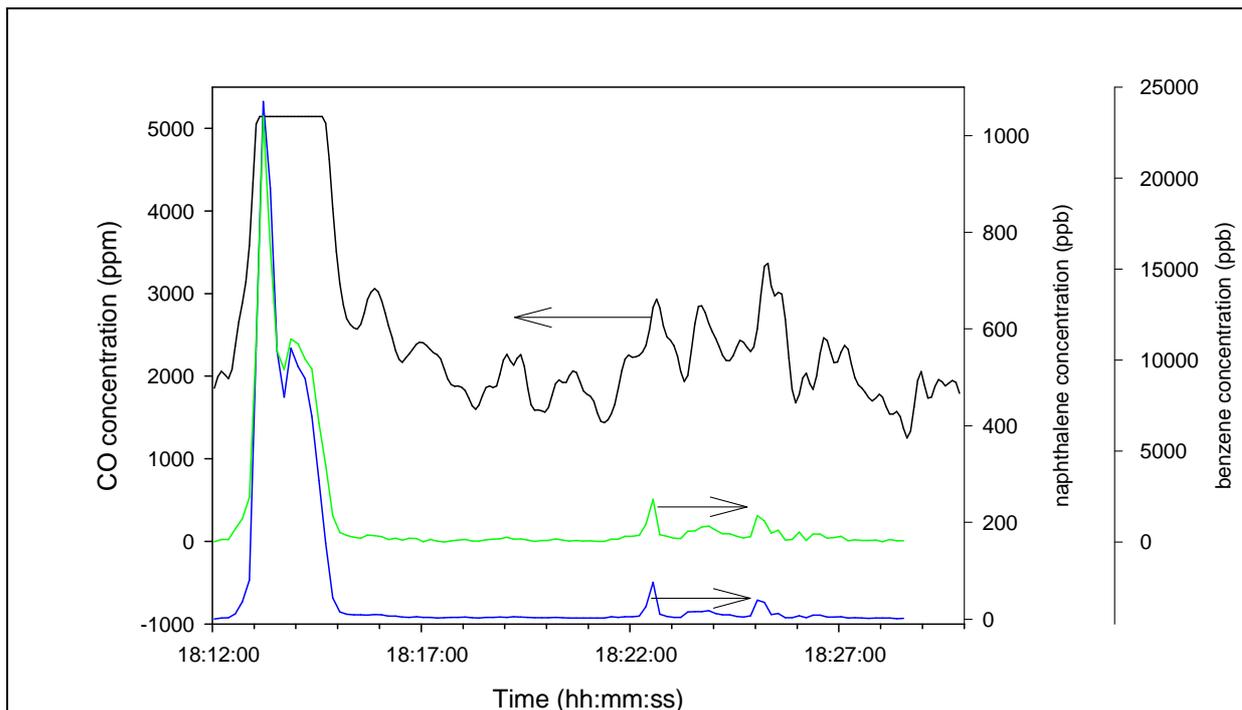


Figure 27. Concentrations of carbon monoxide (upper black line), naphthalene (lower blue line) and benzene (green line in between) vs time on 26/3 (no additive) between 18:12 and 18:30. Carbon monoxide is measured using the FTIR and the aromatic compounds were determined using the REMPI-MS.

7 Further discussions

7.1 Sulphur and chlorine

Analyses of the fuel, bark, gave a value below level of quantification for chlorine (0.01 % D.S.) for most samples and a value of ca 0.04 % D.S. for sulphur. The molar ratio of sulphur to chlorine in the bark fuel is then at least 4.4:1 in the reference conditions, no sulphur additives. With sulphur additives the molar ratio becomes larger, at least 8.5:1 for 3 kg/g additive sulphur, at least 12:1 for 5.8 kg/h additive sulphur and at least 15.6:1 for the maximum dose of additives. These are very large ratios in comparison with those, 0.5:1 or 1:1, in Aurell et al [13].

Computing a chlorine balance is difficult, because the input as fuel is unknown. There is practically no impact of the sulphur additives on the chlorine content of ashes and the figures for the hydrogen chloride content of the flue gases reflect more a natural variation between days and within days than an impact of a dosage. The sulphur content of the fuel here is probably already enough to effect the changes in ash composition and flue gas that one uses additives to obtain in combustion units with comparatively larger chlorine content in the fuel. The plant where the full-scale experiments in this investigation have been performed has not experienced corrosion problems in the superheaters due to deposits of chlorides.

At 35 MW_{th} fuel is fed to the grate at the rate of ca 8 t/h D.S. The input of sulphur is then ca 3.3 kg/h and the input of ash is ca 265 kg/h. Using figures on the relative quantities of ESP ash and bottom ash obtained for this plant in another context [19] the flow of ESP ash may be estimated to 39 kg/h. Taking into account the total carbon content in the analyses, which carbon mainly is charred fuel, the flow of bottom ash is estimated to 585 kg/h.

In the reference case, no additives, the input of sulphur is ca 3.3 kg/h and sulphur taken out of the system with the ashes is ca 0.9 kg/h. The main part of the sulphur input is in the flue gases. Results for low and high doses of additive are given in Table 10.

Table 10. Sulphur balance (kg/h) in the experiments computed for 35 MW

Additive	None	Ammonium sulphate		Elemental sulphur	
		25 l/h	95 l/h	2.9 kg/h	11.6 kg/h
Input (fuel + additive)	3.30	6.30	14.3	6.2	15.0
Output as fly ash	0.57	1.27	2.06	0.82	2.50
Output as bottom ash	0.35	0.35	0.35	0.35	0.48
Total output as ash	0.92	1.52	2.41	1.17	3.08
Output with flue gas	2.38	4.78	11.9	5.0	11.9
SO₂ in flue gas	3.2 ppm	1.8 ppm	15.8 ppm	2.6 ppm	17.4 ppm

If these computations are correct, the ratio between sulphur content in the flue gases at the highest dose and that without additive should be ca 5. This agrees approximately for the elemental sulphur series, the concentrations of sulphur dioxide being 17.4 ppm and ca 3 ppm respectively. Although the sulphur dioxide concentration in the flue gases at the highest dose is 15.8 ppm⁹, the agreement is less good in the case of the complementary ammonium sulphate series in April. The cause is probably statistical variations that raised the sulphur dioxide content in reference conditions, no additive, to 5 ppm in the complementary ammonium sulphate series. The extent of variation may also be seen in the sulphur dioxide figures for the low dose cases.

The sulphur in the additives injected is then to some extent found in the ashes, but the major part leaves the furnace with the flue gases. At low doses of additives, up to 5.8 kg S/h, the impact on the emissions of sulphur dioxides is low.

7.2 Overview of results

Results analysed in two sections are reviewed in this section once again in order to extract further conclusions.

When concentrations were averaged over several hours as well as when their patterns were examined in a time scale of 1 minute or less, the relationship between organic substances (TOC and methane) and carbon monoxide was quite clear. When combustion is incomplete all emissions become higher. The dominating contribution to the averages is in the peaks or puffs of incompletely combusted gases.

Sulphur additives act on the combustion process. The reduction of TOC, which consists mainly of volatile species, is from ca 24 ppm without additives to ca 1 ppm at the highest doses in the present investigation. The volatile part of the naphthalene content in the flue gases (that determined using the REMPI-TOF MS) decreases at the same time from tens or hundreds of ppb down to ca 0.5 ppb.

Data for the gaseous PAH's from the mass spectrometer show a threshold-like behaviour in the correlation: the concentration in the gas phase is very low and almost constant as long as the carbon monoxide concentration is below a threshold value, estimated to be ca 4000 ppm here on the time scale of 1 minute. When averaging over six hours, the threshold value is of the order of 1000 ppm.

The correlation is less clear when looking at results for gas samples, Figure 8. These include also the contribution from small particles that were filtered out before the mass spectrometer. The total content of naphthalene in the gas samples is also higher, ca 10 µg/m³ or more, than in the mass spectrometric data, typically ca 3 µg/m³, which value corresponds to an average of 0.5 ppb from the REMPI-MS data. A major part of the PAH's are then on particles. The difference between samples from port A and those

⁹ 22.4 ppm for the main ammonium sulphate series

from port B reflects probably differences in particle concentration in the raw gases at these locations. Emissions of PAH's will then depend on the efficiency with which particles are removed by the ESP and the flue gas condensing system.

The TOC of the ESP ashes increased with increasing doses of sulphur, which is consistent with a mechanism where sulphur is also hindering the combustion of char. In that case the decrease of PAH in gas samples with increasing additive sulphur doses would mean that the production of PAH from the char is reduced. The decrease of total PCDD/F in Figure 9 might be interpreted similarly.

7.3 Value of additives

The value of using sulphur additives to reduce corrosion and emissions of carbon monoxide, taken as a marker for organic substances, has been calculated by several authors [7], [10], [13]. Repeating these calculations is none too meaningful as conditions in different plants may be different. General remarks may be more appropriate.

The main reasons for injecting sulphur in the plants of Lindau and Skog and of Aurell et al would be to reduce the risk for corrosion. In Lindau and Skog [7] the carbon monoxide concentration was lowered from ca 200 ppm to 100 ppm at 5.2 % oxygen and the TOC from 160 ppm to 20 ppm. In Aurell et al the reduction is from 70-120 ppm at ca 5 % oxygen to ca 6 ppm at 3.5 % oxygen [13]. In Kassman et al the reduction of carbon monoxide concentration was approximately the same at ca 3 % oxygen in the flue gases [20]. The TOC could not be detected in the flue gases. All these furnaces are fluidised bed furnaces.

In the grate furnace used in this investigation there is apparently no need for additives from a corrosion point of view. Emissions of sulphur dioxide must be taken into account. The lower doses (2.9 kg S/h and 5.8 kg S/h or ca 20 mg S/MJ and ca 45 mg S/MJ) do not increase the emissions very much: the increase may be of the same order of magnitude as the fluctuations in the sulphur content of the fuel. However, the highest dose yields a significant increase in emissions. It is then not possible to exploit the effect of additives more than a reasonable dose allows.

In the experiments with the lower doses, the carbon monoxide concentration was reduced by ca 70 % from a level of ca 1700 ppm at ca 13 % oxygen¹⁰. TOC was reduced ca 90 % from ca 24 ppm. In order to calculate a reduction in the PAH's emitted, the efficiency of the particle removal has to be taken into account as the results presented here are for the raw gas.

The impact of sulphur additives is then large in absolute terms, but with these high carbon monoxide concentrations rebuilding the furnace may be a better and more relevant measure. Dosing additives would in this case be a stopgap measure.

¹⁰ The concentration is ca 3500 ppm at 6 % oxygen.

8 Conclusions

The results presented in this report lead to the conclusions summarized below.

