

**Sulphur dioxide
emissions from oil
refineries in Europe
(2006)**

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ABSTRACT

This report describes the results of the 2006 year survey into the sulphur pathways in European refining. This includes the distribution of sulphur in products, the capture and recovery of sulphur in refineries and the emission of sulphur oxides as part of the refining process. The archived results of surveys carried out for the years 1998 and 2002 have also been reanalysed to ensure use of consistent methodology when establishing trends and to better understand caveats made in the 2002 survey report. This survey covered a limited dataset and as a consequence, it was not known if it was fully representative.

In 2006 67 surveys representing a crude throughput equivalent to 68% of the Organisation for Economic Co-operation and Development (OECD) European refining capacity were analysed. The results confirm a downward trend in the sulphur content of major product streams and a reduction of sulphur emitted from refinery operations to ~3.7% of total sulphur intake. This is a factor 2 lower than in 1998. About 45% of all sulphur taken into refineries as crude and other products was recovered as elemental sulphur in 2006.

The results of the reanalysis of earlier surveys were consistent with previous reports. Importantly we were able to establish that, despite concerns over the small survey size, the 2002 survey was generally representative. An important exception was the sulphur content of Marine Bunker Fuels. The 2002 survey suggested a decrease in the sulphur content of marine fuels. However the 2006 and 1998 data were very similar. It therefore seems unlikely that the 2002 survey was representative of all of the European marine bunker production.

KEYWORDS

Emissions, oil industry, petroleum products, refinery, sulphur, sulphur dioxide, survey, crude

INTERNET

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SUMMARY

The CONCAWE Sulphur survey has been run at approximately 4 year intervals since 1979 and provides an overview of the distribution of sulphur across all of the main refinery product streams in relation to the refinery crude diet. Additionally it reports on sulphur emitted to atmosphere and sulphur recovered as a product.

Survey data has been somewhat limited from 1998 onward. The reasons for this are not very clear - it may be related to the ongoing automation of data gathering at the refineries, making it more difficult and cumbersome to access the data in the format requested for the survey. To provide a measure of representativeness we have looked at the ratio of the crude volumes to the OECD Europe crude refining capacity which is a readily available statistic that approximates the European capacity. The response to requests for data decreased from 87% of OECD Europe processed crude in 1998 to 46% in 2002 and up to 68% in 2006.

The survey time spacing of 4 years is also rather long which makes it difficult to retain a "memory" of the survey process. For this report, it was decided that retained data from the 1998 and 2002 surveys should be analysed alongside the 2006 data in a consistent way to establish trends. This was considered important for the 2002 survey which had a small size. The smaller the survey response the greater the possibility that some elements may not be entirely representative.

The data reanalysis of the 1998 and 2002 surveys gave essentially the same results as those reported in CONCAWE reports 10/02 [6] and 02/07 [7] respectively.

It was found that the trends reported in CONCAWE report 02/07 [7] for 2002 relative to 1998 were mostly correct despite the small survey size. One important case where it was not was the view on marine bunkers. A marked reduction in sulphur content was reported. This is not seen at all in the 2006 survey which gives almost exactly the same response as in 1998. We therefore conclude that the 2002 survey was not representative for this product.

The results of the survey show continued reduction in sulphur emitted to atmosphere with an overall increase in sulphur capture. An estimated 45% of the sulphur in the refinery intake is now recovered as elemental sulphur. A further 12% is sequestered in products that are not burned. The amount of sulphur emitted by refineries themselves has halved since 1998 and this is due to both less oil burning and a reduction in the sulphur content of internal fuels. The proportion of sulphur in products destined for combustion has decreased from 37 to 32.5% of intake reflecting the progress of fuel quality legislation.

The annually averaged crude diet for Europe is unchanged since 2002 and very similar to that in 1998 with only a small decrease in the average sulphur content from 0.97 to 0.91%.

The sulphur content of produced fuels closely matches the market requirements of fuels regulated by the Sulphur in Liquid Fuels Directive and the Directive on Automotive Fuel Quality.

The 2006 refinery output will change substantially to meet 2008 requirements for 0.1% sulphur heating fuel and 2010 requirements for 1% marine fuel in emission control areas and we would expect the next survey in 2010 to reflect these drivers.

ACKNOWLEDGEMENTS

CONCAWE would like to express its gratitude to all its member companies whose contribution to the survey has made this work possible.

1. INTRODUCTION

CONCAWE has reported the distribution of sulphur between refinery products and refinery emissions at 4 yearly intervals since 1979 by means of what is known as the Sulphur Survey report. (See references CONCAWE (1984) [1], CONCAWE (1986) [2], CONCAWE (1991) [3], CONCAWE (1996) [4], CONCAWE (1998) [5], CONCAWE (2002) [6], CONCAWE (2007) [7])

The report provides information on the typical sulphur content of the main refinery product streams, the amount of sulphur recovered and the amount of sulphur emitted in the course of refining those products. Results from the Sulphur Survey are useful in assessing how the industry responds to regulation (e.g. on changing fuel specifications, environmental legislation, etc.).

The survey asks for more data than is typically gathered for regulatory and corporate reporting purposes and the overall response has tended to decrease in time with the 2002 survey having a rather small coverage. The reasons for this are not known but, with the ongoing automation of data gathering at the refineries, it may have become more difficult and cumbersome to access the data in the format requested for the survey.

There were several caveats made in the 2002 survey report warning that some conclusions may not be robust or representative because of the (relatively) small sample size. CONCAWE report 02/07 [7] also made reference to some partial reanalysis of the 1998 survey data. It reported "corrected" values from those given in CONCAWE report 10/02 [6] but did not explain why.

Because of the above it was decided to reanalyse data for all of the three surveys for which data are held electronically (1998, 2002, 2006). A standard methodology was used to better determine trends. This allowed natural gas usage to be reported separately from refinery fuel gas usage whereas in earlier surveys a distinction was drawn only between the principal liquid and gaseous fuels. A trend in the efficiency of sulphur recovery plants has also been added.

2. REFINERY INTAKE AND OVERALL SULPHUR BALANCE

Refineries take in both crude oil and intermediate products for processing. The totals reported in the last three survey years are given below compared with the total refinery intake in OECD Europe. This is a readily available statistic that approximates the European refining capacity. The intake in the surveys analysed was 87% of the OECD figure in 1998, 46% in 2002 and 68% in 2006. The survey results should therefore be representative of the industry in 2006 and, by examining trends we can attempt to assess where the 2002 survey was representative and where not.

Table 1 Refinery hydrocarbon intake

	1998	2002	2006
Number of refineries participating in survey	77 ¹	46 ²	67
Crude Intake, Mt	502	277	417
Other Intake, Mt	38	35	55
Total Intake Mt	550	312	472
OECD Europe Total refinery Intake. Mt	635 ³	684 ⁴	696 ⁵
CONCAWE/OECD %	87%	46%	68%

The refinery overall sulphur intake and the distribution of sulphur output is shown in **Table 2** below. The units are kt of sulphur. The categories are:

- products destined for combustion (fuels);
- products (non-combustion) where the sulphur remains in the product and is retained and not further converted (e.g. bitumen);
- sulphur recovered from refinery streams as elemental sulphur;
- sulphur recovered in non-oil products (e.g. gypsum.);
- sulphur emitted from refinery processes and combustion

The largest sulphur output stream for each year studied, is recovered sulphur. The next largest is the sulphur present in products.

¹ CONCAWE Report 10/02 reports 79 refineries completing the questionnaire with a crude input of 507 Mt.

² CONCAWE Report 02/07 reports 47 refineries and a total intake of 331 Mt/a – one survey return appears to have been counted twice in that analysis. We obtain 331 Mt/a using all archived spreadsheets, one name appearing twice.

³ From CONCAWE report 10/02 citing BP statistics as source

⁴ From IEA Energy Statistics 2006 – this is larger than that reported in CONCAWE report 02/07 by 2 Mt/a but the IEA annual reports do sometime show slightly revised values for historic years.

⁵ From IEA Energy Statistics 2007.

The most inconsistent return is for sulphur recovered, not as elemental sulphur but as other products (e.g. gypsum). In the 2002 survey this has a comparatively high value and in 2006 a relatively low value compared to 1998.

The overall average sulphur content of the European crude intake is below 1% and had a value of 0.91% w in both 2002 and 2006 compared with 0.97% w in 1998. The reanalysed data for 1998 and 2002 agree with the earlier reports. The sulphur content of the other intakes was 0.81% in 1998⁶, 0.55% in 2002 and 0.72% in 2006.

The sulphur mass closures were good, noting that for individual refineries they are very sensitive to the value given to the annual average sulphur value in the crude intake. The value of 99.5% for 1998⁷ is very good. The recomputed value of 97% in 2002 is better than the originally reported 91.9% and the 2006 figure is 93.2%. The individual refinery balances were more varied.

Table 2 Refinery sulphur intake and output

		1998	2002	2006
Intake	S in Crude kt(S)	4901	2515	3788
	Other kt(S)	307	194	395
S content	Crude %	0.97	0.91	0.91
	Other %	0.81	0.55	0.72
Output	Products for combustion kt(S)	1926	809	1361
	Products for non-combustion kt (S)	757	233	493
	Recovered as elemental sulphur kt(S)	2053	1289	1880
	Recovered as other sulphur compounds kt(S)	71	149	9
Emitted at Refinery	All sources kt(S)	374	150	156
TOTAL	OUT kt(S)	5181	2629	3900
	IN kt (S)	5207	2709	4183
	RATIO %	99.5	97.0	93.2

A sensitivity study was carried out that eliminated refineries having a sulphur balance of less than 80%. This changed the balances to (98.8%, 99.2%, 96.1%) and the number of refineries excluded were: 7, 12, 8 in the years 1998, 2002, 2006.

⁶ Reported as 0.69% in CONCAWE report 10/02,

⁷ Reported as 97.3% in CONCAWE report 10/02 with very slight difference in output 5122 c.f. 5181 kt(S)

To better establish trends in the distribution of sulphur between the different output modes we normalised the elements in this table to the sulphur intake. For robustness we repeated this with the sensitivity test data shown in brackets. If the “all” data and the “sensitivity” data have a similar value then the data can be considered robust.

Table 3 Fraction of sulphur intake going to different sources

		1998	2002	2006
Output	Products for combustion %S	37.0 (36.5)	29.8 (35.1)	32.5 (32.5)
	Products not for combustion %S	14.5 (14.6)	8.6 (10.4)	11.8 (12.6)
	Recovered %S	39.4 (39.2)	47.6 (45.1)	45.0 (46.9)
	Retained %S	1.4 (1.3)	5.5 (3.2)	0.2 (0.2)
Emitted at Refinery	All sources %S	7.2 (7.2)	5.5 (5.4)	3.7 (3.9)
Balance		99.5 (98.8)	97.0 (99.2)	93.2 (96.1)

This normalisation and sensitivity test very usefully confirm the robustness of the 1998 and 2006 data. It seems likely that the 2002 survey did not capture full information about sulphur in fuel products from some refineries surveyed, most likely in the higher sulphur content fuels such as bunkers. The sensitivity test results for 2002, which excludes 12 surveys, are much more consistent with the trend across the years.

We conclude that the survey shows:

- a progressive reduction in the amount of sulphur going out in products from ~37% of intake in 1998 to 32.5% of intake in 2006.
- an increase in the amount of sulphur recovered from 39.4% of intake in 1998 to ~46% of intake in 2006
- A decrease in the amount of sulphur emitted to atmosphere from refinery direct use from 7.2% in 1998 to 3.8% in 2006.

The sensitivity test figures for 2002 are everywhere consistent with the trend but do imply that there was a more marked increase in sulphur recovery in the period 1998 to 2002 than between 2002 and 2006.

The refinery emissions to atmosphere of oxidised sulphur arise from several combustion sources. The survey requests emissions from Stacks, Fluid Catalytic Cracking Units (FCCU), Sulphur Recovery Units (SRU) and Flares to be disaggregated and for remaining emissions to be categorised as Miscellaneous. The overall distribution of emissions from these sources is given in **Table 4** as a fraction of the refinery sulphur intake. It can be seen that the overall reduction in sulphur emissions derives mainly from a reduction in stack emissions by nearly 60% from 4.6% of intake in 1998 to 1.8-1.9% in 2006. FCCU emissions were fairly flat at a fraction 0.4% of intake, emissions from SRU decreased from 0.8 to 0.6% of intake, flaring decreased from 1.0% to 0.8%. Miscellaneous sources decreased from 0.4%

to 0.2% of intake. Again the numbers in brackets are from the sensitivity analysis removing those responses with the poorest sulphur balance. The biggest sensitivity is for the SRU emissions in 2002 and it seems likely that emissions were overstated for that year.

