EPOW European Pathway to Zero Waste
Demonstrating the route to zero landfill

CHANGES TO THE PROPOSED QUALITY PROTOCOL FOR BIOMETHANE FOLLOWING PUBLIC CONSULTATION

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Contents

1.0 Executive Summary

We consulted on the development of a Quality Protocol for biomethane in the summer of 2012. The development of the Quality Protocol was supported by an environmental risk assessment, which considered the risks to human health and the environment that would result from implementation of the proposed Quality Protocol.

The consultation invited comments on the requirement to meet specific conditions and the monitoring associated with this. As a result of the comments received and following their consideration by the Quality Protocol's Technical Advisory Group, we have reviewed the draft Quality Protocol, its environmental risk assessment and related documents, including the considerations made in deriving the proposed conditions and monitoring in the proposed Quality Protocol.

This document explains the analysis undertaken and the outcome of that review. We are consulting upon the revisions arising from that review in February 2013.

Summary of revisions to the draft Quality Protocol for biomethane

- The original designated application of biomethane as 'a fuel for road vehicles' has been amended to 'a fuel in appliances suitably designed and operated for natural gas.' This change in definition covers use as a fuel in vehicles but has the advantage of allowing the Quality Protocol to apply to use of biomethane in a wider range of applications
- The definition of biomethane for the purposes of the Quality Protocol has been revised to better reflect the designated end uses
- The standards and specifications for determining Quality Protocol compliant biomethane and its associated sampling regime have been revised, due to calculation changes and taking into account international comparators. The requirements contained in the revised draft Quality Protocol are set out in Table 1 below.
- A clarifying amendment note has been added to the environmental risk assessment where some of the text was found to be unclear.

The original designated application of biomethane for injection into the gas grid is unchanged.

Table 1 – Revised limits for biomethane to grid and for appliances and sampling frequencies in the revised draft Quality Protocol for biomethane

Trace Gas	Limit indicated in risk assessment (mg m^{-3})	Limit (mg m^{-3})	Minimum frequency of sampling
Total Sulphur	405	30	annual
Hydrogen Sulphide	319	5	annual
Ammonia	5,824	20	annual
Hydrogen Chloride	527	1.5	annual
Hydrogen Fluoride	113	5	annual
Halogenated Hydrocarbons	1.5	1.5	annual
Xylene	13,932	100	annual
Arsenic	0.37	0.1	annual

2.0 Background: Quality Protocols

Waste recovery processes involve the treatment of materials to render them capable for reuse. Quality Protocols define the point in the recovery process where the material moves from a waste to a product. This is the stage where legislation covering the treatment of wastes no longer applies and legislation regarding products becomes applicable.

The development of Quality Protocols is supported by environmental risk assessments to ensure that, where needed, measures are put in place to ensure the 'product' neither has a detrimental effect on the environment nor poses a risk to human health. Where possible, these conditions are integrated with 'product' standards or production controls to reduce any discrimination between products derived from waste or products derived from virgin materials.

During the development of the Quality Protocol for biomethane, the environmental risk assessment undertaken indicated that a number of substances may present risks and, accordingly, measures were proposed in the draft Quality Protocol to manage the risks by proposing maximum concentration limits for substances in biomethane. Feedback from the UK consultation has led us to review the process for deriving the proposed limits and make changes to the Quality Protocol. This review has been undertaken under the scrutiny of the Technical Advisory Group associated with the development of this Quality Protocol, details of which can be seen in Appendix 1. The Technical Advisory Group includes members representing the interests of regulators, biomethane gas producers and potential industrial users.

This document contains the results of this review.

3.0 Review of methodology and proposed amendments

The review identified two main amendments to the derivation of the proposed control limits (which are highlighted within the process flow diagrams at Figures 1 and 2 below) and one change regarding the defined use of biomethane. In addition, it is proposed that an amendment note be added to the environmental risk assessment to clarify any ambiguity in the terms originally used.

Please note that changes in Figures 1 and 2 are indicated in orange, with solid-lined boxes indicating additions and dashed-lined boxes indicating removals.