Regarding the relationship between carbon monoxide and organic substances:

- There is a relationship between the concentration of carbon monoxide in the raw gases and the concentration of organic substances represented by TOC or of individual substances such as methane or the PAH's.
- The concentrations of all substances fluctuate in concert. Carbon monoxide, TOC, methane and the lighter gaseous PAH's all peak simultaneously and relax simultaneously and so does sulphur dioxide originating from the fuel. This indicates that these peaks are puffs of partially combusted gases.
- The main contribution to emissions of e.g. PAH is in these puffs. Keeping a steady level of carbon monoxide or allowing wide variations around that level will yield very different levels of PAH in the emissions.
- The reason for the importance of puffs is that there are threshold values, primarily in carbon monoxide, for concentrations of organic substances (both those at comparatively high concentration determined as TOC and trace substances such as PAH's). When the carbon monoxide concentration increases, the increase in concentration of organic substances is weak below that threshold but much stronger above it.

Regarding sulphur additives:

- The more sulphur additive is injected, the lower the concentration of all products of incomplete combustion in the raw flue gas, i.e. carbon monoxide, organic compounds including PAH. There is though a diminishing return for increases in dosage, i.e. there is an economic optimum.
- In this investigation, at equal sulphur dosage there is no major difference between the two additives ammonium sulphate and elemental sulphur or between injection in the gas volume above the grate and mixing into the fuel regarding their effect on carbon monoxide and organic substances in the flue gases.
- For this furnace, the curve describing TOC, representing organic compounds, as a function of carbon monoxide is the same whether an additive is used or not. Therefore, whatever method is used to lower the carbon monoxide concentration (sulphur additives or a better control of combustion), the concentration of organics will be lowered.
- The decrease in concentration of carbon monoxide and organic substances with injection of sulphur additives is accompanied by an increase in TOC in the fly ash. However, this effect should be confirmed in an independent investigation.

Regarding PAH and PCDD/F

- Injecting sulphur additives reduces PAH concentrations in this investigation. The rather large variation in concentration for the same dose of additive may be caused by the variation in particle loading between samples.

- As already stated above, the PAH concentration in the gas phase depends slightly on carbon monoxide concentration below a threshold value in this concentration and increases strongly above this threshold.
- The PCDD/F concentrations in the flue gases are already very low without any additive and they are at the detection limit, probably because of the low chlorine content in the fuel. Any effect of sulphur additives disappears in the natural variation.

9 Recommendations and applications

The first step towards reduced emissions of carbon monoxide and organic substances with the flue gases is taking measures on the primary side, i.e. to optimize the combustion process and its control. This may involve rebuilding the furnace, e.g. air staging, in order to provide tools to improve the combustion.

A particular goal for these measures should be the reduction or avoidance of puffs of partially combusted gases, which in this furnace probably originate from a fluctuating intensity of the processes in the fuel bed on the grate and from the flow pattern of gases in the combustion chamber. This probably does more for reducing emissions than just lowering the overall level.

Injecting a sulphur additive or using an auxiliary fuel with a high content of sulphur may then be a means to further reduce the carbon monoxide emissions. As far as their effect on carbon monoxide and organics is considered, there is no difference between these. Avoiding emissions should be considered as one of the desired effects, as reducing corrosion by alkali chlorides or the possibility to reduce nitrogen oxides may be equally or more important. At least a halving of the concentration of carbon monoxide and of organics counted as TOC may be expected in general (if the sulphur content of the fuel is not already too high), but for an accurate estimate trial runs need to be performed over a reasonably long period of time. The value of this halving depends also on the level of emissions before dosage of additives.

10 Suggestions for continued research

The mechanisms for the effect of sulphur on carbon monoxide and organic substances in emissions are still unknown, even if some components are beginning to appear. To try to understand them, the first step should be to investigate the basic reactions in the laboratory. When the possible reaction paths have been mapped, measurements may be done in a furnace, from the combustion zone to the flue gas duct.

Although a limit to the reduction of carbon monoxide concentrations could not be found in this investigation, one was found in other studies. One question that should be answered is what this limit is and under which circumstances sulphur leads to increased emissions of organic substances, e.g. the increased PAH emissions with sulphur dosage observed in [12] and [13].

The topic of sulphur additives and PCDD/F in large combustion systems is still unresolved. Before launching a dedicated full-scale experimental study, one should identify a furnace or boiler with larger emissions, where an effect would not be drowned by the natural variability. It is probably not meaningful to continue investigating PCDD/F emissions from furnaces or boilers with clean wood or bark as fuel since the emissions are already low.

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Appendices

- A CONDITIONS IN THE BOILER – AT A GLANCE**
- B PAH, PCBZ AND PCDD/F RESULTS**

A Conditions in the boiler – at a glance

The purpose of this appendix is to provide a survey of the conditions in the boiler during the experiments:

- Carbon monoxide concentration in the raw gas
- Periods when additives were injected (ammonium sulphate solution and elemental sulphur respectively)
- Periods when as samples were taken for later analysis (PAH, PCBz and PCDD/F)
- Load on the boiler
- When fuel oil was burned in the furnace

The information is presented graphically in a series of diagrams, one per day. As the FTIR instrument was not in working order during the best part of the first week, CO data from the SCADA system at the plant are used. When the FTIR instrument was back in working order, from 24/3, the CO data from the FTIR are used.

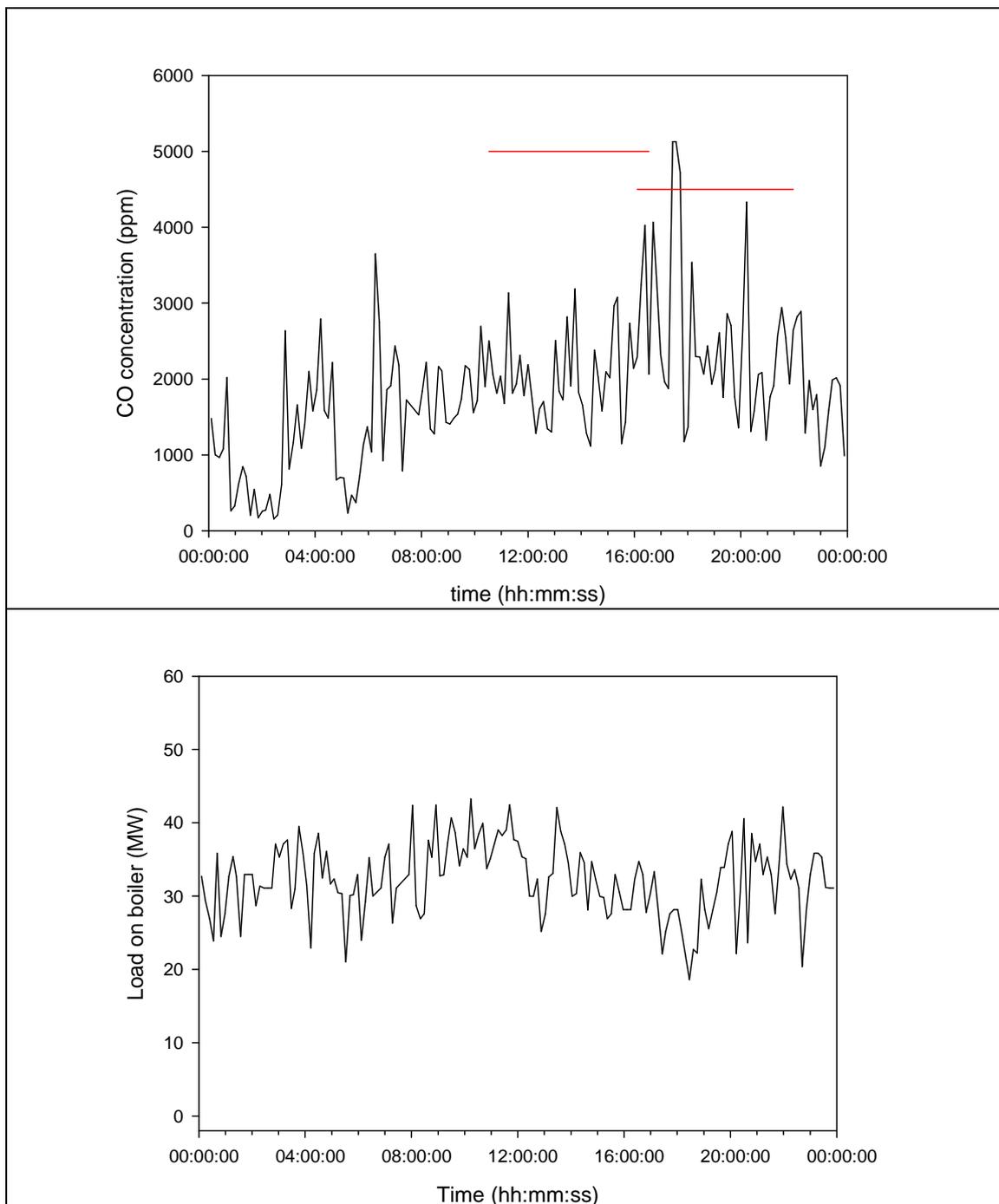


Figure 28. Conditions during the first reference day (19/3). Upper diagram, CO concentration as a function of time with the gas sampling periods superimposed on the diagram. Lower diagram: load on the boiler (black line) and load supplied by oil burners (red line).