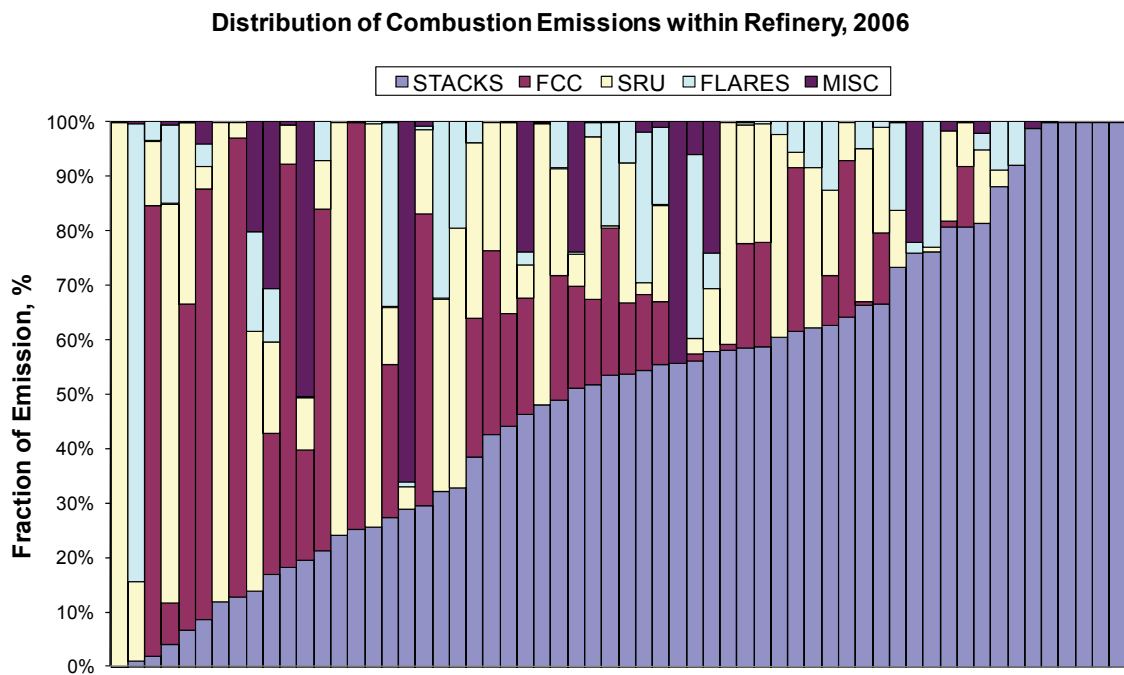
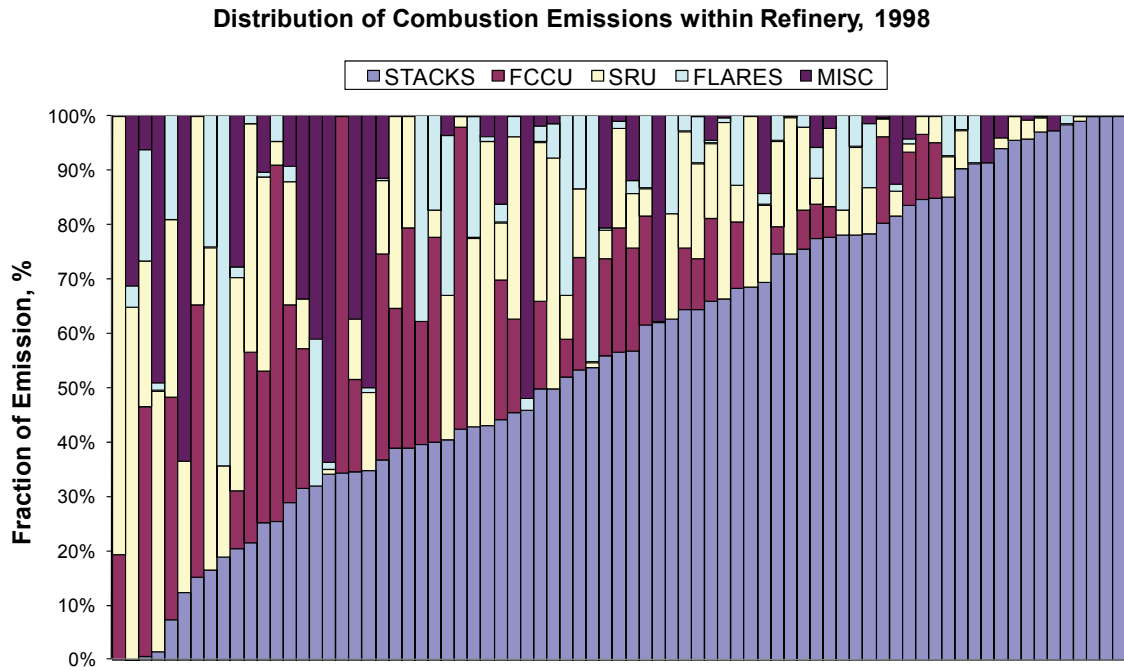
Table 4 Distribution of oxidised sulphur emissions between refinery sources as % of intake

Emissions from Combustion % of sulphur intake	1998		2002		2006	
Stacks	4.6%	(4.6%)	3.1%	(3.3%)	1.8%	(1.9%)
FCCU	0.4%	(0.4%)	0.2%	(0.3%)	0.4%	(0.4%)
SRU	0.8%	(0.8%)	1.3%	(0.8%)	0.6%	(0.6%)
Flares	1.0%	(1.0%)	0.6%	(0.7%)	0.8%	(0.8%)
Misc	0.4%	(0.4%)	0.2%	(0.3%)	0.2%	(0.2%)
All sources %S	7.2%	(7.2%)	5.5%	(5.4%)	3.7%	(3.9%)

The figures above are industry-wide aggregates. The distribution of these emission sources between refineries is highly variable because some refineries do not have a FCCU, some refineries are natural gas fired and have a lower stack sulphur emission as a consequence, some have cokers that add to the miscellaneous emission etc.

This heterogeneity is shown for the years 1998 and 2006 in **Figure 1**. The data is for all survey returns and these have been arranged in order of increasing stack emission as a proportion of total emission. A trend is evident and in 2006 stack emissions comprise a smaller fraction of the total emission for many refineries compared with 1998.

Figure 1 Distribution of refinery sulphur emissions between stacks, FCCU, SRU, flares and other sources. Results ordered by stack emission as fraction of total emission.

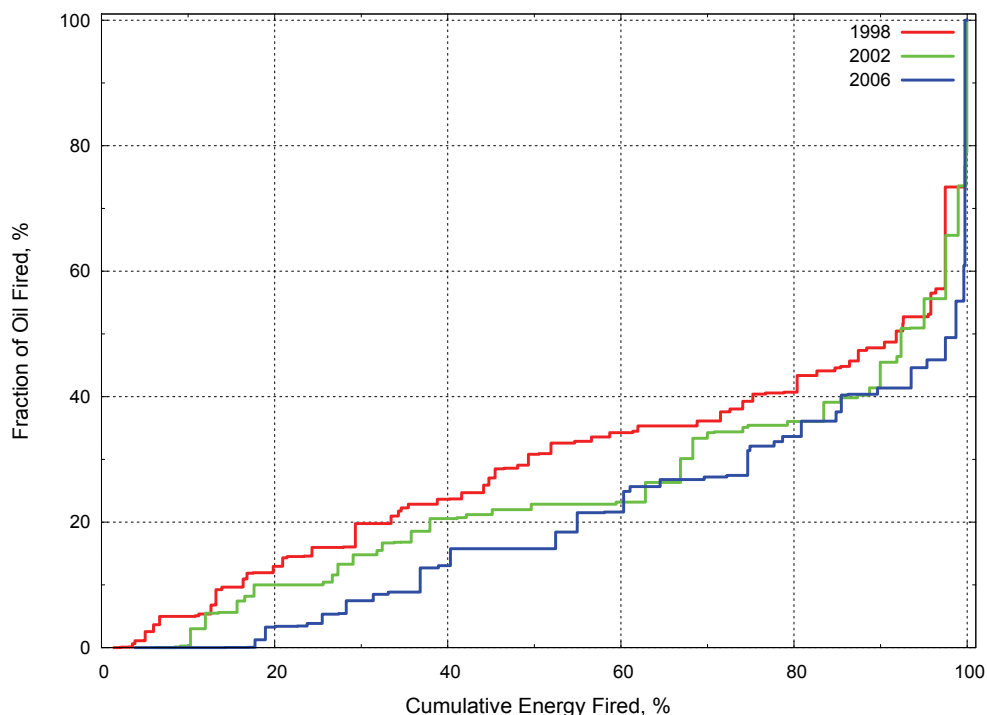


3. COMBUSTION EMISSIONS

Emissions that are a direct consequence of burning refinery fuels are of high regulatory importance. The main fuels used are oil, refinery fuel gas and imported natural gas. Sites with catalytic crackers recover energy by burning carbon deposited on the catalyst (coke). Data on this thermal input is not requested by the survey. There are other combustible streams that may have a low heating value due to their high nitrogen or carbon-dioxide content. The category “other fuels” encompasses such usage but may not capture the contribution from FCC coke.

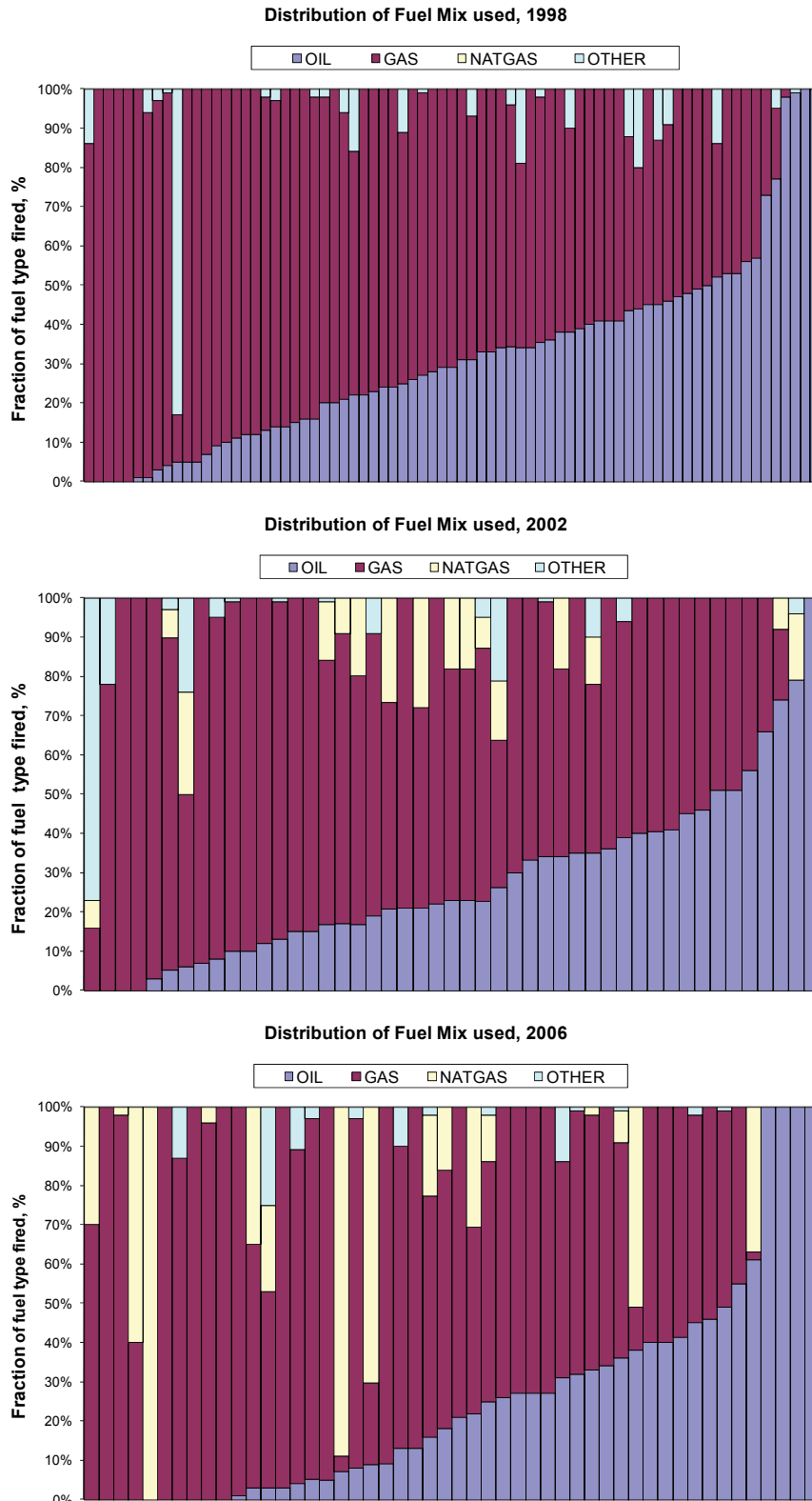
The amount of fuel oil fired in refineries has been steadily decreasing. The constraints on emissions imposed by emission limit values (e.g. for particulate matter) and the provision of the majority fuel concept under the large combustion plant directive realistically limits oil use to 50% of the thermal input of plants sized 50 MW or more. **Figure 2** shows the evolution in oil use over the period 1998 to 2006. There has been a general reduction since 1998 and the increase in the use of gas (almost 20% of heat fired was gas only in 2006) is evident.