Amendment 1 – Upgrade Factor

Good data on the composition of biomethane (from either AD or landfill) is not available. In conducting the risk assessment, our consultants used data on the composition of landfill gas adjusted with some limited data on biogas from anaerobic digestion plants. During the upgrading from biogas to biomethane in the waste recovery process, the concentration of the methane increases. In completing the risk assessment, our consultants concluded that the concentration of the trace gases would increase in a similar way and indicated that contaminants would need to be multiplied by a factor of 2 when modelling this process. This is the 'upgrade factor'.

Where a pollutant of particular concern is identified in the source gas, the most sensitive health criterion value for that substance is used to derive an acceptable concentration. This represents the concentration within biomethane that permissibly could be released without breaching the health criterion. In the environmental risk assessment our consultants included 'the upgrade factor' in the calculation of the acceptable concentration, (although this was not clear in the report). When we derived the proposed limits in the Quality Protocol, we applied the upgrade factor a second time. This mistake meant that a number of the potential contaminants appeared to be present at a level that was significant and therefore needed to be controlled in the Quality Protocol.

This calculation has now been revised and, as a result, a number of contaminants are now not considered to be significant. For those contaminants still categorised as significant, the limits have changed. Of course, this does not mean that we have changed the safe limits for human or environmental exposure to chemicals (those are fixed), it is just that we have corrected the safe levels for substances in the biomethane. This does not simply result in a doubling of the revised limit, compared to the previous proposed limit for each substance. Some substances will be screened-out for consideration because they will no longer be regarded as posing significant health or environmental risks. The remaining substances will then pass forward through the risk assessment process, where they will be compared with calculated safe environmental levels for instantaneous, short and long term exposures. Because the expected concentration of each substance in the biomethane will have changed in relation to these various safe exposure criteria, the applicable most stringent criterion of the three will also have changed. Thus, the relationship between the previous and revised limits is not a simple doubling factor.

Amendment 2 – Combustion Factors

Since there is a total absence of data on the composition of the combustion products of the burning of biomethane, our consultants considered alternative sources to provide data that could be used in the assessment. These include:

- Destruction Factors: these result from models of how substances are destroyed in the combustion process.

- Combustion Factors: these are derived from the measurement of substances during the combustion of natural gas
- Limit Factors: these consider that particular elements are not destroyed within the combustion process but are converted from one compound to another.

A number of substances exist in natural gas which are not present in biomethane or biogas. Limits that were included in the Quality Protocol, based on a risk assessment relating to the combustion of natural gas, rather than biomethane, are therefore inappropriate. These include:

- Polycyclic Aromatic Hydrocarbons (with the exception of Naphthalene and Benzo-a-pyrene) are not present in biogas, will not, therefore, occur in biomethane and are not likely to be formed in the combustion process at significant concentrations due to the low concentration of the longer chain hydrocarbons.
- Metals (with the exception of Arsenic and Mercury) are not found to occur in biogas.

Accordingly, these substances were removed from consideration in the revised environmental risk assessment.

Amendment 3 – change in definition of use from transport to appliances

In discussing the proposed Quality Protocol, its consultation responses and, in particular, how conformance with the required limits may be demonstrated, the Technical Advisory Group determined to clarify the definition relating to use of biomethane in transport. The Group proposed that a more effective description is **Biomethane used in Appliances**, since this better aligns with both industrial specifications and terminology within environmental permits applicable to the sector. The application will, therefore, be:

- Use as a fuel in an appliance that is suitably designed and operated for natural gas which includes :
    - compression and spark ignition engines;
    - gas turbines;
    - fuel cells; and
    - heating appliances.

Note that use of biomethane as a fuel in suitably designed appliances covers its use in vehicles.

In making this proposal, the Technical Advisory Group considered any implications for the financial risk assessment and the environmental risk assessment. In relation to the former, the conclusion of the Group is that, although there may be slight additional benefits arising from the potential increase in scope, these will not make a material difference to the outcome of the financial risk assessment, and that any change would be positive owing to a widened scope of potential end users. A further review of the financial risk assessment is therefore not warranted on the grounds of the costs and benefits of doing this.

In making this change, we have undertaken a review of any specific additional industry groups that may be affected, and will be making specific representations as part of a second consultation starting in February 2013.