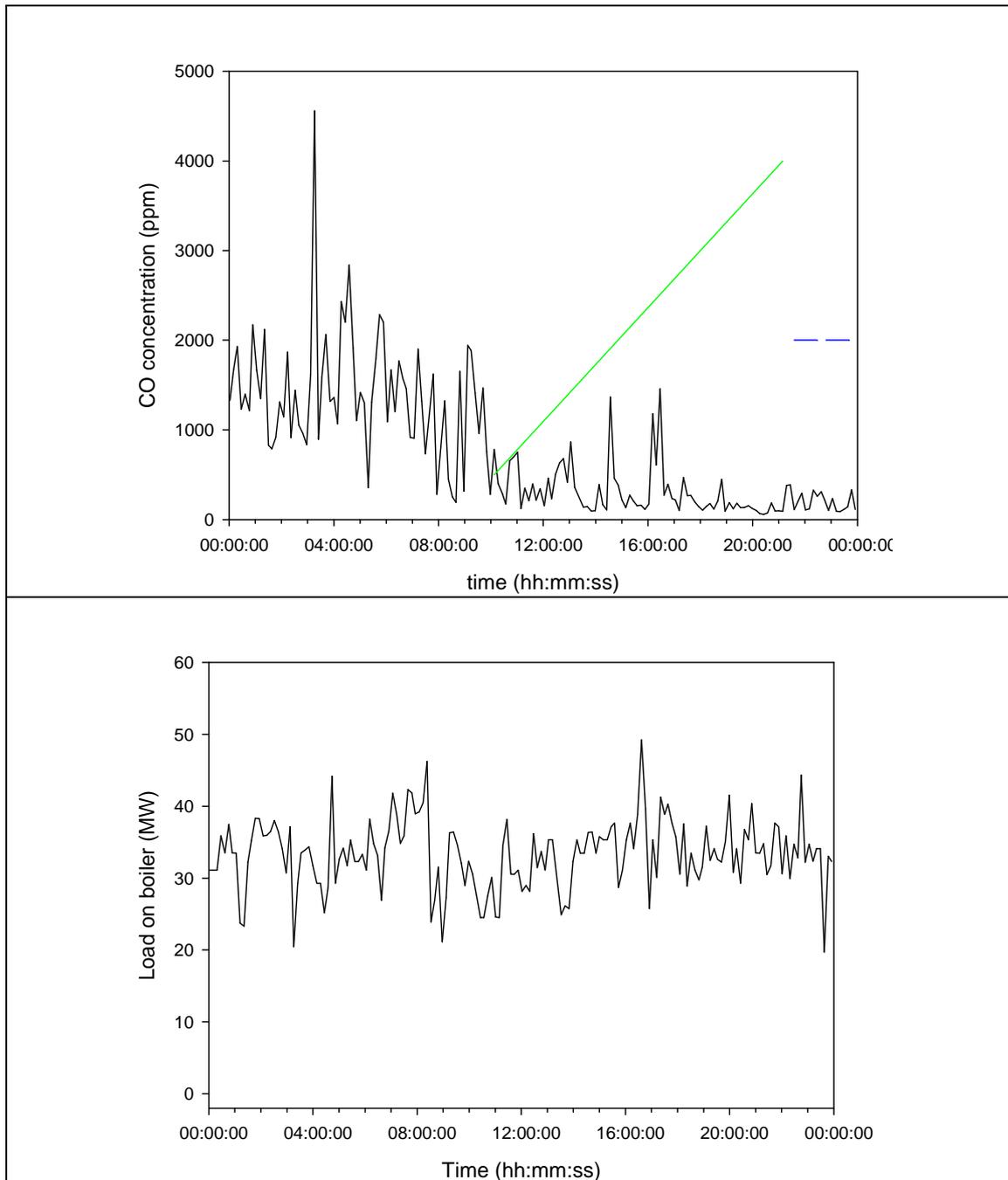


Figure 29. Conditions during the dose-response mapping experiment with ammonium sulphate (20/3). Upper diagram: CO concentration as a function of time. The ramping period is shown with a green line. Dosage with 49.5 l/h (blue dashed line) commenced at ca 21:30. Lower diagram: load on the boiler (black line) and load supplied by oil burners (red line).

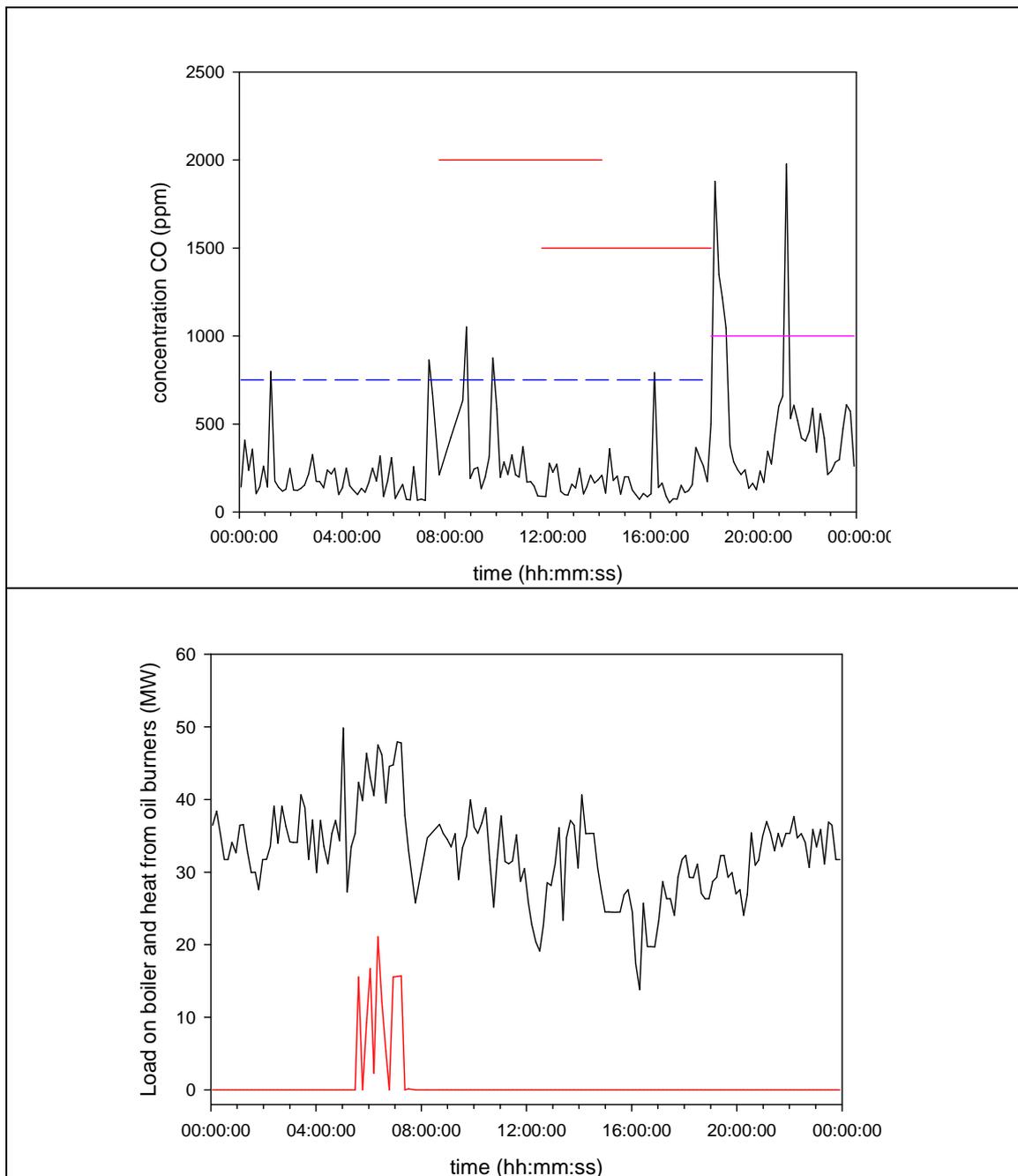


Figure 30. Conditions during the first ammonium sulphate day (21/3), 49.5 l/h (blue dashed line) and 25 l/h (pink line). Upper diagram, CO concentration as a function of time with the gas sampling periods (red lines) superimposed on the diagram. Lower diagram: load on the boiler (black line) and load supplied by oil burners (red line).

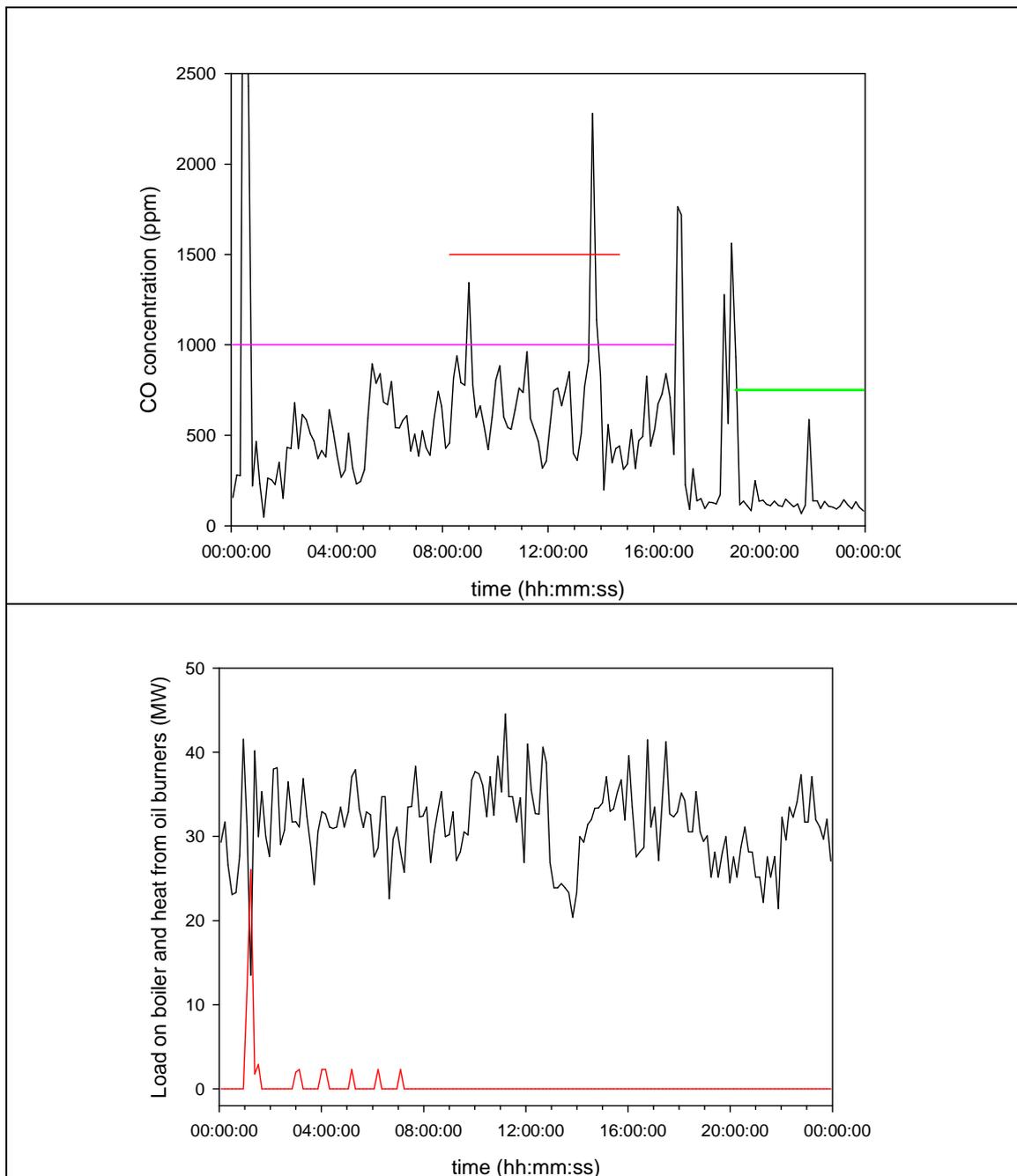


Figure 31. Conditions during the second ammonium sulphate day (22/3), 25 l/h (pink line) and 95 l/h (green line). Upper diagram, CO concentration as a function of time with the gas sampling periods superimposed on the diagram. Lower diagram: load on the boiler (black line) and load supplied by oil burners (red line).

