Research Report: Measurements of emissions to air of particulate matter (PM_{10}), nickel and polycyclic aromatic hydrocarbons (PAHs) at three UK oil refineries

1st edition

RESEARCH REPORT: MEASUREMENTS OF EMISSIONS TO AIR OF PARTICULATE MATTER (PM_{10}), NICKEL AND POLYCYCLIC AROMATIC HYDROCARBONS (PAHs) AT THREE UK OIL REFINERIES

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FOREWORD

Measurements of the concentration of PM_{10}, nickel (total and in particulate phase), total PAHs and B[a]P have been made in stacks at three UK refineries. Measurements were made on two dual-fired combustion units and on two FCCU regenerators. These data were used to calculate the mass emissions of these pollutants.

All of the measured concentrations of PAH and B[a]P, for both combustion units and FCCUs, were below the limit of detection of the analytical equipment used.

For each pollutant a review of the contribution of the oil refining sector contribution to the UK national air emissions inventory for 2010 has been undertaken. Refineries provide minor contributions of both PM_{10} and PAHs: 1,0 % and 0,9 % respectively. Combustion of residual fuel oils in refineries, however, results in their nickel emissions being relatively significant in the overall inventory compared to other heavy metals. Oil refining contributed 7,4 % of the national atmospheric nickel inventory in 2010.

From information supplied by the refineries on the properties and quantities of fuels fired and on operating data from the FCCUs, the mass emissions have been estimated for each campaign measurement run. These estimates have been made using the methodologies provided in the UKPIA protocol published by the Environment Agency in its Petroleum Activities Guidance Note on pollution inventory reporting. This protocol is used by UK refineries in developing their inventory submissions. In addition, for comparison, other emission estimation factors published in internationally recognised guidance documents have been used.

The project has shown, assuming the limited measurements are representative, that the oil industry is over-estimating its emissions of PM_{10} from both combustion and FCCUs and also nickel emissions from FCCUs. It is probably also over-estimating PAH emissions as all of the measurements were reported to be below the limit of detection values. Where the industry may be under-estimating is the quantity of nickel emitted from fuel oil firing. Recommendations have been proposed to improve the accuracy of the refinery submissions to the UK inventories.

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The following members of the Energy Institute's Emissions Working Group have been associated with the production of this report:

Steve Cross	Shell
Beate Hildenbrand	Energy Institute
Kevin Lenthall	Total
Graham Neal	ExxonMobil
Paul Shawcross	ConocoPhillips
Brian Smithers	Consultant

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1 INTRODUCTION

In 2004, at the request of the Environment Agency (EA), boundary-fence monitoring of benzo[a]pyrene (B[a]P) was undertaken at two UK refineries[1]. That project concluded that there were no significant differences between the concentrations measured upwind and downwind of the refineries. Furthermore the average B[a]P concentrations were relatively low, being comparable to those expected at urban sampling locations within the UK polycyclic aromatic hydrocarbons (PAH) monitoring network.

During the PPC permitting discussions in 2007, it was agreed with the EA to undertake stack measurements at three refineries to permit a further assessment of the emissions of PAHs. B[a]P was chosen to be the focus of this campaign as this compound is used as a surrogate for total PAHs in ambient air quality monitoring. For the latter, B[a]P is measured in the PM_{10} fraction of the particulate phase. This contains the great majority of the emissions, the concentrations in the vapour phase being significantly lower due to the low volatility of B[a]P. To obtain a full understanding of the emissions, however, the scope of the measurement campaigns was widened to include a limited number of measurements of total PAHs.

In addition the EA requested an assessment of emissions of a heavy metal. Nickel was selected to be measured as refineries are one of the major industrial emission sources of this pollutant due to the combustion of heavy fuel oil. Again the focus was on the particulate phase (PM_{10} fraction), although limited measurements of total (both particulate and gas phase) nickel emissions were included in the measurement campaigns.

As particulate sampling is a necessity to determine the concentrations of both nickel and B[a]P in their solid phases, the project was extended to report and assess the measured concentrations of the PM_{10} fraction of the particulate emissions.

The main sources of refinery emissions of PAHs and nickel are from fuel oil combustion and from FCCU regenerators. Due to the constraints of the Large Combustion Plant Directive [2] the sole firing of fuel oil is now very rarely practised in UK refineries. Measurements were made, therefore, on dual-fired combustion units in which refinery fuel gas and fuel oil are burnt simultaneously.

Monitoring campaigns were undertaken between September 2009 and February 2010. Concentration measurements of the following pollutants were made:

From dual-fired combustion units:

Refinery A – PM_{10}, Ni and B[a]P in PM_{10} fraction, total Ni and total PAHs.
Refinery B – PM_{10}, Ni and B[a]P in PM_{10} fraction, total Ni.

From FCCU regenerators:

Refinery B – PM_{10}, Ni and B[a]P in PM_{10} fraction.
Refinery C – PM_{10}, Ni and B[a]P in PM_{10} fraction, total Ni and total PAHs.

Stack monitoring was carried out by accredited consultants (RPS Consultants Ltd) in accordance with documented procedures and using the reference methods listed in Appendix 1. The sample analyses were undertaken at UKAS accredited laboratories; the majority at RPS Laboratories (Manchester), with the PAH analyses carried out at Marchwood Scientific Services Ltd. Stack gas flow rates were also determined allowing mass emission fluxes to be calculated over the monitoring periods.

The operating conditions of the combustion units and FCCUs during the period of the surveys were provided by the refineries. These permit the emissions to be estimated using

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