With regard to any risks to the environment or health, the Technical Advisory Group determined that the environmental risk assessment has already considered the elements which would now be required for the proposed change of definition, and therefore again, no further specific review of the environmental risk assessment would be needed to make this change,

other than a note within the environmental risk assessment to indicate this change. Essentially, the conservative approach adopted in the risk assessment for biomethane to grid applications means that the exposures calculated are equally applicable to the use of biomethane in appliances. Therefore, the limits we have derived can be equally assigned to the use of biomethane in appliances, including vehicles.

Other amendments

The Quality Protocol now also includes a template for the demonstration of conformity with the proposed limits, to aid consistent demonstration of compliance with legislation. This is guidance only, and not mandatory.

We have also reviewed similar approaches to these protocols in other countries (Sweden, The Netherlands, Germany, Switzerland, Austria and California). The review revealed that limit values for contaminants in biomethane for grid injection and for use in vehicles exist in Sweden, The Netherlands, Germany, Switzerland, Austria and California (USA). These have been conveniently reviewed by a Health & Safety Executive research publication[1] and the range of contaminants considered and their respective limit values are summarised in Table 2.

Table 2 – Contaminant Limits for Biomethane in Other Countries

Substance	Concentration Range	Source
Ammonia	3 – 20 mg m^{-3}	All
Total Sulphur	23 – 30 mg m^{-3}	SE, DE, CH,
H_2S	<5 – 5 mg m^{-3}	NL, DE, CH, AUT
Mercaptan	10 mg m^{-3}	NL
Cl-compounds	0.1 – 50 mg m^{-3}	NL
F compounds	25 mg m^{-3}	NL
HCl	1 ppm	NL
Benzene, toluene, xylene	500 ppm	NL
Aromatics	1 mol.%	NL
Dust	Technically free of dust	NL, US
Siloxanes	5 ppm	NL
Halogen compounds	<1 mg m^{-3} as Cl	DE, CH, US
Heavy metals	<5 mg m^{-3}	DE, CH
Silicon	<10 mg m^{-3}	AUT
F compounds	25 mg m^{-3}	NL
HCl	1 ppm	NL
Aldehydes, ketones	<0.1 ppm	US
Mercury	0.01 µg m^{-3}	US
Volatile metals	0.01 µg m^{-3}	US
PCBs	<0.1 ppb	US
Pesticides	<1 ppb	US

Where the approaches have specified limits on potential chemicals of concern identified in our risk assessment, we have adopted limits which are consistent with those proposed in other European countries. This is because harmonisation of gas composition requirements between Member States is an important issue that is currently being considered under the EU specifications for the high calorific gas cross-border transportation initiative. We have also considered the limits contained in the Gas Safety (Management) Regulations 1996 (GSMR)

[1] HSE (2011) Hazards arising from the conveyance and use of gas from Non-Conventional Sources (NCS). Research Report RR882.

and the network entry agreements and have adjusted the limits proposed in the revised Quality Protocol to align with these. In some cases, this has also involved the aggregation of individual compounds within a generic family group under one generic limit. For example, instead of specifying individual limits for a range of sulphur- and chlorine-containing compounds, we have specified one "umbrella" limit for each of these two classes of substances. In addition, we have also, in the interests of consistency, produced a unified set of limits that applies to biomethane to grid and biomethane for appliances.

In the original Quality Protocol document consulted upon in 2012, it was indicated that the REACH Regulations would potentially apply to biomethane. We have now received confirmation from the Competent Authority (in this case, the Health & Safety Executive) that these Regulations will not apply to biomethane[2].