Figure 2 Oil firing as a fraction of overall refinery fuel combustion



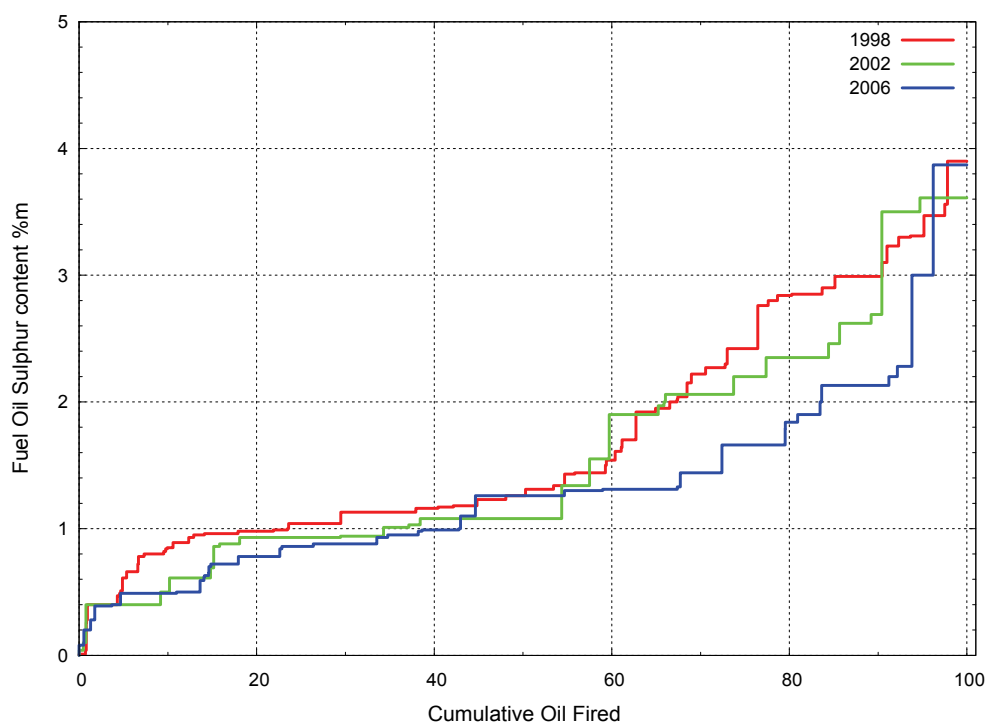
The results for 2002 seem consistent with the trend. The average oil use in 1998 was 28.5% of firing, in 2002 it was 23.5% and in 2006 19.1%. The survey has requested a split between refinery fuel gas and refinery natural gas usage although this has not been reported previously. There were no returns showing natural gas use in 1998 but some penetration in 2002 and more in 2006 with one refinery showing only natural gas use. Results are shown in **Figure 3**.

Figure 3 Evolution of fired fuel mix, 1998 - 2006



The sulphur content of the oil used in refineries is shown in **Figure 4**. About 50% of oil fired has a sulphur content of ~1% or less and this fraction has been remarkably consistent over the surveys but what is marked is the decline in the “high” sulphur usage with only 10% of refineries using oil with more than 2% sulphur in 2006 compared with 20% in 2002 and 35% in 1998. The average sulphur content was 1.7% in 1998, 1.34% in 2002 and 1.33% in 2006.

Figure 4 Sulphur content of refinery fuel oil



An actual breakdown of fuel use is given in **Table 5**. Results for 2006 are based on a subset of returns as a breakdown of emissions/fuel use by stack height was not available for several refineries. This shows a rise in the use of gas⁸ and redistribution of energy use across the process plants. Gas use has increased most in the smaller (< 50 MW) units with a corresponding fall in oil use. Results for 2002 are not consistent with the trend between 1998 and 2006 showing less gas use in the large combustion plant and more in the small combustion plant. The reported sulphur content is also lower than a linear trend would suggest.

⁸ Sum of refinery fuel gas and natural gas

Table 5 Breakdown of energy use and of fuel sulphur content by fuel type and stack size

	1998		2002		2006	
	Energy %	Fuel sulphur content %m	Energy %	Fuel sulphur content %m	Energy %	Fuel sulphur content %m
Oil < 50MW	2.2%	1.73%	6.9%	0.75%	2.7%	0.95%
Oil > 50MW	26.3%	1.70%	16.7%	1.59%	16.5%	1.39%
All Oil	28.5%	1.70%	23.6%	1.34%	19.1%	1.33%
Gas < 50MW	12.6%	0.11%	29.3%	0.03%	22.7%	0.14%
Gas > 50MW	53.2%	0.07%	39.3%	0.04%	56.4%	0.05%
All Gas	65.8%	0.08%	68.7%	0.04%	79.2%	0.07%
Other < 50MW	0.3%	0.51%	2.9%	0.27%	0.5%	0.72%
Other > 50MW	5.4%	0.78%	4.8%	0.12%	1.2%	0.19%
All Other	5.7%	0.77%	7.7%	0.18%	1.7%	0.34%

It is useful to construct a refinery combustion bubble concentration for SO₂ from the results although this can only be imperfectly done using annual emissions. It is necessary to assume representative average fuels and to calculate an equivalent dry flue gas volume at 3% oxygen for each tonne of fuel use. This methodology is described in **Appendix 1**.

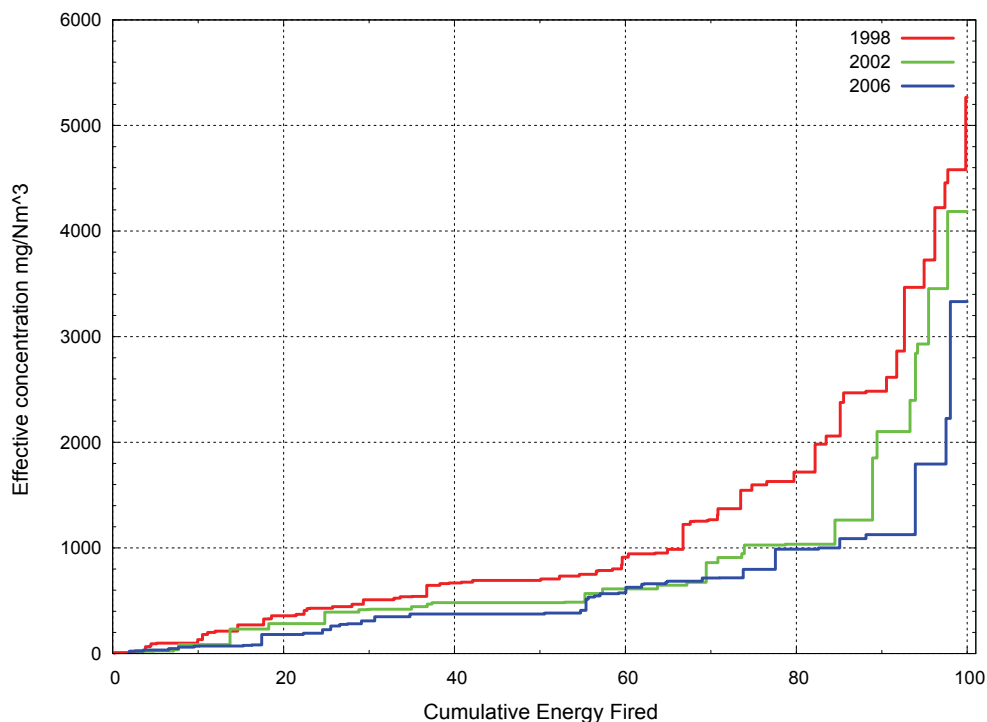
The bubble presented here follows the definition in the Large Combustion Plant Directive (LCPD). It is calculated from the emissions from stacks with connected plant of 50 MW or more thermal capacity. The bubble concentration is estimated using the annual emission of sulphur (as SO₂) divided by the total fuel burned (expressed as a fuel oil equivalent (foe)) itself multiplied by a typical flue gas volume (Nm³/kg foe) at 3% oxygen. The survey results are ordered by the bubble value and plotted against the cumulative heat fired (foe) normalised by the total foe fired.

The bubble excludes emissions from catalytic crackers, from sulphur recovery units, stacks having less than 50 MW thermal input and flares. We note that CONCAWE has proposed a broadening of the bubble definition in the reference document for Best Available Techniques for Refineries (refinery BREF), consistent with some national regulations, to include all sources of SO₂ emission. In this respect it would be useful for future surveys to include sufficient information on dilutions and associated heat release for the whole bubble to be calculated.

Figure 5 shows how the bubble for large combustion plant on refineries has evolved since 1998. A value of 1000 mg/Nm³ is a bubble applicable to existing units > 50 MW in size burning internal refinery fuels as defined in the LCPD. It is clear that much progress has been made to reduce the higher values and refineries accounting for ~90% of energy fired for process purposes meet the LCP bubble limit of 1000 mg/Nm³.

The average⁹ LCP combustion bubble concentration for 1998 was reported to be 1125 mg/Nm³ in CONCAWE report 10/02 [6] and recalculated as 1249 mg/Nm³ in CONCAWE report 02/07 [7]. It was calculated here to be 1116 mg/Nm³. The average for 2002 was reported to be 800 mg/Nm³ in CONCAWE report 02/07 [7] and is calculated here to lie between 791 and 816 mg/Nm³ according to whether all surveys are used or whether refineries with a poor sulphur balance are excluded. For 2006 the calculated value was 594 mg/Nm³. Note: this was based on only 80% of the overall refinery oxidised sulphur emission due to missing stack and fuel information in some responses. Some degree of caution therefore has to be exercised when citing a value for 2006 but the implication is that the average LCP bubble concentration could have reduced by a factor of almost 2 since 1998.

Figure 5 Estimated distribution of annual average LCP SO₂ concentrations



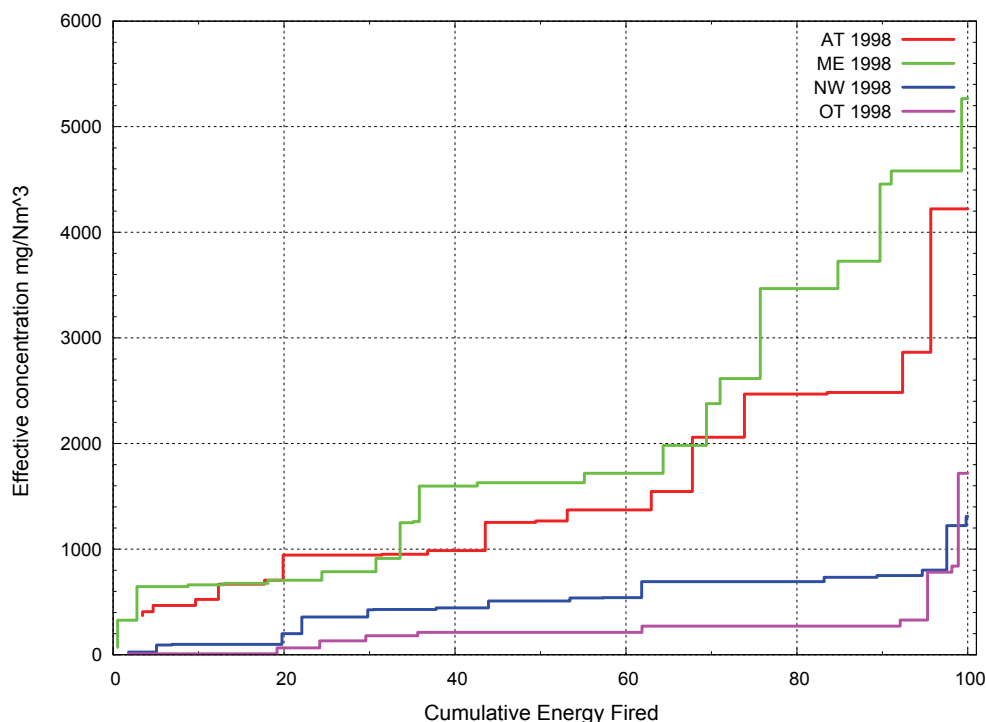
⁹ This is a weighted average using all refinery production not an arithmetic average across refineries.

In previous reports a regional distribution of average LCP SO₂ concentrations was reported dividing refinery groups into regions following the model of a 1995 study on refinery sulphur management for the European Commission. At that time there were 12 members of the European Community:

- Northwest Europe (defined as Belgium, Netherlands, Germany and Denmark)
- Atlantic (defined as Ireland, United Kingdom, Portugal and the Atlantic Coasts of France and Spain)
- Mediterranean (the Mediterranean coast of Spain, France, Italy and Greece)
- Others (remaining surveyed areas).

The following figures show the evolution of the geographic pattern over the period 1998 to 2006. It is evident that the historic variation between the refineries in the Mediterranean and Atlantic regions where there is less environmental sensitivity to sulphur deposition and those in the North-West region where sensitivity is higher has reduced significantly in time. The number of reports is rather low in this disaggregation to present results in this way but of the reporters in 2006 only 2 in the Mediterranean and 2 in the Atlantic and 1 in the North West had an average SO₂ concentration¹⁰ greater than the 1000 mg/Nm³ option to be met by 2008 under the LCPD.

Figure 6 Regional variation in average LCP SO₂ concentration in 1998



¹⁰ Note we make important fuel mix assumptions in calculating the average LCP SO₂ and for two of the enumerated refineries (Atlantic, North West) the deviation we calculate from 1000 mg/Nm³ is very small.