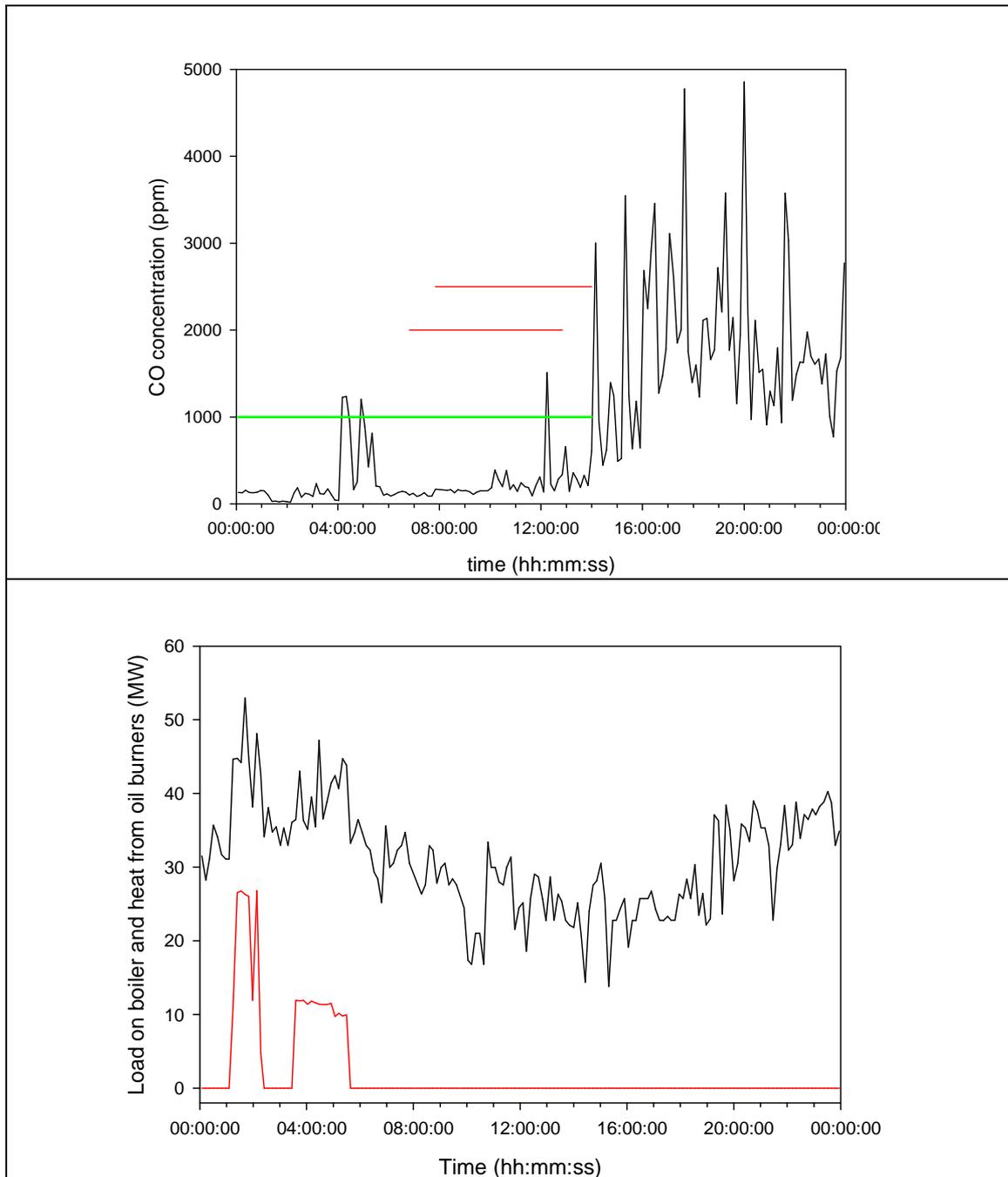


Figure 32. Conditions during the last ammonium sulphate day (23/3), 95 l/h (green line). Upper diagram, CO concentration as a function of time with the gas sampling periods superimposed on the diagram. Lower diagram: load on the boiler (black line) and load supplied by oil burners (red line).

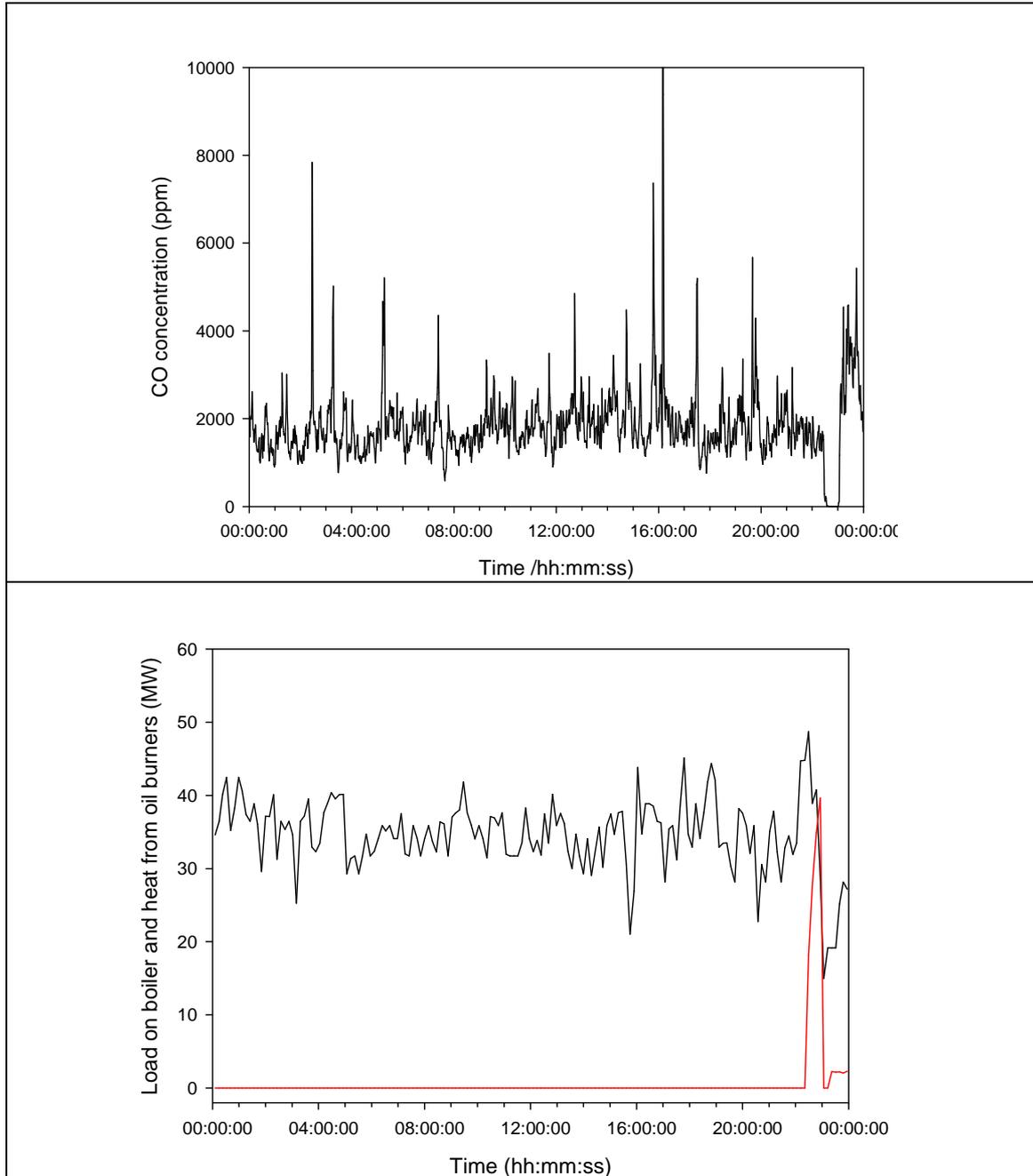


Figure 33. Conditions during the first weekend day (24/3), no dosage. Upper diagram, CO concentration as a function of time. Lower diagram: load on the boiler (black line) and load supplied by oil burners (red line).

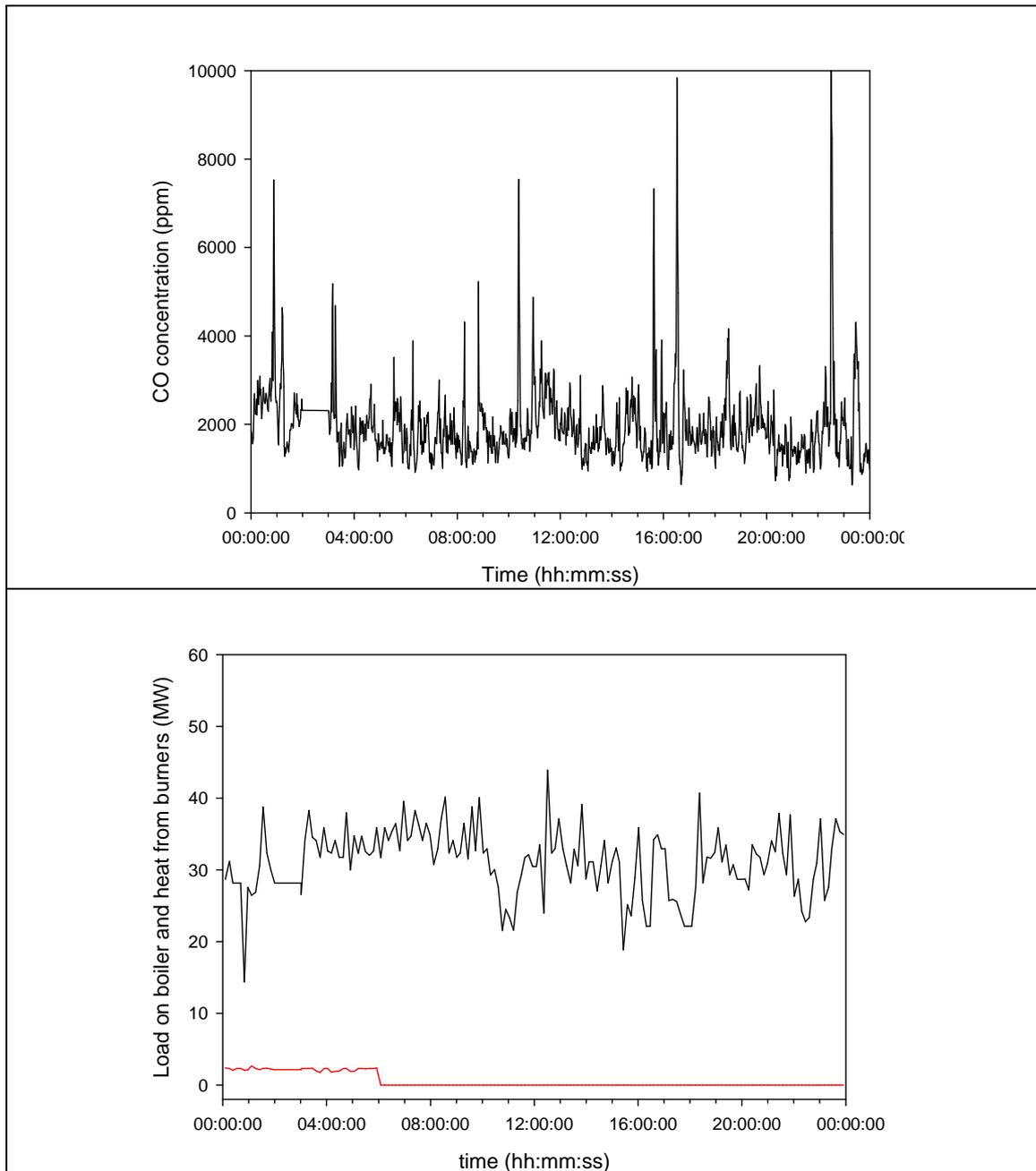


Figure 34. Conditions during the second weekend day (25/3), no dosage. Upper diagram, CO concentration as a function of time, the straight section corresponds to the change over from winter time to summer time. Lower diagram: load on the boiler (black line) and load supplied by oil burners (red line).