[2] http://www.hse.gov.uk/reach/resources/waste.pdf and http://www.hse.gov.uk/reach/resources/exemptions.pdf

Figure 1 - Process flowchart for the raw gas risk assessment for the derivation of limits for the draft Quality Protocol for Biomethane

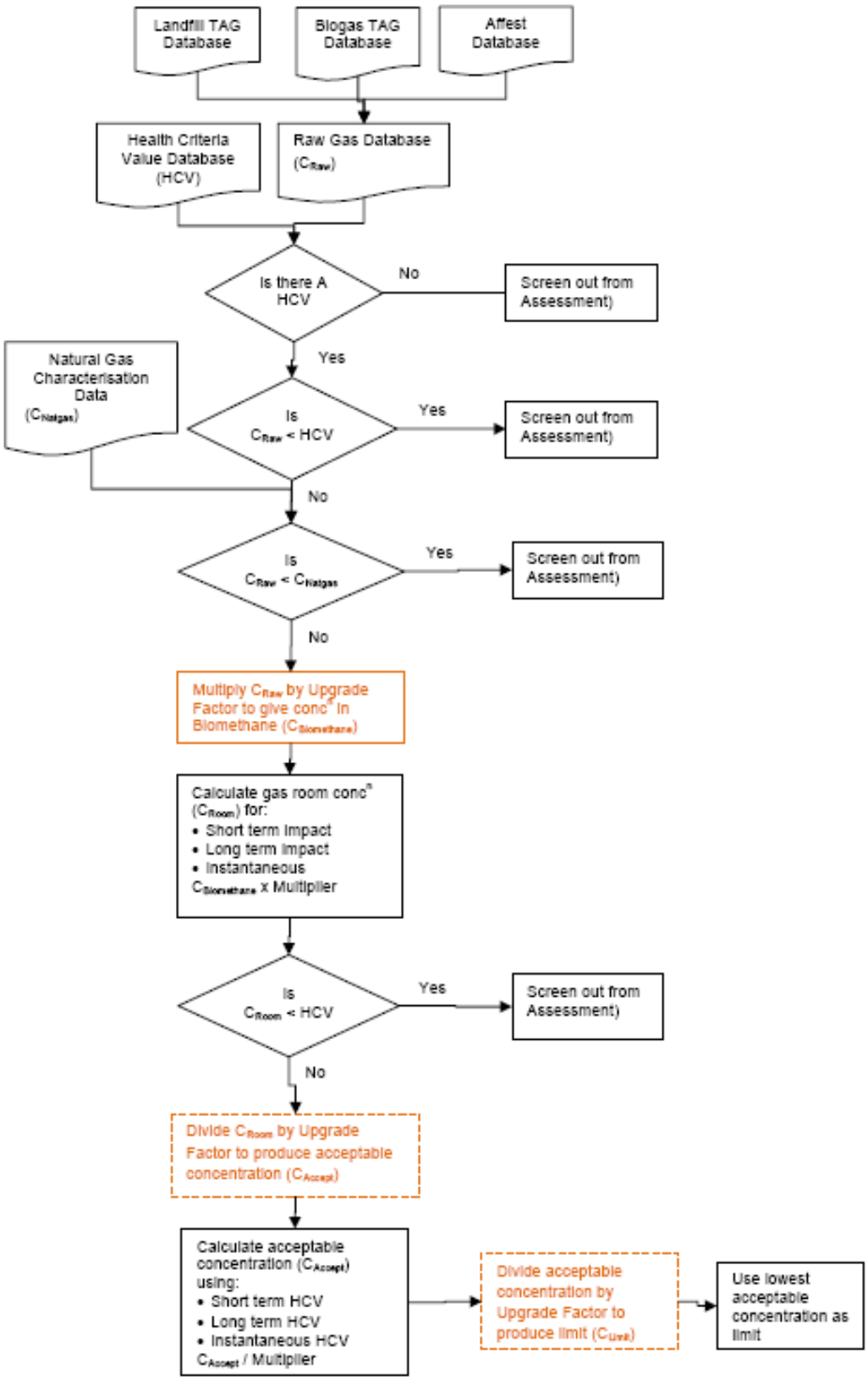
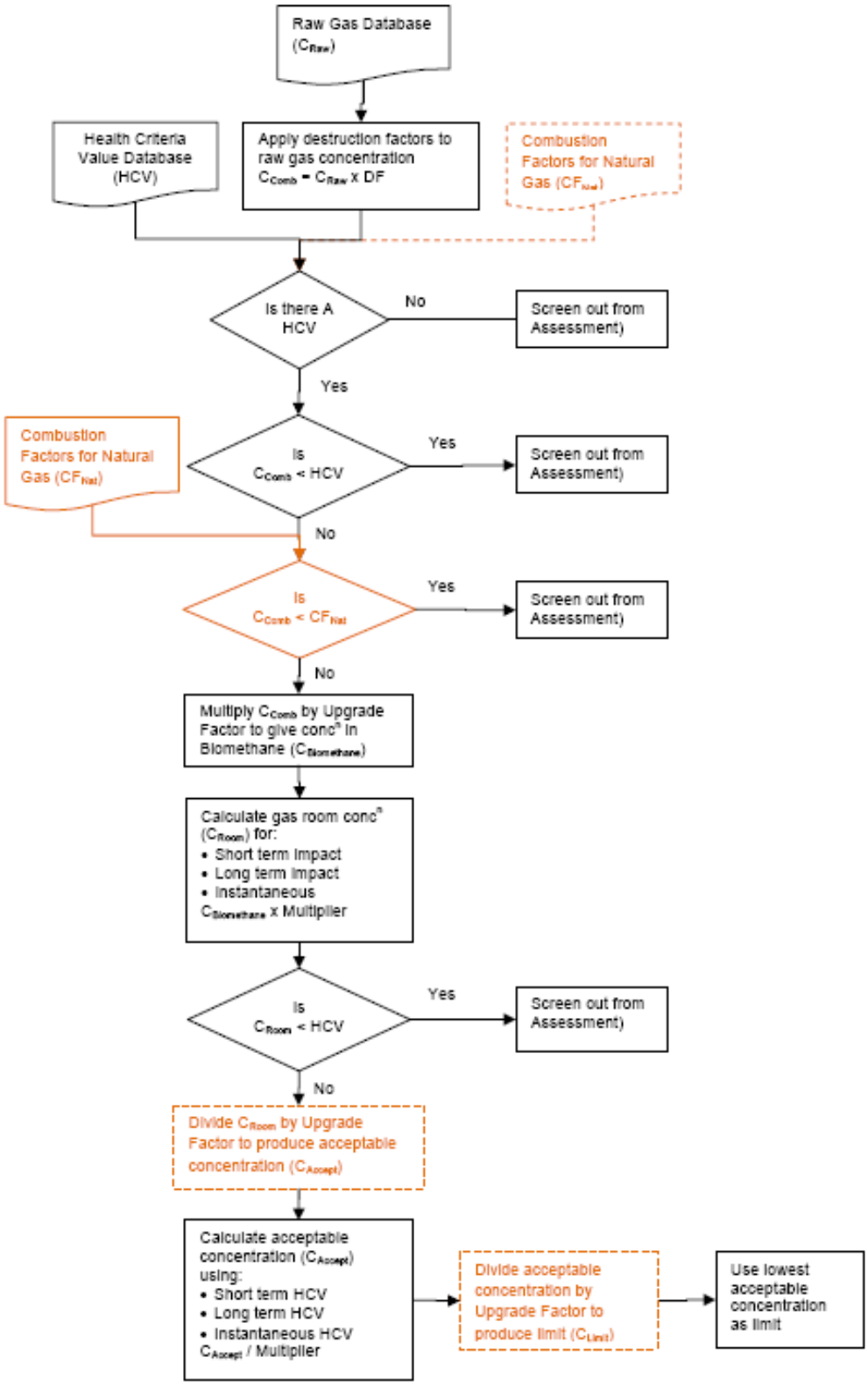