Figure 7 Regional variation in average LCP SO₂ concentration in 2002

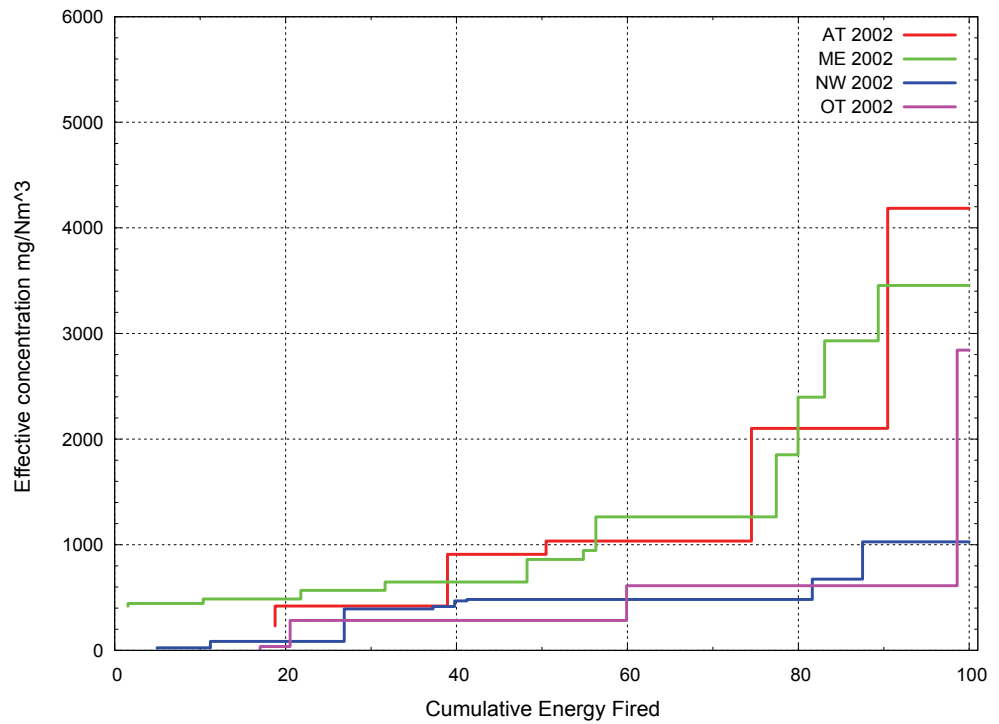
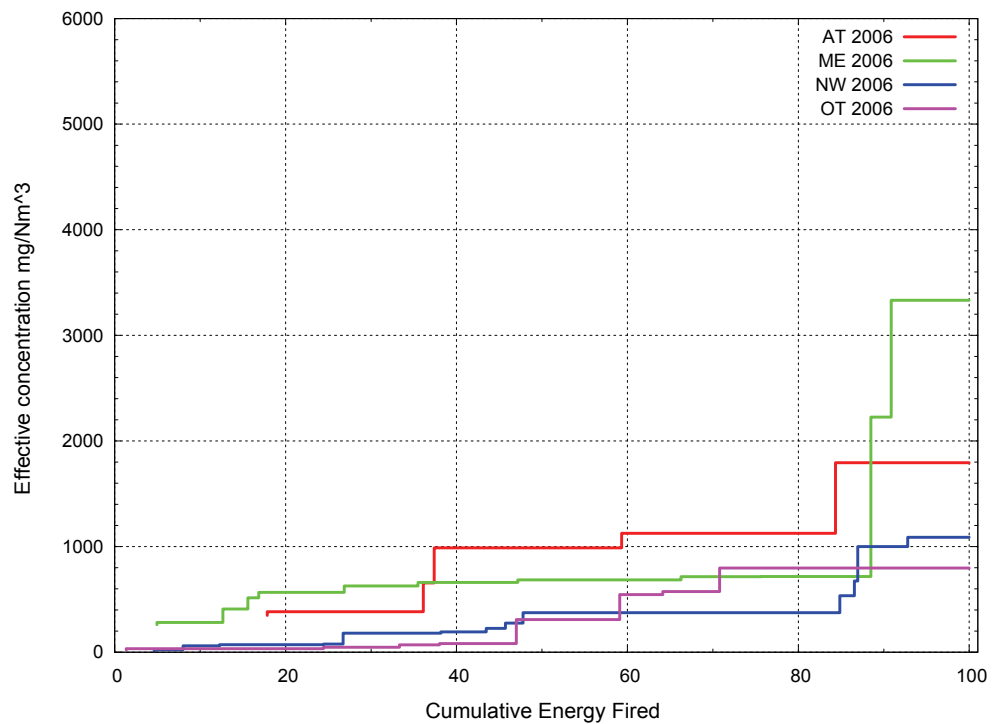


Figure 8 Regional variation in average LCP SO₂ concentration in 2006

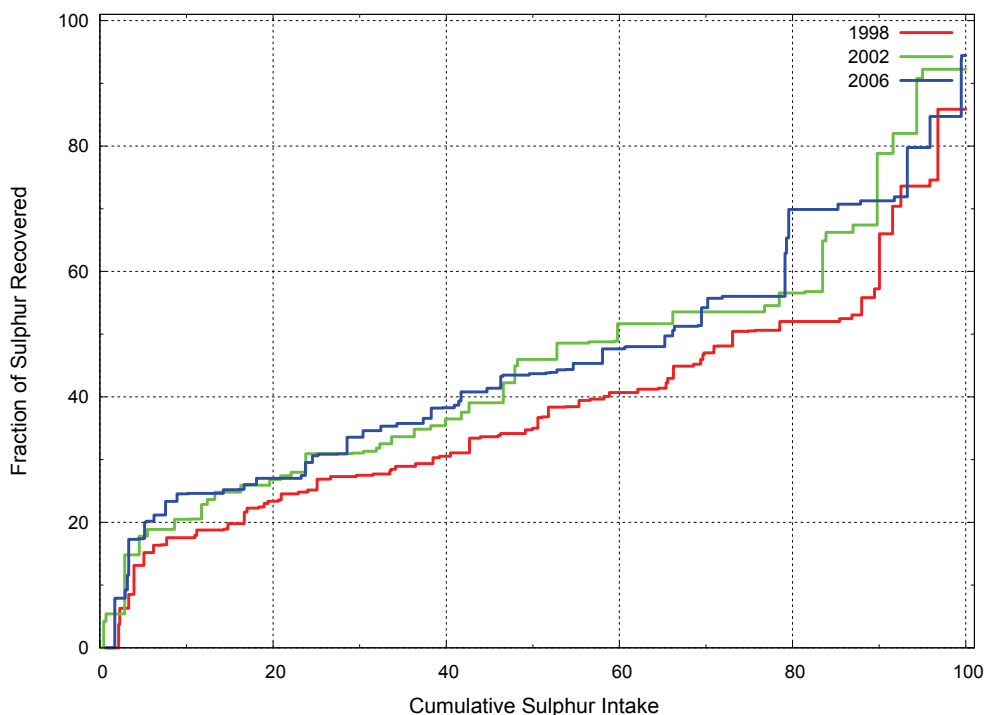


4. SULPHUR RECOVERY

The reduction in both refinery atmospheric emissions and in the product sulphur content while maintaining throughput with a given crude slate means that sulphur recovery must improve. As shown in **Table 3**, the recovery¹¹ in 1998 was calculated to be 39.3% of total sulphur intake, in 2002 to be 46.3% and in 2006 to be 46%.

The distribution of recovery achieved on a per-refinery basis is shown in **Figure 9**. The returns for 2006 give a very similar profile to the returns for 2002 and both show the shift to increased recovery compared to 1998.

Figure 9 Distribution of sulphur recovered



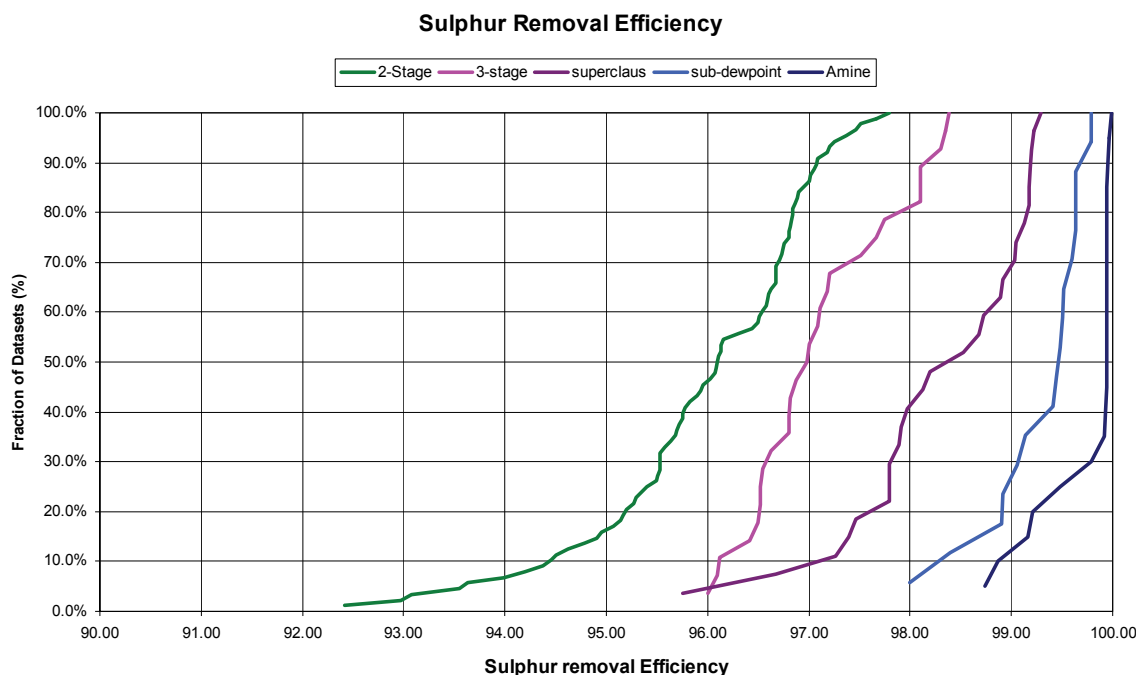
We can investigate how the sulphur recovery process itself has changed in this period. The sulphur survey allows the annual efficiency of the installed sulphur removal capacity to be assessed by taking the ratio of the sulphur recovered as a solid product to the sulphur entering the sulphur recovery unit (SRU) as feed-stock.

The SRU generally comprises a two or three stage Claus unit followed by a tail-gas treatment unit. The ability of these units to remove sulphur was investigated for the CONCAWE contribution to the refinery BREF review [8] by Sulphur Experts. Their consultancy advises on operability of SRU and they make measurements from which efficiency can be derived as part of their diagnostic work. **Figure 10** shows the distribution of measured efficiencies for the different plant components starting with the 2 and 3-stage Claus plants and then adding a tail gas

¹¹ These figures are the average of the whole survey results and the reduced survey results in Table 3.

units considered were the SuperClaus unit, the generic type sub-dew point unit and the generic type amine treatment unit.

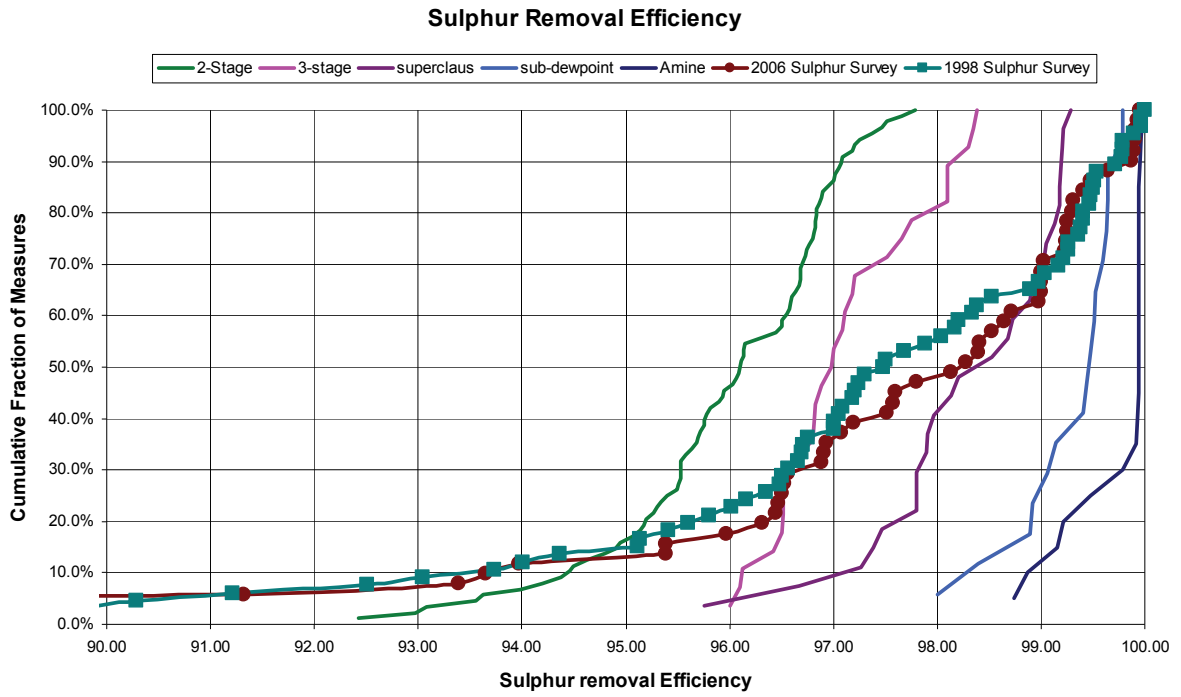
Figure 10 Efficiency of the different SRU components – Claus and Claus + tail gas unit combined



It can be seen that the removal efficiencies up to 97.5% can be achieved with a 2-stage Claus unit and the median efficiency is 96%. A 3-stage unit improves the maximum efficiency to 98.4% and the median to 97%. To go further requires a tail-gas unit. A SuperClaus unit will increase efficiency to 99.3% at maximum and the median to 98.4%. Sub-dewpoint process to 99.7% maximum and 99.5% median and amine units to greater than 99%. These figures come from short duration measurement campaigns on European refinery units.