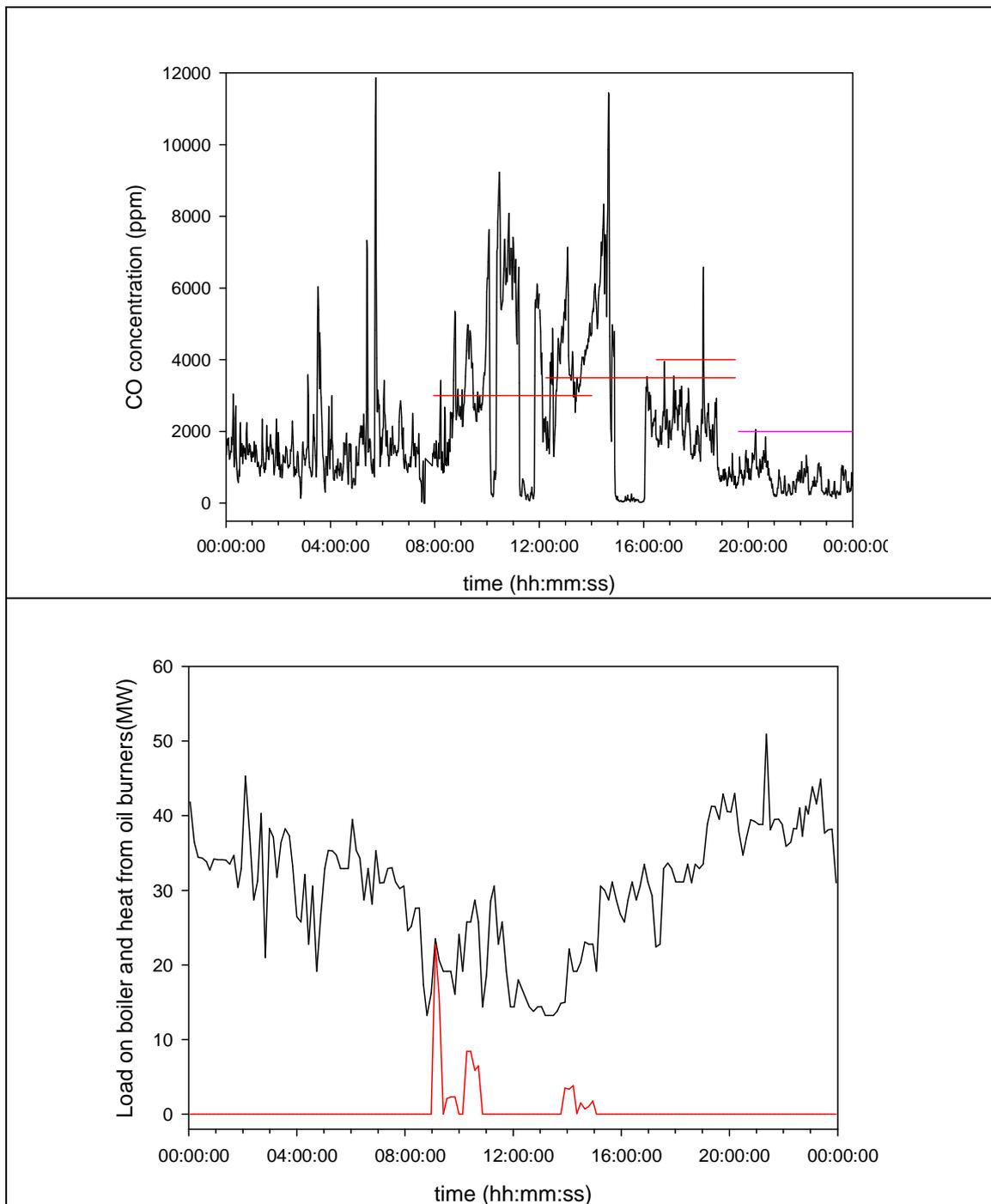


Figure 35. Conditions during the second reference day (26/3), no dosage and 2.9 kg/h elemental sulphur after 20:30 hrs (pink line). Upper diagram, CO concentration as a function of time with the gas sampling periods superimposed on the diagram. Please note that when the instruments were shut down at times (zero values of CO). Lower diagram: load on the boiler (black line) and load supplied by oil burners (red line).

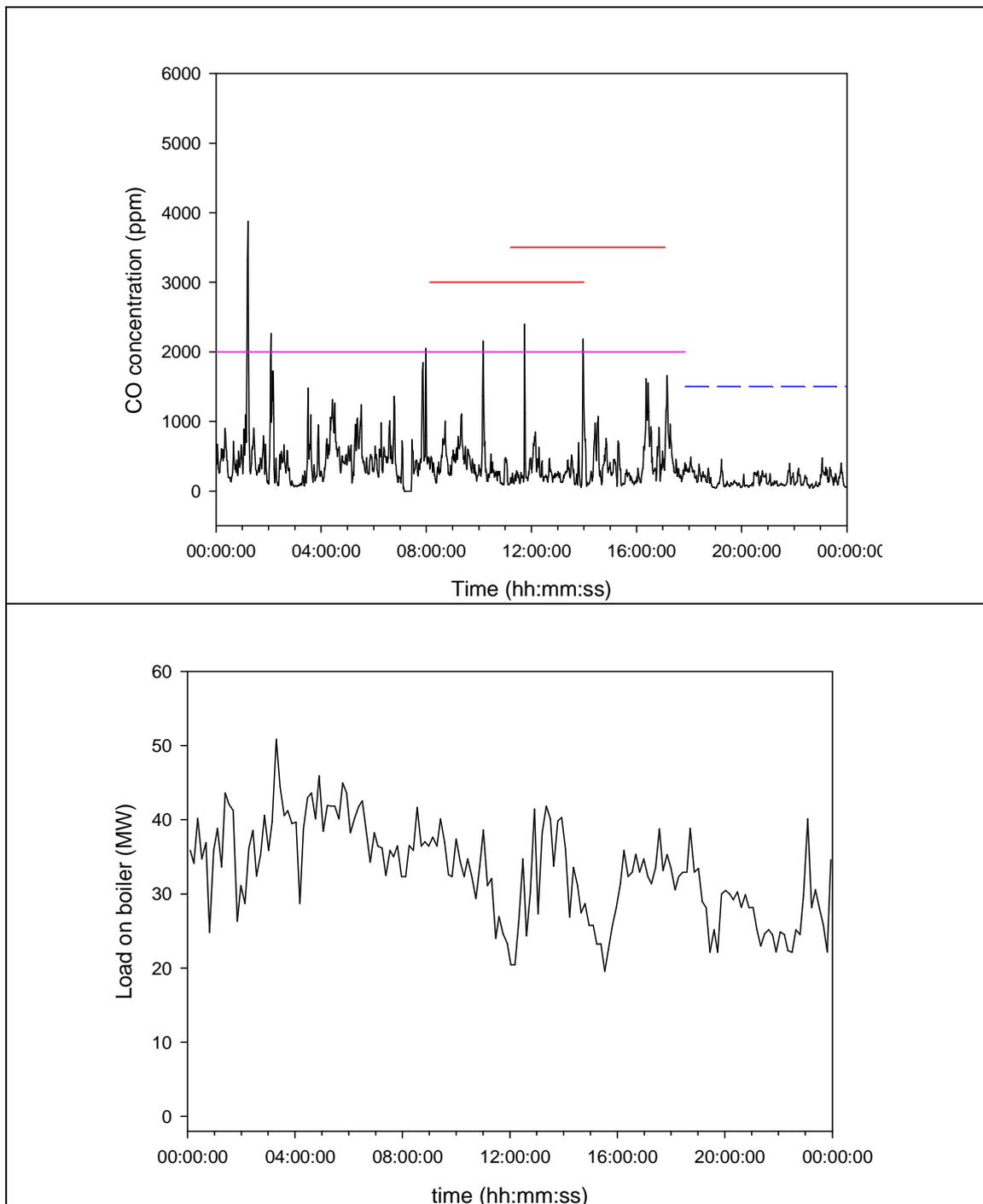


Figure 36. Conditions during the first elemental sulphur day (27/3), 2.9 kg/h (pink line) and 5.8 kg/h (blue dashed line). Upper diagram, CO concentration as a function of time with the gas sampling periods (red lines) superimposed on the diagram. Lower diagram: load on the boiler (black line) and load supplied by oil burners (red line).