Although the annual efficiency estimates are not necessarily comparable to the short duration measures it is interesting to overlay the 1998 and 2006 survey results on the data of **Figure 10**. The results are shown in **Figure 11**. There is a marked improvement in the recovery efficiency in the mid ranges between 97% and 99%. This could indicate a preferred investment in SuperClaus units as, to generate the observed increase in efficiency would require upper quartile performance of a 3 stage Claus unit. Some 20% of sites were reporting annual efficiencies above the SuperClaus maximum and 10% above the sub-dew point process maximum. Overall this could indicate a majority use of SuperClaus as a tail gas treatment and approximately equal sub-dew point process and amine treatment units. About 50% of returns indicated efficiencies lower than the bottom quartile of the SuperClaus curve in 2006 and this possibly indicates that there is a substantial base of SRUs comprising a Claus process only.

Figure 11 Overlay of sulphur survey results on the SRU performance curves

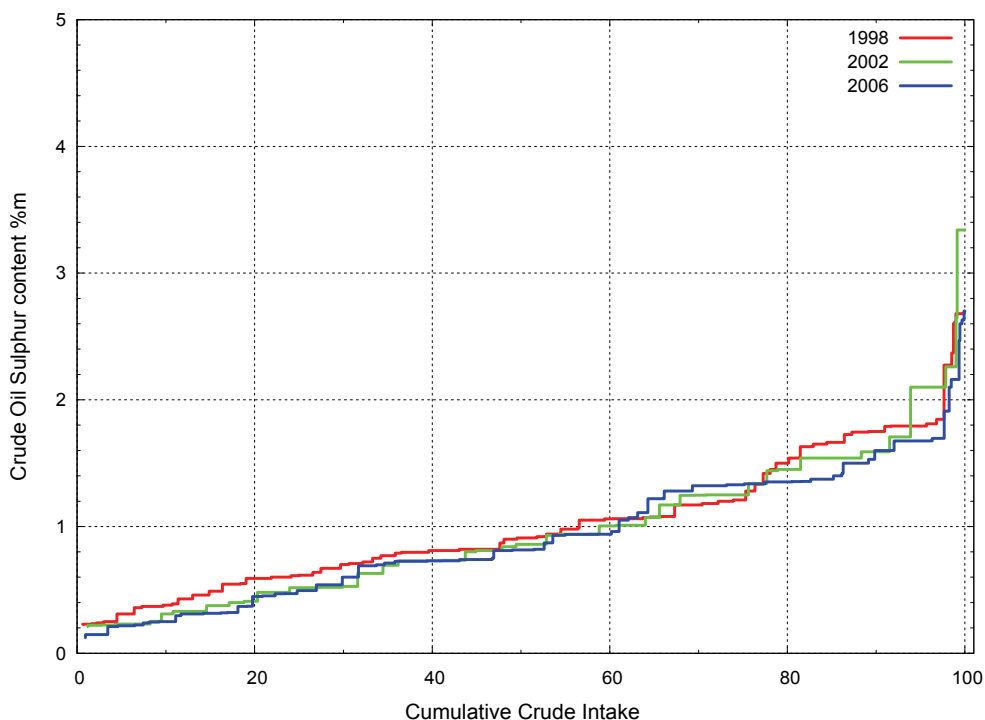


5. DISTRIBUTION OF SULPHUR IN STREAMS

A third of the sulphur entering the European refineries still leaves in the fuel product streams so it is of interest to examine the overall distribution of sulphur in these streams and in the crude intake.

Figure 12 shows that the annually averaged crude slate for sulphur for Europe has hardly changed between 1998 and 2006. This is to be expected because refineries are designed to cope with a relatively narrow crude diet and crude will be procured to meet this requirement. The average crude sulphur content from **Table 2** is 0.90% in 2006 and 2002, down from 0.97% in 1998. About 60% of refinery throughput is lower sulphur crude. A small fraction of refineries appears to specialise in treating high sulphur crude, although since 1998 there appears to be a trend to sweeten the annual average crude diet in the 20% of crude with the highest sulphur content (crudes with a sulphur content above ~1.4%).

Figure 12 Distribution of sulphur in crude oil



Previous reports presented the European distribution of crude oil sulphur content in order to show that there are important geographic variations in crude oil supply. **Figure 13 - Figure 15** confirm that there is continued variation in the sulphur content in crude intake across Europe. The Mediterranean refineries use a higher sulphur content crude than the Atlantic refineries. The variation across the years 1998 to 2006 is comparatively small.

Figure 13 Regional variation in the sulphur content of refined crude 1998

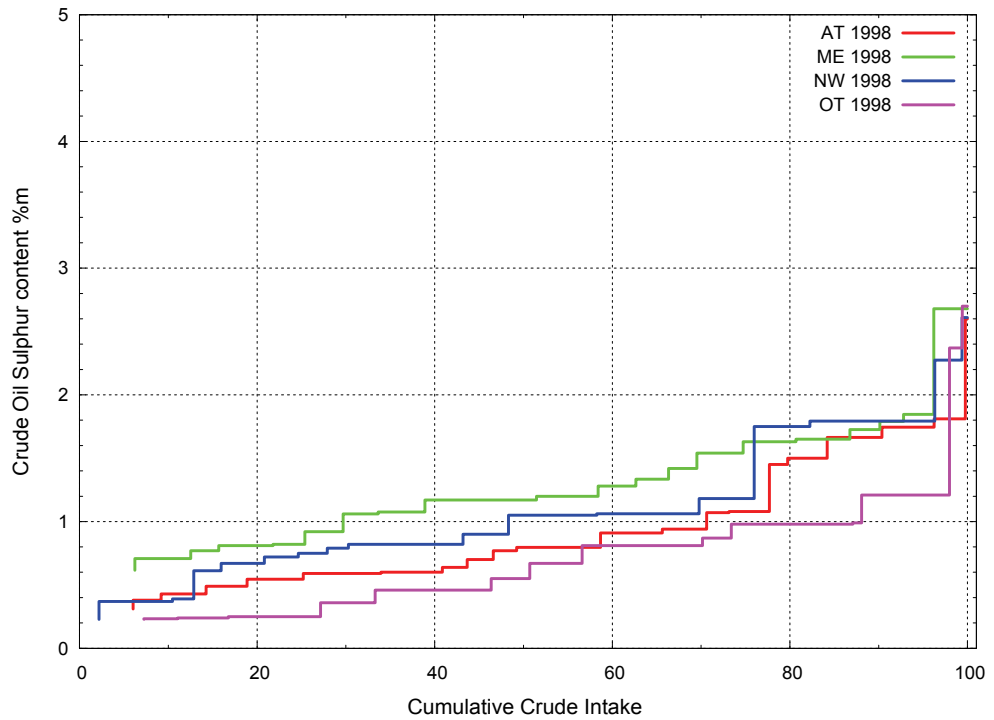


Figure 14 Regional variation in the sulphur content of refined crude 2002

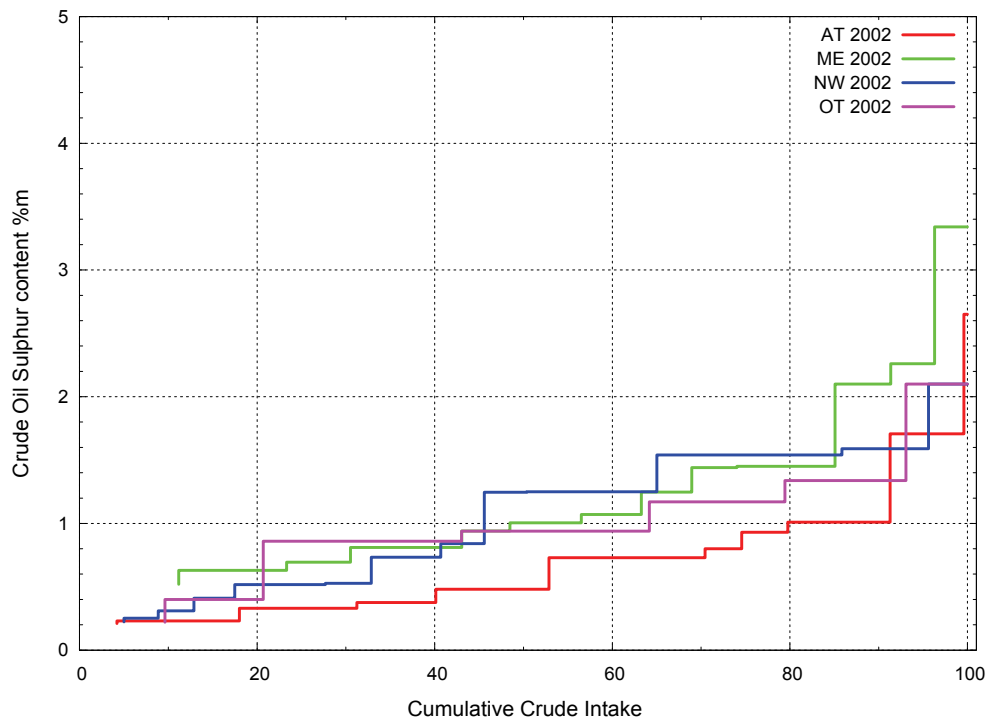
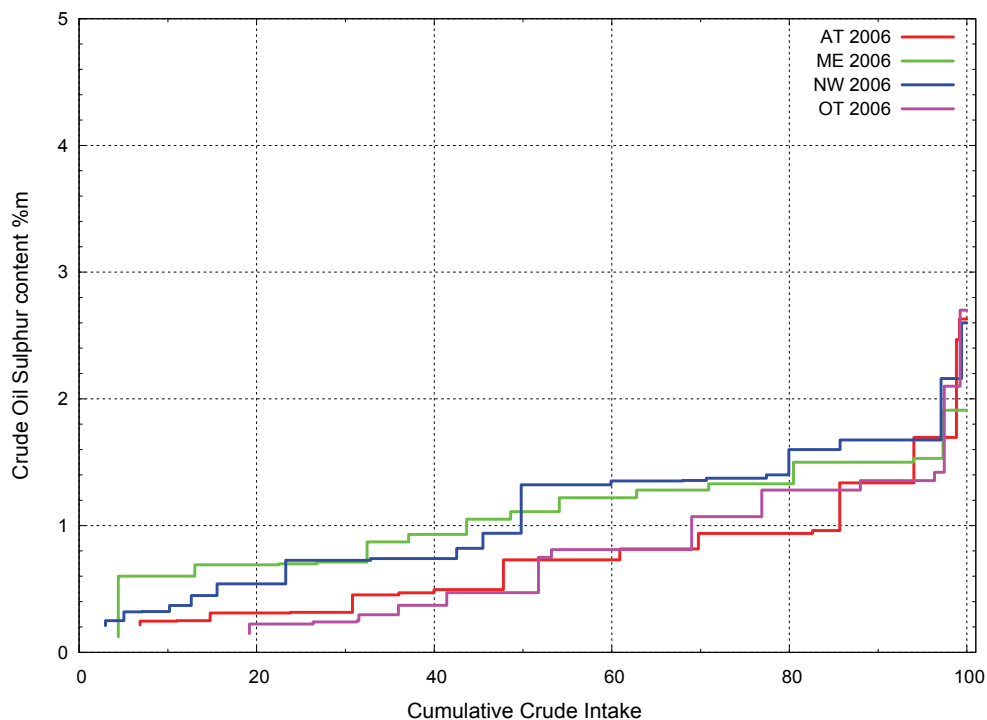
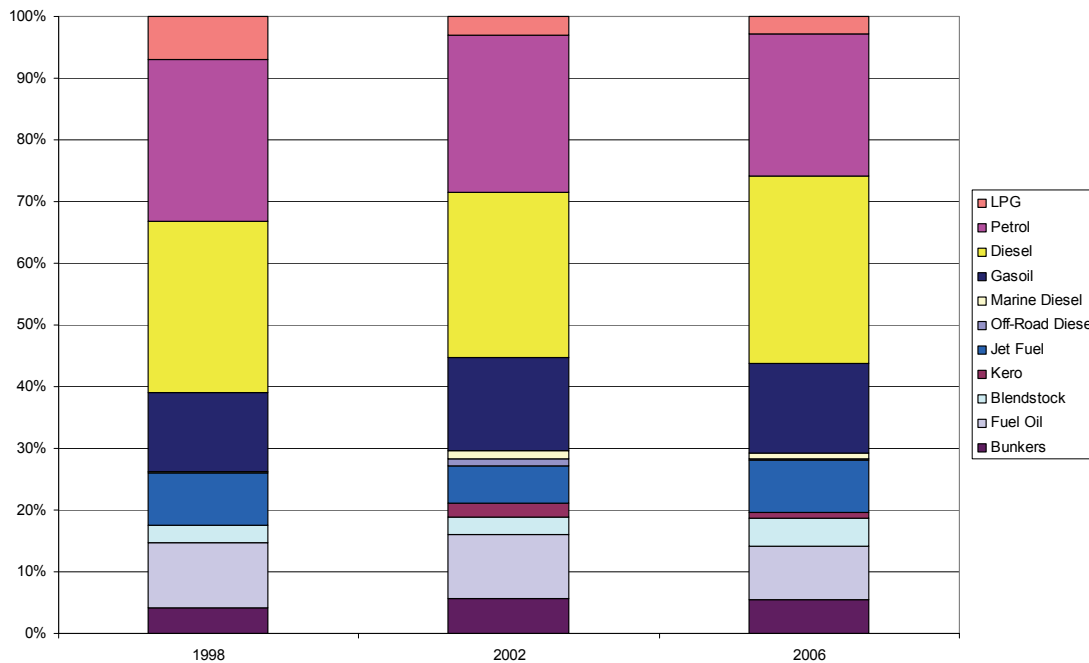