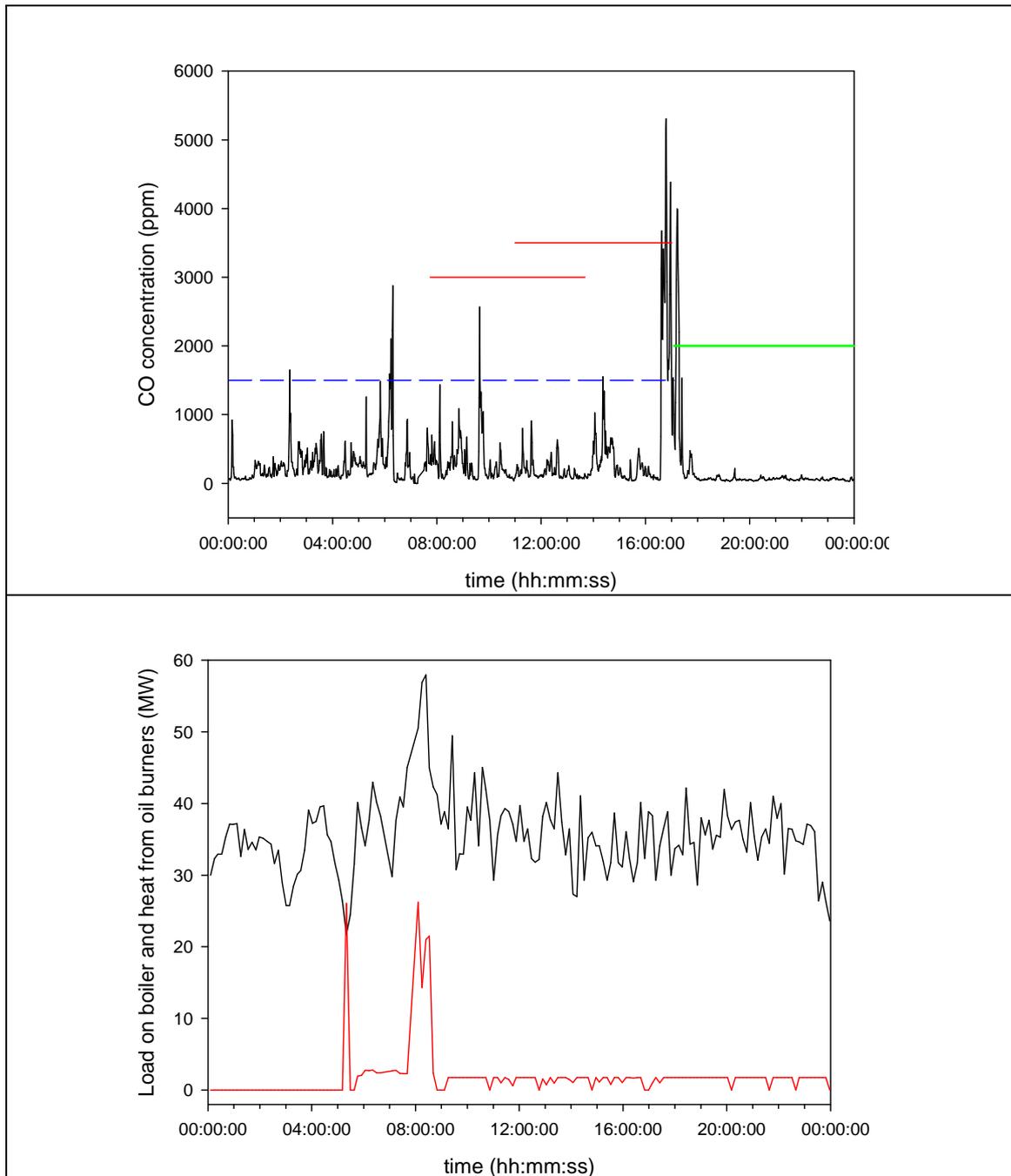


Figure 37. Conditions during the second elemental sulphur day (28/3), 5.8 kg/h (blue dashed line) and 11.6 kg/h (green line). Upper diagram, CO concentration as a function of time with the gas sampling periods (red lines) superimposed on the diagram. Lower diagram: load on the boiler (black line) and load supplied by oil burners (red line).

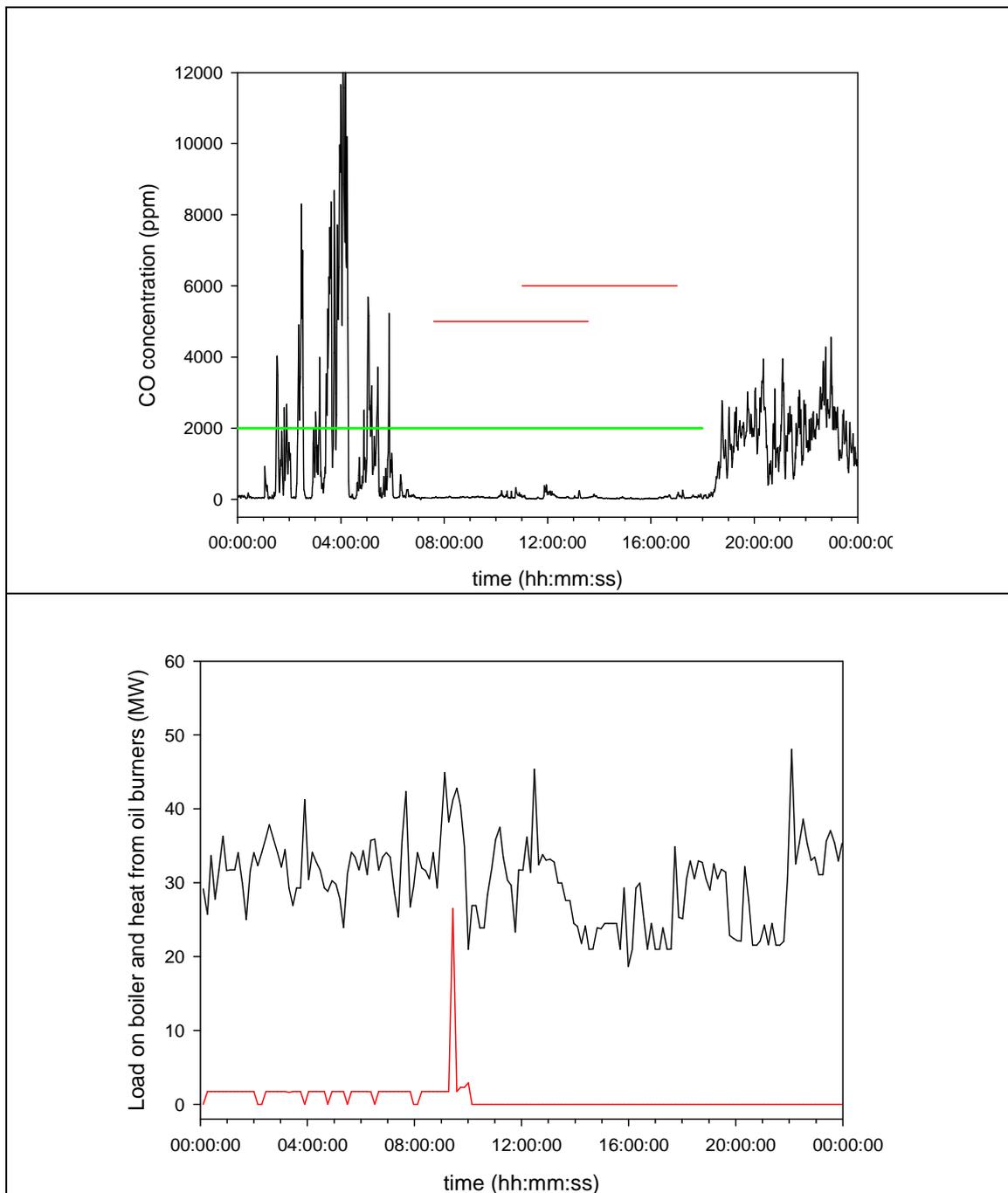


Figure 38. Conditions during the last elemental sulphur day (29/3), 11.6 kg/h (green line). Upper diagram, CO concentration as a function of time with the gas sampling periods (red lines) superimposed on the diagram. Lower diagram: load on the boiler (black line) and load supplied by oil burners (red line).

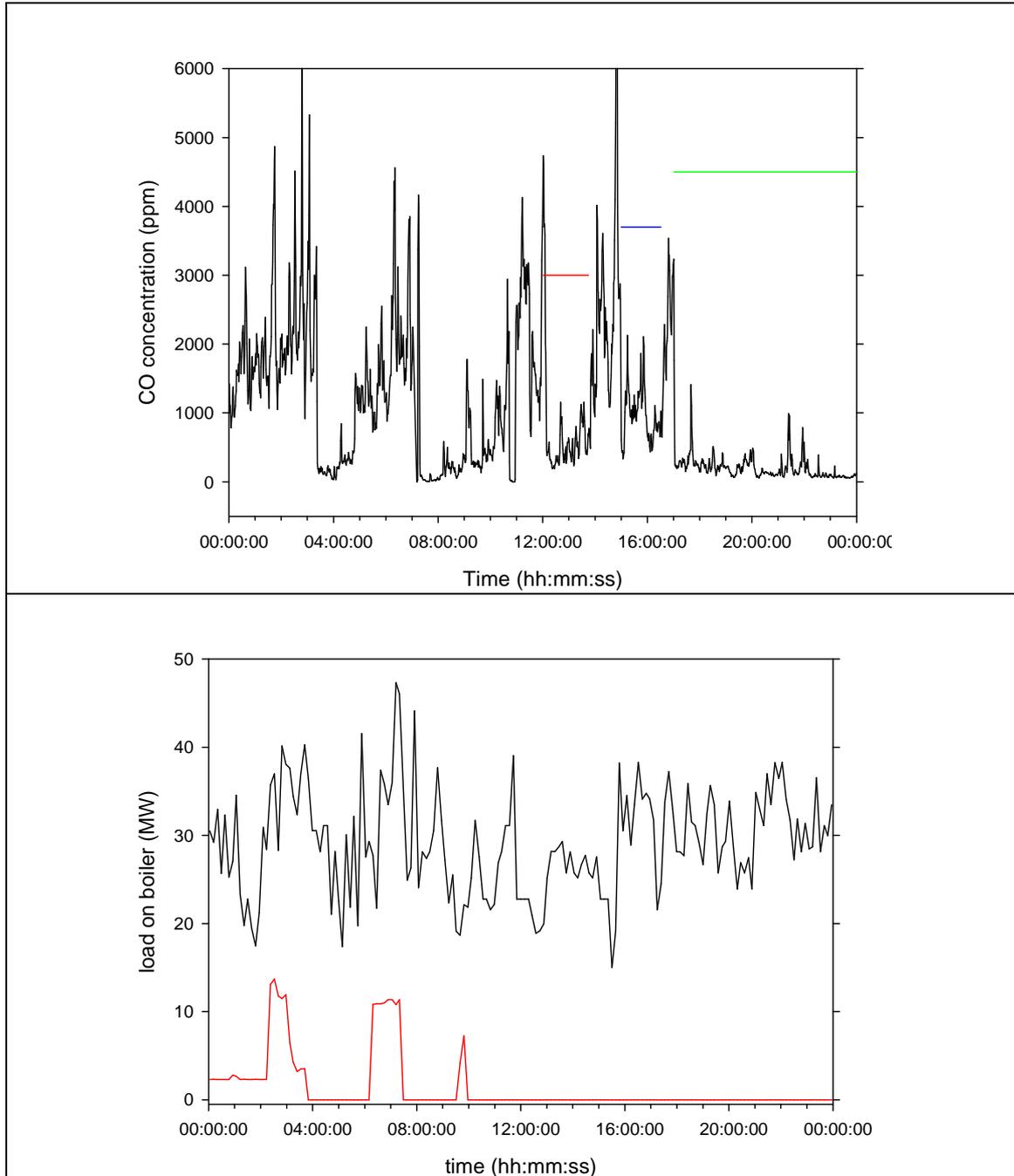


Figure 39. Conditions during the repeat experiments with ammonium sulphate (24/4), 11.6 kg/h. Upper diagram, CO concentration as a function of time with the gas sampling periods superimposed on the diagram. Lower diagram: load on the boiler (black line) and load supplied by oil burners (red line).

B PAH, PCBz and PCDD/F results

In this Appendix are collected the detailed data of PCDD/F and other analyses on the same gas samples.

Regarding the values reported for the PCDD/F, the blank value for the total procedure, including sample handling and transport, is ca 0.00001 I-TEQ/m³ when non-detects are assigned the value zero. When assigning the level of quantification (LOQ) as value to the non-detects, the blank value is ca 0.0005 I-TEQ/m³, mainly for OCDD and Cl7DF. The blank values exceeding LOQ have been taken into account when quantifying the results.

B.1 Summary of samples taken

Table 11. Summary of samples taken for off-site analysis of PCDD/F and of PCBz and PAH

Date	Nr	start	end	duration	Sampling port	Gas volume
		hh:mm	hh:mm	hh:mm		m ³ STP dry
19/3 ¹	070319-1	10:31	16:32	06:01	A	13.05
	070319-2	16:02	22:00	05:58	B	10.67
21/3 ¹	070321-1	07:46	14:05	06:19	B	11.36
	070321-2	11:45	18:20	06:35	A	13.37
22/3 ¹	070322-1	08:13	14:40	06:27	B	11.59
	070322-2	09:36	11:30	01:54	A	4.64
	070322-3	12:10	15:49	03:39	A	6.64
23/3 ¹	070323-1	06:50	12:50	06:00	A	10.77
	070323-2	08:00	14:00	06:00	B	9.96
26/3 ²	070326-1	07:57	14:00	06:03	B	7.44
	070326-2	12:15	19:30	07:15	A	6.57
	070326-3	16:29	19:30	03:01	B	3.86
27/3 ²	070327-1	08:08	14:00	05:52	B	12.11
	070327-2	11:13	17:05	05:52	A	10.26
28/3 ²	070328-1	07:44	13:41	05:57	B	11.91
	070328-2	11:00	17:00	06:00	A	11.35
29/3 ²	070329-1	07:35	13:34	05:59	B	12.18
	070329-2	11:00	17:00	06:00	A	11.71

Footnotes, REMPI-MS data available:

¹ Between 17:10 and 19:25 on 19/3, between 08:30 and 19:25 on 21/3, between 08:40 and 17:20 on 22/3 and between 07:05 and 16:05 on 23/3

² Between 18:10 and 21:15 on 26/3, between 08:25 and 17:00 on 27/3, between 08:20 and 17:00 on 28/3 and between 08:00 and 17:15 on 29/3

B.2 PCDD/F results

The PCDD/F results are reported as three tables:

- Samples taken at port B during the ammonium sulphate week, Table 12
- Samples taken on the same day at port A and B, during that week, Table 13
- Samples taken during the elemental sulphur week, only port B, Table 14

Aggregated results are reported in Table 3 and Table 4 of section 5.1 and illustrated graphically in the analysis of averaged data, section 5.3.2.

Taking into account non-detects in sums is as always a source of uncertainty. In the case of PCDD/F here, choosing to set their values to zero or choosing LOQ, the level of quantification (the highest possible value), does not seem to have any importance at least as far as the ammonium sulphate series is concerned. In the case of the elemental sulphur series choosing to zero the concentration of non-detects yields a value that is different from that obtained when setting the value of non-detects as LOQ. The latter provides an upper bound for the PCDD/F concentrations, which anyhow are quite low.

Table 12. Results for the PCDD/F samples taken during the ammonium sulphate week from port B in the flue gas duct. All results are stated as ng/m³ STP except for the feed rate which is in l/h. Sum 1 is the I-TEQ value when taking the LOQ as value for the non-detects, Sum 2 is the I-TEQ value when giving the non-detects the value 0.

	19/3	21/3	22/3	23/3
Rate of injection	0 l/h	49.5 l/h	25 l/h	95 l/h
2,3,7,8-TCDD	< 0.0001	< 0.0004	0.0010	0.0005
1,2,3,7,8-PeCDD	0.0001	< 0.0002	< 0.0003	0.0006
1,2,3,4,7,8-HxCDD	0.0001	< 0.0001	0.0001	0.0006
1,2,3,6,7,8-HxCDD	0.0001	< 0.0003	0.0003	0.0016
1,2,3,7,8,9-HxCDD	0.0001	< 0.0002	0.0002	0.0013
1,2,3,4,6,7,8-HpCDD	0.0011	0.0006	0.0013	0.0043
OCDD	0.0022	0.0014	0.0028	0.0035
2,3,7,8-TCDF	0.0016	0.0070	0.0254	0.0117
1,2,3,7,8-PeCDF	0.0003	0.0006	0.0028	0.0025
2,3,4,7,8-PeCDF	0.0006	0.0011	0.0023	0.0019
1,2,3,4,7,8-HxCDF	0.0005	0.0004	0.0003	0.0009
1,2,3,6,7,8-HxCDF	0.0004	0.0004	0.0005	0.0009
1,2,3,7,8,9-HxCDF	0.0001	< 0.0001	< 0.0001	0.0002
2,3,4,6,7,8-HxCDF	0.0005	0.0003	0.0004	0.0014
1,2,3,4,6,7,8-HpCDF	0.0018	0.0008	0.0010	0.0019
1,2,3,4,7,8,9-HpCDF	0.0003	< 0.0003	< 0.0003	0.0004
OCDF	0.0012	0.0009	< 0.0001	0.0010
Sum MCDD	<0.115	<0.004	<0.004	<0.01
Sum DCDD	0.652	1.127	0.016	0.006
Sum TriCDD	0.037	0.460	0.021	0.011
Sum TCDD	0.0009	< 0.006	0.0135	0.035
Sum PeCDD	0.0009	< 0.001	0.0041	0.035
Sum HxCDD	0.0009	< 0.001	< 0.002	0.022
Sum HpCDD	0.0022	0.0012	0.0025	0.010
OCDD	0.0022	0.0014	0.0028	0.0035
Sum MCDF	<0.077	<0.126	<0.002	0.29
Sum DCDF	0.004	0.01	1.73	0.62
Sum TriCDF	0.01	0.01	1.54	0.52
Sum TCDF	0.0141	0.087	0.31	0.15
Sum PeCDF	0.0039	0.010	0.030	0.023
Sum HxCDF	0.0037	0.003	0.0029	0.005
Sum HpCDF	0.0019	0.001	0.0013	0.008
OCDF	0.0012	0.0009	< 0.0001	0.0010
I-TEQ Sum 1	0.0008	0.0019	0.0052	0.0038
I-TEQ Sum 2	0.0006	0.0018	0.0052	0.0038
Average chlorination	1.88	2.25	2.58	2.39

Table 13. Results for the PCDD/F samples taken during the ammonium sulphate week. All results are stated as ng/m³ STP. Sum 1 is the I-TEQ value when taking the LOQ as value for the non-detects, Sum 2 is the I-TEQ value when giving the non-detects the value 0. Samples taken at port B are also found in the previous table, but are entered here for the sake of comparison

	19/3, port A	19/3, port B	23/3, port A	23/3, port B
Rate of injection	0 l/h	0 l/h	95 l/h	95 l/h
2,3,7,8-TCDD	< 0.0001	< 0.0001	0.0005	0.0005
1,2,3,7,8-PeCDD	0.0002	0.0001	0.0011	0.0006
1,2,3,4,7,8-HxCDD	0.0002	0.0001	< 0.001	0.0006
1,2,3,6,7,8-HxCDD	0.0008	0.0001	0.0021	0.0016
1,2,3,7,8,9-HxCDD	0.0002	0.0001	< 0.001	0.0013
1,2,3,4,6,7,8-HpCDD	0.0063	0.0011	0.0118	0.0043
OCDD	0.0155	0.0022	0.0104	0.0035
2,3,7,8-TCDF	0.0013	0.0016	0.0155	0.0117
1,2,3,7,8-PeCDF	0.0007	0.0003	0.0040	0.0025
2,3,4,7,8-PeCDF	0.0015	0.0006	0.0071	0.0019
1,2,3,4,7,8-HxCDF	0.0009	0.0005	0.0048	0.0009
1,2,3,6,7,8-HxCDF	0.0011	0.0004	0.0053	0.0009
1,2,3,7,8,9-HxCDF	0.0002	0.0001	< 0.001	0.0002
2,3,4,6,7,8-HxCDF	0.0014	0.0005	0.0147	0.0014
1,2,3,4,6,7,8-HpCDF	0.0032	0.0018	0.0249	0.0019
1,2,3,4,7,8,9-HpCDF	0.0007	0.0003	< 0.003	0.0004
OCDF	0.0028	0.0012	< 0.013	0.0010
Sum MCDD	0.12	<0.115	<0.01	<0.01
Sum DCDD	0.26	0.652	0.012	0.006
Sum TriCDD	0.018	0.037	0.071	0.011
Sum TCDD	0.0009	0.0009	0.046	0.035
Sum PeCDD	0.0021	0.0009	0.039	0.035
Sum HxCDD	0.0055	0.0009	0.030	0.022
Sum HpCDD	0.0114	0.0022	0.023	0.010
OCDD	0.0155	0.0022	0.0104	0.0035
Sum MCDF	<0.004	<0.077	0.35	0.29
Sum DCDF	<0.004	0.004	0.96	0.62
Sum TriCDF	<0.004	0.01	0.59	0.52
Sum TCDF	0.0142	0.0141	0.217	0.15
Sum PeCDF	0.0089	0.0039	0.051	0.023
Sum HxCDF	0.0064	0.0037	0.052	0.005
Sum HpCDF	0.0047	0.0019	0.089	0.008
OCDF	0.0028	0.0012	< 0.013	0.0010
I-TEQ Sum 1	0.0016	0.0008	0.0097	0.0038
I-TEQ Sum 2	0.0016	0.0006	0.0097	0.0038
Average Chlorination	2.15	1.88	2.57	2.39

Table 14. Results for the PCDD/F samples taken during the elemental sulphur week from port B in the flue gas duct. All results are stated as ng/m³ STP, except for the rate of injection which is in kg/h. Sum 1 is the I-TEQ value when taking the LOQ as value for the non-detects, Sum 2 is the I-TEQ value when giving the non-detects the value 0.