Figure 15 Regional variation in the sulphur content of refined crude 2006



The product slate obtained from the three surveys is shown in **Figure 16**. In 1998 the marine diesel, off road diesel and kerosene streams were not disaggregated. The main refinery products are road transport fuels, heating gasoils, aviation fuel and heavy fuels (fuel oil and bunkers). The evolution of the slate can be seen. There is a reduction in gasoline (26.4% to 23%) and increase in on-road diesel (from 27.7 to 30.55%) in the period 1998 to 2006. The gasoil pool increases from 40.6% to 46.2% over the period. The fuel oil pool (heavy fuel + bunkers) decreases slightly from 14.7% in 1998 to 14.1% in 2006. Reported jet fuel is the same in 1998 and in 2006 but the overall kerosene pool increase slightly from 8.6% to 9.4%. The production of LPG decreases from 6.9% to 2.8%, perhaps linked to the increased use of refinery fuel gas. The fraction of blend stocks increases from 2.8% to 4.5%.

Figure 16 Product slate from 1998 to 2006, proportion by mass %



5.1. ROAD TRANSPORT FUELS

In previous sulphur survey reports the road diesel component was not presented as a separate item with the explanation that disaggregation was not reliable. Instead all gasoil items were combined and reported as a general gasoil pool. In this report the on-road diesel and heating gasoil streams have been disaggregated although we must introduce the caveat that there may be some unappreciated inadequacies in the reporting from previous years. The generalised gasoil pool is reported for consistency with earlier reports and comprises the combination of the above with off-road diesel and marine gasoil streams but these latter are minor contributors overall.

Figure 17 Distribution of sulphur in gasoline

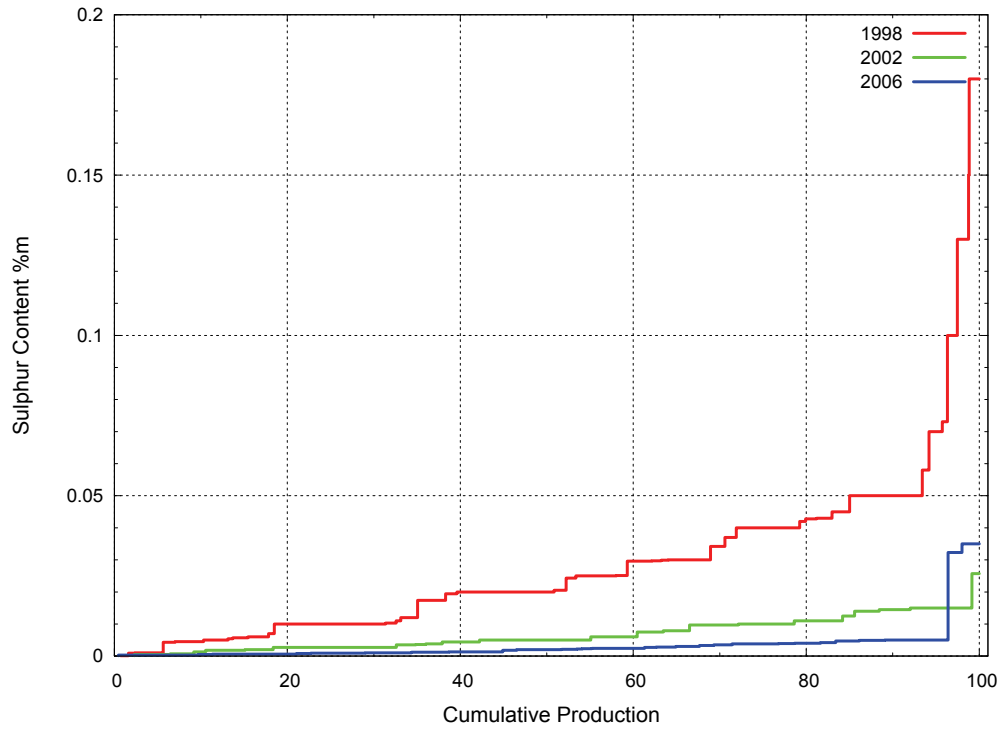


Figure 17 shows the evolution of sulphur in produced gasoline. In 2006 95% of production had a sulphur content of 0.005% m (50 ppm) or lower. The substantial decrease since 1998 reflects EU legislation for the sulphur content to decrease to 150 ppm in 2000 and 50 ppm in 2005. There was also a requirement for 10 ppm fuel to be widely available from 2005. The survey gives 30% of production meeting this specification in 2006.

Figure 18 Distribution of sulphur in on-road diesel

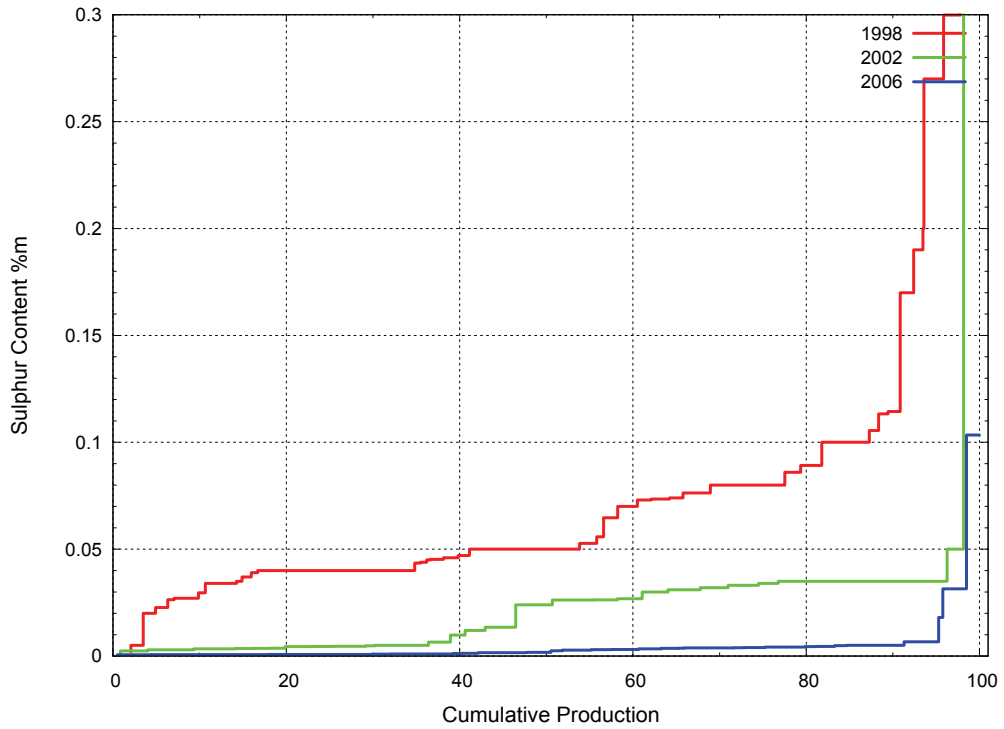


Figure 18 shows the distribution of sulphur in on-road diesel. As for gasoline the changes reflect the requirements of the EU market which requires that from 2005 the maximum sulphur content of diesel shall be 50 ppm and that substantial supplies of 10 ppm fuel should be made available ahead of full implementation in 2009. Of the production in 2006, 98% had a sulphur content below 50 ppm and 40% below 10 ppm.

Figure 19 Distribution of sulphur in marine fuel

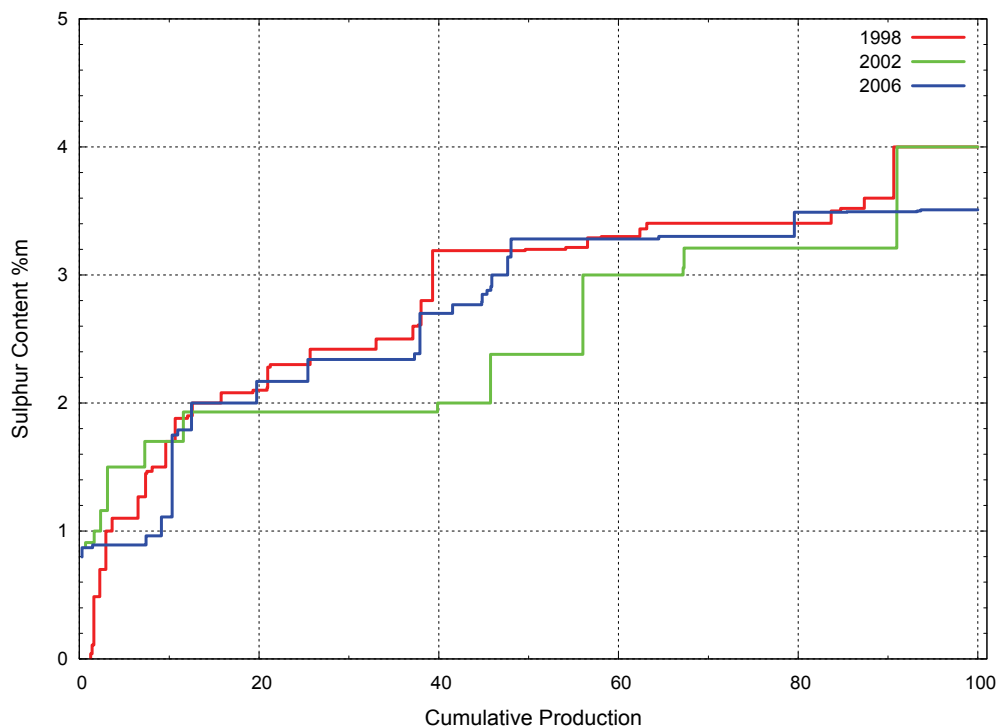


Figure 19 shows the distribution of sulphur in marine bunker fuels. The distribution for 1998 and for 2006 are very similar whereas the results for 2002 show generally lesser values. It was concluded in CONCAWE report 02/07 [7] from the 2002 analysis that there was a downward trend in the sulphur content of bunker fuel. As the current analysis reproduces the 1998 and 2002 results reported in CONCAWE report 02/07 [7] we suspect these differences reflect the smaller number of respondents. Not all refineries produce marine bunker fuel and the number of responses for marine fuels was 44 in 1998, 17 in 2002 and 27 in 2006. The finding that the marine bunker content is predominantly above 2% sulphur is significant given the ratification of Marpol Annex VI in 2005 which required that only fuels having a sulphur content below 1.5% could be used in Sulphur Emission Control Areas from the Autumn of 2007. The results of the next Sulphur Survey will be especially interesting with regard to the further requirement to reduce the sulphur in fuel burned in special areas to 1% in 2010 and 0.1% in 2015.

Figure 20 Sulphur distribution in kerosene

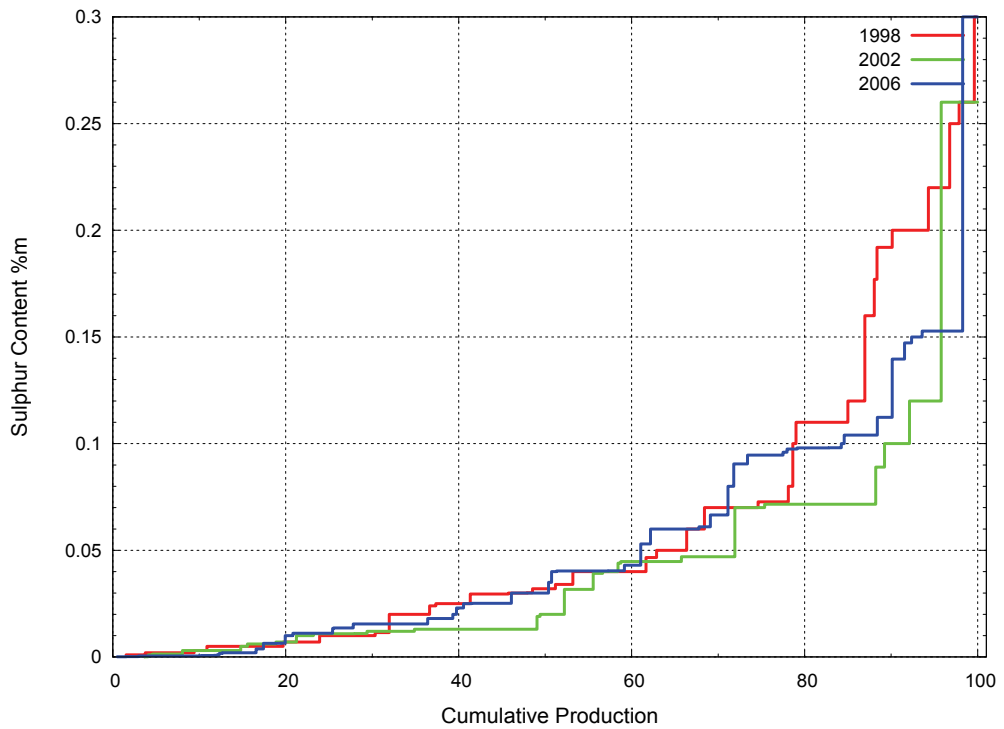


Figure 20 shows the distribution of sulphur in kerosene. The world-wide specification for Jet fuel is 0.3%. The results of the three surveys suggest very little change in the production of sulphur below certainly 0.05% m sulphur (500 ppm) and probably 0.1% m (1000 ppm) if the limited nature of the 2002 survey is accounted for. There does seem to be a reduction in the production of fuel having a sulphur content above 0.1% sulphur which comprises about 20% of the total. The sulphur in liquid fuels directive limits heating oil sulphur content to 0.2% sulphur in 2000 and 0.1% sulphur in 2008 and, in some European markets, kerosene can be used for this purpose.

5.2. FUEL OILS

Figure 21 shows the distribution of sulphur in gasoils used for heating purposes. The sulphur limit is 0.2% sulphur (since 2000) to decrease to 0.1% in 2008. The survey shows very little evolution in the distribution since 1998 with substantially all production less than 0.2% m. About 25% is less than 0.1% so we would expect to see a significant change in the next survey.

Figure 21 Distribution of sulphur in heating gas-oil

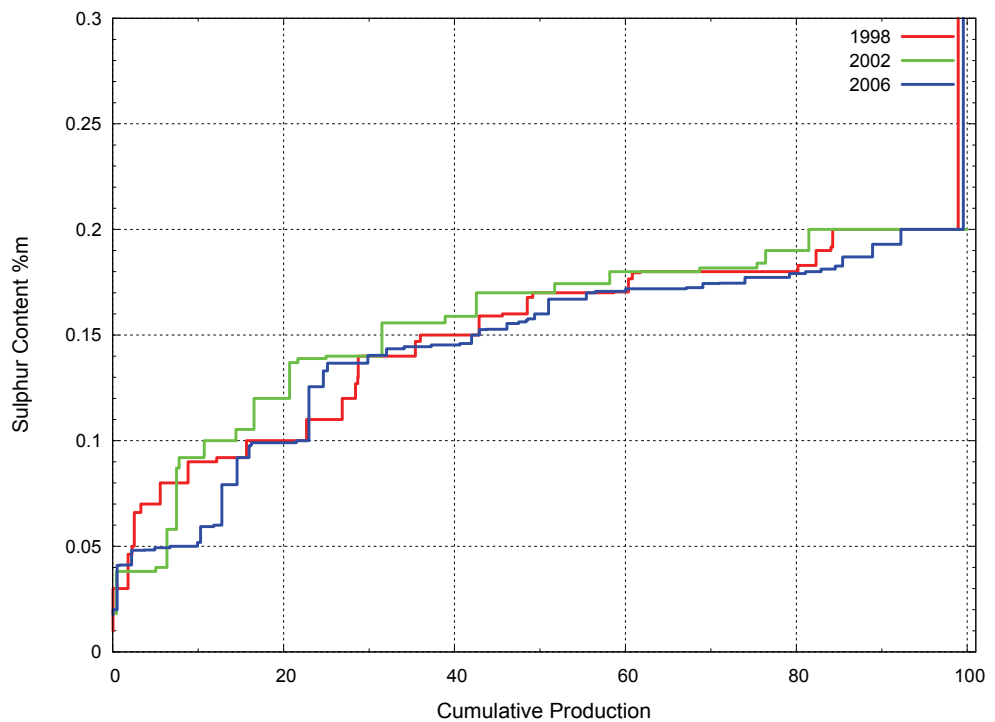
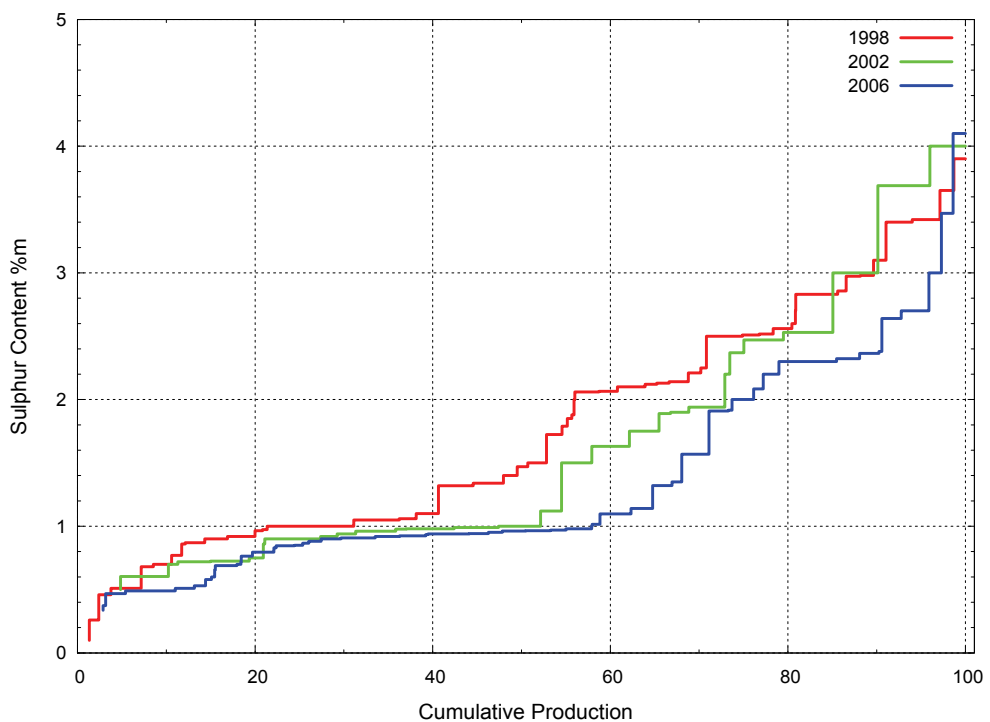


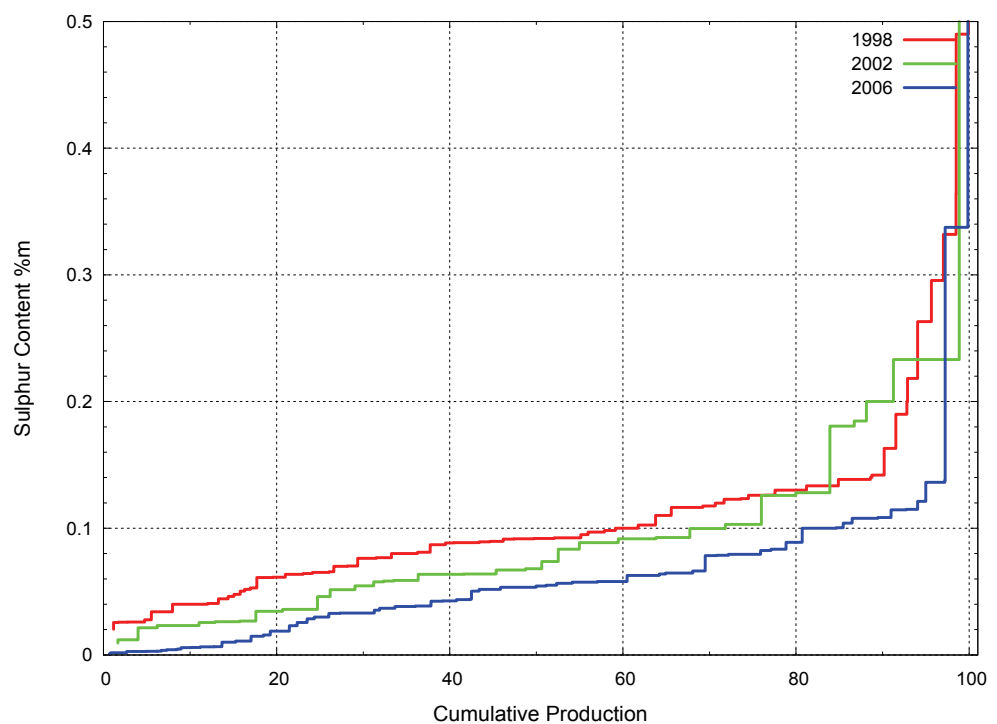
Figure 22 shows the distribution of sulphur in fuel oil. Under the terms of the Sulphur in Liquid Fuels Directive, since 2003, heavy fuel oil has had to have a maximum sulphur content of 1% for general use in Europe. Fuel oil having a sulphur content greater than 1% but less than 3% is can be used under permit in installations with appropriate emissions abatement equipment or it may be exported. **Figure 22** shows that the fraction of production meeting this specification has increased from ~ 30% in 1998 to 50% in 2002 to over 60% in 2006.

Figure 22 Distribution of sulphur in fuel oil



For completeness with previous surveys the sulphur content of the overall gasoil pool is shown in **Figure 23**. The sulphur content is evaluated as the weighted average of all the gasoil streams (heating oil, automotive diesel, off-road diesel and marine gasoil). The results show a progressive reduction since 1998 and in 2006 the overall pool has 90% of production less than 0.1%. This is heavily influenced by the automotive fuel production as we have seen and should NOT be interpreted as indicating the widespread availability of 0.1% sulphur fuel.

Figure 23 Sulphur in the overall gasoil pool



5.3. OTHER

The sulphur content of produced butanes and propanes is shown in **Figure 24**. The 2006 and 2002 results are very similar and show an overall drop so that 70% of the production has a sulphur content of 0.2 ppm or less (data rounded to 1 decimal place) showing a reduction since 1998 across the whole production range.

Figure 24 Sulphur content of LPG

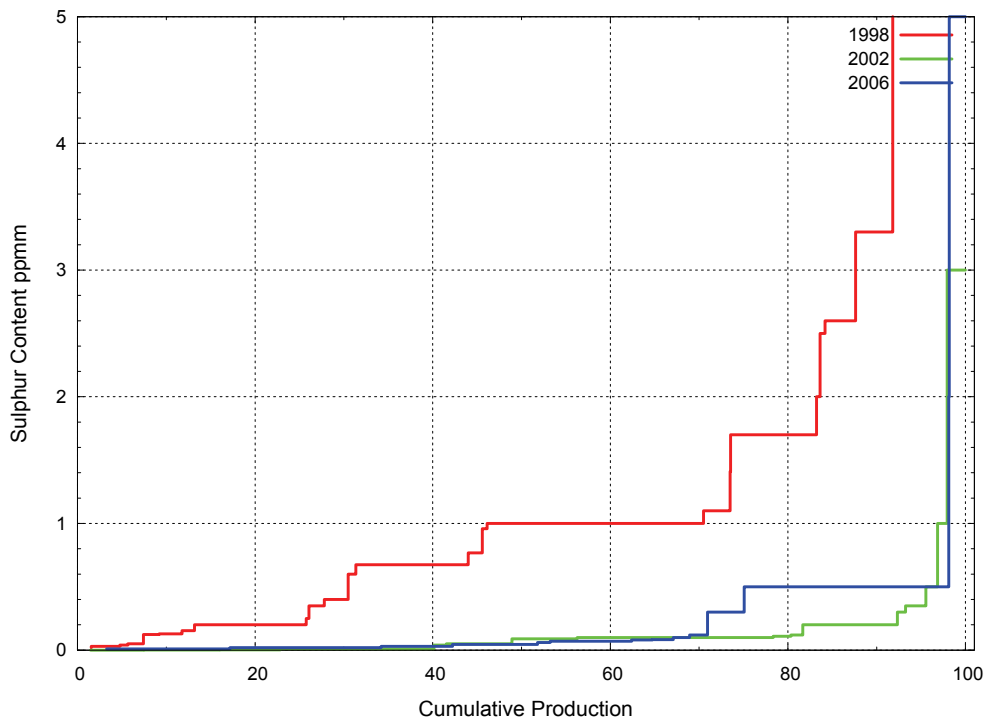
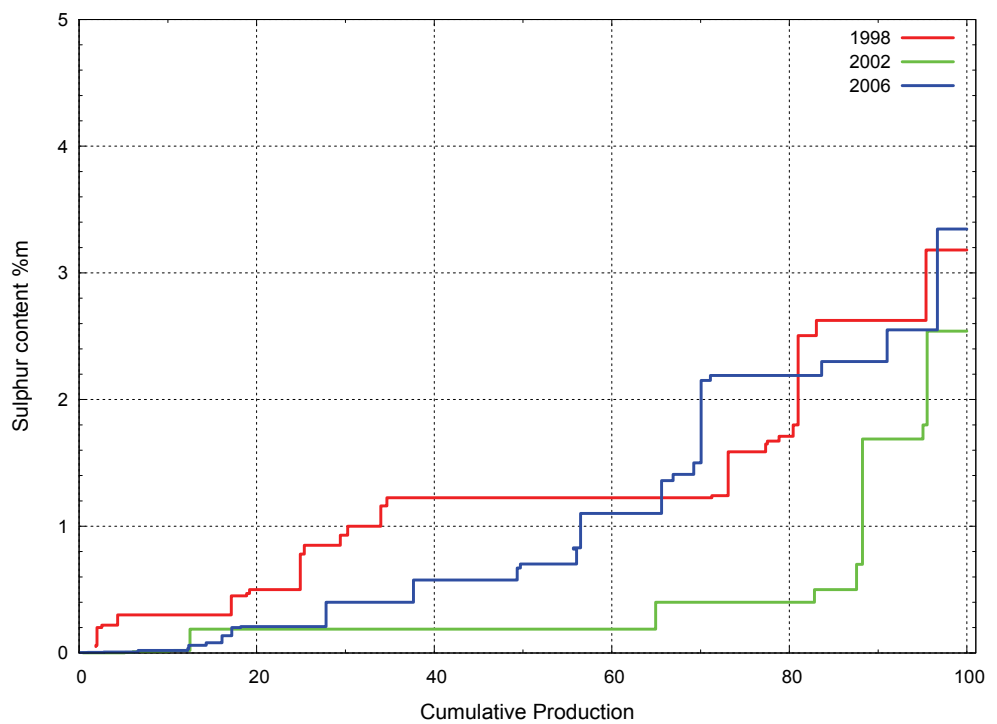