	26/3	27/3	28/3	29/3
Rate of injection	0 kg/h	2.9 kg/h	5.8 kg/h	11.6 kg/h
2,3,7,8-TCDD	0.0010	< 0.000	0.0002	< 0.000
1,2,3,7,8-PeCDD	0.0010	< 0.000	0.0002	< 0.000
1,2,3,4,7,8-HxCDD	0.0013	< 0.000	0.0002	< 0.000
1,2,3,6,7,8-HxCDD	0.0052	< 0.000	0.0002	< 0.000
1,2,3,7,8,9-HxCDD	0.0052	< 0.000	0.0002	< 0.000
1,2,3,4,6,7,8-HpCDD	0.0026	< 0.001	0.0005	< 0.000
OCDD	0.0052	< 0.001	0.0008	< 0.002
2,3,7,8-TCDF	0.0070	0.0097	0.0042	0.0017
1,2,3,7,8-PeCDF	0.0023	< 0.002	0.0003	0.0002
2,3,4,7,8-PeCDF	0.0060	0.0016	0.0005	0.0007
1,2,3,4,7,8-HxCDF	0.0013	< 0.001	0.0003	< 0.000
1,2,3,6,7,8-HxCDF	0.0013	< 0.001	0.0003	< 0.000
1,2,3,7,8,9-HxCDF	0.0013	< 0.000	0.0003	< 0.000
2,3,4,6,7,8-HxCDF	0.0013	< 0.001	0.0003	< 0.000
1,2,3,4,6,7,8-HpCDF	0.0026	< 0.002	0.0003	< 0.000
1,2,3,4,7,8,9-HpCDF	0.0026	< 0.000	0.0003	< 0.000
OCDF	0.0026	< 0.001	0.0008	< 0.001
Sum MCDD	-	<0.002	<0.002	0.003
Sum DCDD	-	1.30	0.76	0.53
Sum TriCDD	-	0.52	0.29	0.13
Sum TCDD	0.0104	0.0010	0.0008	< 0.003
Sum PeCDD	0.0104	0.0008	0.0008	< 0.001
Sum HxCDD	0.0259	0.0008	0.0008	< 0.001
Sum HpCDD	0.0078	0.0038	0.0008	< 0.001
OCDD	0.0052	< 0.001	0.0008	< 0.002
Sum MCDF	-	0.178	0.027	0.043
Sum DCDF	-	0.010	0.0078	0.0042
Sum TriCDF	-	0.016	0.021	0.0057
Sum TCDF	0.0357	0.0917	0.047	0.0294
Sum PeCDF	0.0104	0.0021	0.0019	0.0021
Sum HxCDF	0.0104	0.0008	0.0008	< 0.001
Sum HpCDF	0.0104	0.0040	0.0008	< 0.001
OCDF	0.0026	< 0.001	0.0008	< 0.001
I-TEQ Sum 1	0.0071	0.0026	0.0011	0.0009
I-TEQ Sum 2	0.0037	0.0021	0.0007	0.0006
Average chlorination	-	2.21	2.30	2.19

B.3 PCBz results

Table 15. Results from analyses of polychlorinated benzenes in the gas samples taken at port B during the ammonium sulphate week. All results are stated as ng/m³ STP except for the rate of injection of solution, which is in l/h.

	19/3	21/3	22/3	23/3
Rate of injection	0 l/h	49.5 l/h	25 l/h	95 l/h
Chlorobenzene	103	n.g	165	155
1,3-Dichlorobenzene	18	60	63	26
1,4-Dichlorobenzene	47	68	83	38
1,2-Dichlorobenzene	11582	7217	8706	4346
1,3,5-Trichlorobenzene	0	5	7	3
1,2,4-Trichlorobenzene	4	28	48	18
1,2,3-Trichlorobenzene	3	6	8	4
1,2,3,5- + 1,2,4,5-Tetrachlorobenzene	1	3	5	2
1,2,3,4-Tetrachlorobenzene	1	1	2	1
Pentachlorobenzene	< 1	< 1	< 3	< 2
Hexachlorobenzene	2	2	3	3
Sum Chlorobenzenes (Cl1 - Cl6):	11660	7391	8929	4443

Table 16. Results from analyses of polychlorinated benzenes in the gas samples taken at port A during the ammonium sulphate week. All results are stated as ng/m³ STP except for the rate of injection of solution which is in l/h. The results at port B in the previous table are also entered for the sake of direct comparison.

	19/3		23/3	
Rate of injection	0 l/h		95 l/h	
Port	A	B	A	B
Chlorobenzene	n.q.	103	80	155
1,3-Dichlorobenzene	14	18	36	26
1,4-Dichlorobenzene	32	47	38	38
1,2-Dichlorobenzene	11201	11582	2210	4346
1,3,5-Trichlorobenzene	0	0	4	3
1,2,4-Trichlorobenzene	4	4	17	18
1,2,3-Trichlorobenzene	3	3	4	4
1,2,3,5- + 1,2,4,5-Tetrachlorobenzene	1	1	3	2
1,2,3,4-Tetrachlorobenzene	1	1	1	1
Pentachlorobenzene	< 1	< 1	< 1	< 2
Hexachlorobenzene	2	2	1	3
Sum Chlorobenzenes (Cl1 - Cl6):	11258	11660	2316	4443

Table 17. Results from analyses of polychlorinated benzenes in the gas samples taken at port B during the ammonium sulphate week. All results are stated as ng/m³ STP except the rate of injection of sulphur which is in kg/h.

	26/3	27/3	28/3	29/3
Rate of injection	0 kg/h	2.9 kg/h	5.8 kg/h	11.6 kg/h
Chlorobenzene	528	104	149	185
1,3-Dichlorobenzene	41	83	94	64
1,4-Dichlorobenzene	194	72	80	52
1,2-Dichlorobenzene	41774	594	1335	977
1,3,5-Trichlorobenzene	1	10	8	5
1,2,4-Trichlorobenzene	33	47	44	32
1,2,3-Trichlorobenzene	4	9	9	6
1,2,3,5- + 1,2,4,5-Tetrachlorobenzene	1	5	4	2
1,2,3,4-Tetrachlorobenzene	1	2	1	1
Pentachlorobenzene	1	< 2	< 3	< 1
Hexachlorobenzene	7	1	1	1
Sum Chlorobenzenes (Cl1 - Cl6):	42057	824	1579	1142

B.4 PAH results

Table 18. Results from analysis of PAH in gas samples during the ammonium sulphate week, all data in $\mu\text{g}/\text{m}^3$ STP except for the feed rate of ammonium sulphate solution, which is in l/h

Species	Date	19/3-1	19/3-2	21/3-1	21/3-2	22/3-1	22/3-2	22/3-3	23/3-1	23/3-2
	Port	A	B	B	A	B	A	A	A	B
Rate of injection (l/h)		0	0	49.5	49.5	25	25	25	95	95
Benzo(a)anthracene		0.01	0.04	< 0.01	0.046	< 0.01	0.037	0.072	< 0.01	< 0.01
Benzo(a)pyrene		0.01	0.03	< 0.01	0.044	< 0.01	0.012	0.046	< 0.01	< 0.01
Benzo(b+j+k)fluoranthene		0.04	0.15	0.0	0.10	0.0	0.086	0.26	0.04	0.04
Chrysene/Triphenylene		0.04	0.15	0.0	0.10	0.0	0.086	0.26	0.04	0.04
Dibenzo(ah+ac)anthracene		< 0.01	< 0.01	< 0.01	0.002	< 0.01	0.001	0.003	< 0.01	< 0.01
Indeno(1,2,3-cd)pyrene		< 0.01	< 0.01	< 0.01	0.002	< 0.01	0.002	0.002	< 0.01	< 0.01
Naphthalene		25	38	29	25	17	34	157	11	5.9
Anthracene		0.11	0.37	0.0	0.33	0.0	0.37	0.79	0.03	0.02
Phenanthrene		2.5	6.6	0.8	2.4	1.3	2.8	9.1	1.0	0.70
Pyrene		0.18	0.56	0.1	0.30	0.2	0.47	0.74	0.14	0.22
Acenaphthene		0.15	0.26	0.1	0.14	0.1	0.08	0.27	0.03	0.02
Acenaphthylene		1.8	3.4	0.5	1.6	0.3	0.58	3.0	0.07	0.05
Fluorene		0.03	0.07	0.1	0.11	0.1	0.04	0.19	0.07	0.04
Fluoranthene		0.25	0.85	0.1	0.47	0.2	0.40	1.3	0.19	0.18
Benzo(ghi)perylene		< 0.01	0.02	< 0.01	0.009	< 0.01	0.006	0.016	< 0.01	< 0.01
Sum EPA 16		30	51	30	30	19	39	173	13	7.2

Table 19. Results from analysis of PAH in gas samples during the elemental sulphur week, all data in $\mu\text{g}/\text{m}^3$ STP except the feed rate of sulphur which is in kg/h

Species	Date	26/3-1	26/3-2	26/3-3	27/3-1	27/3-2	28/3-1	28/3-2	29/3-1	29/3-2
	Port	B	A	B	B	A	B	A	B	A
Rate of injection (kg/h)		0	0	0	2.9	2.9	5.8	5.8	11.6	11.6
Benzo(a)anthracene		29	20	0.28	< 0.01	0.055	< 0.01	0.055	< 0.01	0.004
Benzo(a)pyrene		13	9.3	0.10	< 0.01	0.006	< 0.01	0.008	< 0.01	0.001
Benzo(b+j+k)fluoranthene		36	28	0.39	< 0.01	0.053	< 0.01	0.081	< 0.01	0.015
Chrysene/Triphenylene		54	42	0.49	0.02	0.066	0.01	0.10	< 0.01	0.012
Dibenzo(ah+ac)anthracene		1.5	8.4	0.026	< 0.01	0.001	< 0.01	0.002	< 0.01	0.0004
Indeno(1,2,3-cd)pyrene		2.9	6.2	0.078	< 0.01	0.001	< 0.01	0.002	< 0.01	0.001
Naphthalene		3726	1944	83	11	73	8	79	2.0	10
Anthracene		742	502	1.0	0.03	0.87	0.04	1.52	< 0.01	0.08
Phenanthrene		1117	693	13.7	0.54	3.5	0.39	3.11	0.25	0.72
Pyrene		172	105	1.9	0.06	0.52	0.03	0.50	0.02	0.11
Acenaphtene		120	53	0.80	0.05	0.32	0.03	0.36	0.02	0.09
Acenaphtylene		1157	539	6.8	0.24	1.5	0.15	1.12	0.07	0.05
Fluorene		280	182	1.0	0.03	0.28	0.03	0.13	0.02	0.05
Fluoranthene		253	177	2.3	0.12	0.67	0.06	0.87	0.04	0.13
Benzo(ghi)perylene		9.5	1.1	0.078	< 0.01	0.008	< 0.01	0.012	< 0.01	0.002
Sum EPA 16		7710	4303	112	12	81	9.1	87	2.5	11

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