Figure 25 shows the distribution of sulphur in intermediates and blend stocks. The reporting on this was relatively sparse and the 2002 returns seem to be out of line with the 1998 and 2006 returns. There seems to be a bimodal distribution with ~30% of production having sulphur content above 2% and ~65% having sulphur content below 1% in 2006. The trend from 1998 is for a decrease in sulphur content for that material having sulphur content less than ~1% and a small increase in the amount of production having sulphur content above 2% sulphur.

Figure 25 Sulphur content of intermediates and blend stocks



6. CONCLUSIONS

The sulphur survey response for the year-end 2006 has been analysed together with the responses for previous surveys in 1998 and 2002. A reanalysis of the previous surveys was performed to ensure a consistent base for trends to be established. Results obtained were very close to those reported previously.

The 2006 survey response was 67 refineries compared¹² to 46 in 2002 and 77 in 1998 and represented a refinery intake equivalent to 68% of the OECD European refinery capacity which we have used as a proxy for the refining capacity across the sulphur survey countries.

The survey provides an overview of the distribution of sulphur between the refinery products, the recovery of sulphur in the refinery and the emission to atmosphere from refinery processes.

This report has evolved from the fixed format of previous survey reports and has included a more detailed description of sulphur recovery units and the product streams as it has disaggregated on-road diesel and gasoil used for heating from the general gasoil pool.

A limited disaggregation by geographic region within Europe, as used in previous reports, has been carried out. It shows convergence of environmental performance as would be expected in the enlarged EU and a continued difference in the sulphur content of refined crudes by region.

The period 1998 to 2006 has seen the following trends:

- to more sulphur recovery (up from 39.4 to 45.0% of input)
- reduction in refinery emissions (down from 7.2% to 3.8% of sulphur intake)
- reduction in sulphur delivered in products for combustion from 37.0% to 32.5% of input.

The sulphur content of the overall crude slate has decreased very little over this time period. There remains a distinct geographic variation in the sulphur content of crude processed.

The product slate has changed with an increase in the overall proportion of middle distillates and a decrease in gasoline production.

The sulphur content of road fuels has decreased markedly since 1998 and reflecting preparation for the introduction of a 10 ppm max sulphur in both petrol and diesel starting in 2009. The requirement for "wide availability" of 10 ppm fuels starting in 2005 is evident in the changes in the 2006 survey compared to 2002.

The sulphur content of inland fuel oil decreased.

There were no changes to the sulphur content of marine bunkers with 2006 and 1998 results being almost identical. It therefore seems likely that the reduction reported for 2002 was not representative because of the relatively small number of refineries involved.

¹² Number of returns used in the analysis.

There has been little change to the sulphur content of heating gasoils. Reduction in the sulphur level of the overall gasoil pool was due to the changes to on-road diesel.

Sulphur recovery efficiency also increased over the period 1998 to 2006. Taking account of the performance of different abatement technologies it seems likely that use of SuperClaus tail-gas units increased.

7. REFERENCES

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8. GLOSSARY

BREF	Best Available Techniques Reference Document
FCCU	Fluid Catalytic Cracking Units
Foe	Fuel oil equivalent
LCP	Large Combustion Plant
LCPD	Large Combustion Plant Directive
OECD	Organisation for Economic Co-operation and Development
SRU	Sulphur Recovery Units

APPENDIX 1 METHODOLOGY

The survey form comprises an Excel spreadsheet distributed to member companies. The spreadsheet comprises 12 worksheets of which 7 are data entry forms and the others contain contextual and summary information. The survey requests inputs and outputs that allow a hydrocarbon and sulphur balance on the refinery to be made. Sulphur emissions through combustion are identified on a per stack basis using the size categories of the Large Combustion Plant Directive.

Fuel use is standardised on an energy rather than a mass basis using a fuel-oil equivalent figure. In previous reports a lower heating value of 40.24 MJ/kg was used for the oil; a value of 52.3 MJ/kg was used for gases and a value of 16.1 MJ/kg was used for the fuel category "other". These figures were based on a 1998 analysis of fuel streams. As discussed below, these have been used again here for consistency and lack of a better approach.

One change to the survey in 2006 is that it sought data on internal fuel consumption in both mass and in energy units. All respondents provided mass data but only a few provided energy data. Some used global conversion factors (constant energy content for liquids, gas and other fuels), others reported different energy contents for fuels by combustion plant size. We note that the survey uses annual total emissions and so either total mass or total energy may comprise use of different fuels over the year.

The distribution of reported heating values for each survey fuel category (liquid, refinery gas, natural gas, other) is shown in **Figure A1**. This has been calculated by dividing the reported energy use by the reported fuel consumption in each reported category and counting the heating values falling into 2 MJ/kg wide bands. Average values have been calculated on both a weighted (amount of energy used) and on an unweighted (number of data points) basis. Results of the averaging are given in **Table A1**.

The fuel oil values are narrowly distributed about a weighted value of 42.03 MJ/kg (41.29 MJ/kg unweighted) which is slightly larger than the value of 40.24 MJ/kg used previously and is close to the IEA standard conversion of 41.86 MJ/kg.

The natural gas value is lower than for pure methane perhaps reflecting the high inert (N₂) content of some natural gases. The average value of 47.97 (46.2) MJ/kg is lower than the value used previously for gas of 52 MJ/kg. The refinery fuel gas value was surprisingly small 37.3 (41.81) MJ/kg on average but it is apparent that some low energy fuels were included in this category and this has depressed the mean value. These lower energy fuels would be better assigned to the category "other". Heating values assigned to gaseous fuels ranged from below 18 MJ/kg to above 54 MJ/kg.

Similarly it seems that two types of "other" fuel are in use having heating values that are very low (10 – 14 MJ/kg) on the one hand and high (44 MJ/kg) on the other hand. The average is 18.29 (34.06) MJ/kg fuel which compares well with the previously used value of 16 MJ/kg.

Figure A1 Distribution of heating value by fuel type, 2006 survey

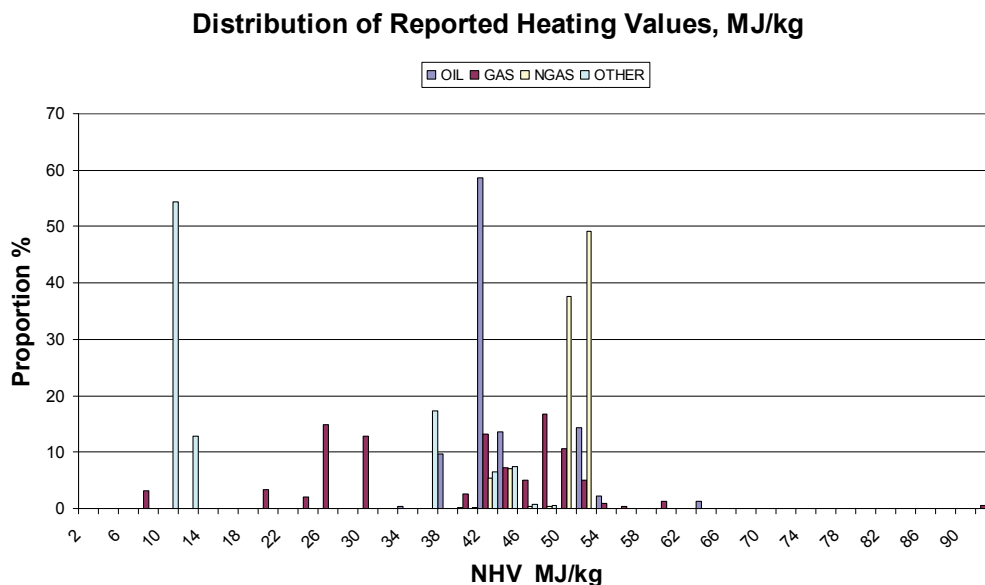


Table A1 Average lower heating values by fuel type (2006 report) compared with previous reports

Fuel	Lower Heating Value MJ/kg		
	weighted mean	unweighted mean	Used in this and earlier reports
Oil	42.03	41.29	40.2
Refinery Fuel Gas	37.34	41.81	52
Natural Gas	47.97	46.2	52
Other	18.29	34.06	16

To perform the survey analysis it is necessary to have a simple method of comparing fuel use in terms of energy content. The data collection was not adequate for this purpose and it was decided to retain the historic heating values, having also advantages of backward compatibility.

The assumptions will result a small margin of error in the estimate of total energy use. They may affect the refinery position in ranked charts but, because refinery name are not used in the study this has no consequence.

We note that the definition of fuel oil equivalent (foe) used in the sulphur survey analysis is different to the IEA definition (40.24 c.f. 41.86 GJ/t). In this appendix we use the standard value of 41.86 GJ/t.

The other aspect of fuel quality is the need to estimate combustion air requirements for the different fuels in order to determine equivalent bubble concentrations.

The commonly used conversion that the Large Combustion Plant Emission Limit Value of 1700 mg/Nm³ for SO₂ corresponds to a fuel oil containing 1% sulphur by weight gives a dry combustion product volume of 11.67 Nm³/kg fuel.

Values for dry flue gas volume used in previous reports (converted to the standard foe at 41.86 MJ/kg) were 12.5 for oil, 11.67 for both Refinery Fuel Gas and Natural Gas and 28.8 Nm³/kg for "other" fuels. These compare well with calculations for some typical refinery fuels.

Table A2 Dry flue gas volume (3% excess oxygen) for several fuels. All on a fuel oil equivalent basis of 41.86 MJ/kg

Fuel Type	Lower Heating Value GJ/t	Standard Flue Gas Volume Nm ³ /kg (foe)	Comment
Refinery Fuel Oil	39.7	12.6	H/C = 1.5 mol ratio.
Refinery Fuel Gas	47	11.67	Alkane mixture (10% C4)
Refinery Fuel Gas	49.7	11.4	Alkane mixture with 40% H2
Natural Gas	50	11.66	Methane
Natural Gas	39.2	11.86	13.7% Nitrogen, typical Benelux
FCC Coke	38	12.3	Low hydrogen
FCC Coke	40.7	11.9	High hydrogen
Low Joule Gas	4.19	16.94	High Nitrogen H2/CO mix
Low Joule Gas	1.88	27.0	5% HC

Original spreadsheets from the 1998, 2002 and 2006 surveys were used directly in the analysis to minimise the possibility of transcription error. The extraction and analysis of the data was performed using a computer program so that the methodology was exactly the same for each year and for each spreadsheet. Some observations can be made. There were 2 fewer spreadsheets compared with the number of refineries reported for 1998 (CONCAWE report 10/02). One spreadsheet appeared twice in the collection for 2002 (CONCAWE report 02/07). Not all of the spreadsheets are complete in every detail but all spreadsheets contain useful data. Measures of integrity that can be used are: non-availability of information – for example a breakdown of emissions by stack size; incompleteness of a hydrocarbon balance or a poor sulphur balance. Generally individual refinery hydrocarbon balances were good and sulphur balances less so. Aggregated balances were good. The analysis was run twice. First using all available data and then after eliminating those returns with the poorest sulphur balance defined as more than 20% deviation. In the 1998 survey this procedure rejected 7 responses, in the 2002 survey it rejected 12 responses and in 2006 it rejected 8 responses.

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