Figure 2 - Process flowchart for the combustion gas risk assessment for the derivation of limits for the draft Quality Protocol for Biomethane



4.0 Revised assessment of limits

Compounds Screened out of the Revised Risk Assessment

As a result of the changes made to the risk assessment methodology under Amendments 1 and 2, described in section 3 above, the number of substances to be considered has reduced. Those substances removed from consideration include polycyclic aromatic hydrocarbons and heavy metals, with the exception of mercury and arsenic, which are still included.

Within the draft Quality Protocol produced for the 2012 national consultation we proposed limits for the following polycyclic aromatic hydrocarbons:

- Naphthalene (0.632 mg m^{-3} for BtG and BfT);
- Acenaphthene (44.2 mg m^{-3} for BtG and BfT);
- Fluorene (29.5 mg m^{-3} for BtG and BfT);
- Anthracene (221 mg m^{-3} for BtG and BfT);
- Fluoranthene (9.27 mg m^{-3} for BtG and BfT);
- Pyrene (22.1 mg m^{-3} for BtG and BfT);
- Benzo-a-anthracene (0.0017 mg m^{-3} for BtG and BfT);
- Chrysene (0.0056 mg m^{-3} for BtG and BfT);
- Benzo-b-fluoranthene (0.0017 mg m^{-3} for BtG and BfT);
- Benzo-k-fluoranthene (0.0017 mg m^{-3} for BtG and BfT);
- Benzo-a-pyrene (0.0017 mg m^{-3} for BtG and BfT);
- Dibenzo-ah-anthracene (0.0001 mg m^{-3} for BtG and BfT);
- Indeno-123-cd-pyrene (0.0021 mg m^{-3} for BtG and BfT).

These have now been discarded because these compounds do not exist in biogas or biomethane and would not be formed in the combustion process.

Within the draft Quality Protocol produced for the 2012 national consultation we also proposed limits for the following metals:

- Arsenic (0.002 mg m^{-3} for BtG and BfT);
- Barium (0.0525 mg m^{-3} for BtG and BfT);
- Cadmium (0.0005 mg m^{-3} for BtG and BfT);
- Copper (0.2105 mg m^{-3} for BtG and BfT);
- Cobalt (0.034 mg m^{-3} for BtG and BfT);
- Chromium (total) (0.0002 mg m^{-3} for BtG and BfT);
- Chromium (hexavalent) (0.00005 mg m^{-3} for BtG and BfT);
- Manganese (0.0158 mg m^{-3} for BtG and BfT);
- Mercury (0.021 mg m^{-3} for BtG and BfT);
- Nickel (0.0068 mg m^{-3} for BtG and BfT);
- Lead (0.0263 mg m^{-3} for BtG and BfT);
- Selenium (mg m^{-3} for BtG and BfT);
- Vanadium (0.0545 mg m^{-3} for BtG and BfT);
- Zinc (5.25 mg m^{-3} for BtG and BfT).

The majority of these metals do not exist in biogas or biomethane (and, therefore, in the combustion gases from biomethane) and have been removed from consideration in the revised risk assessment. The exceptions are arsenic and mercury, which have been found in biogas. These two metals have been retained in the revised risk assessment.

Results of Revised Risk Assessment

The result of the revised risk assessment included a reduced number of substances requiring control. Following advice from the Technical Advisory Group, we have aggregated the

substances into common chemical groups, thereby allowing the use of a single limit for the chemical group in some cases. In the original risk assessment, limits applied to the original designated applications of biomethane as a fuel for injection to the national gas grid (Biomethane to Grid, BtG) and as a fuel for use in vehicles (Biomethane for Transport, BfT). The revised limits are for use in BtG and in the revised designated applications of Biomethane for Appliances (BfA).

Sulphur Based Compounds

Within the draft Quality Protocol produced for the 2012 national consultation we proposed limits for the following sulphur based compounds:

- Total Sulphur (13.15 mg m^{-3} for BtG and BfT);
- Hydrogen Sulphide (5 mg m^{-3} for BfT);
- Dimethyl Sulphide (79.5 mg m^{-3} for BtG and BfT);
- Dimethyl Disulphide (79.5 mg m^{-3} for BtG and BfT);
- Carbon Disulphide (58 mg m^{-3} for BtG and BfT);

Following review of the use of the 'upgrade factor' (see section 3 above, under Amendment 1) the outcome of the revised risk assessment indicates that we need to set limits for the following substances at the following maximum levels:

- Sulphur Dioxide = 815 mg m^{-3} (equivalent to 405 mg.m^{-3} S);
- Hydrogen Sulphide = 340 mg m^{-3} (equivalent to 349 mg.m^{-3} S);
- Carbon Disulphide = 233 mg m^{-3} (equivalent to 197 mg.m^{-3} S).

For the Biomethane to Grid application, gas providers are required to comply with the total sulphur and hydrogen sulphide limits within the Gas Safety (Management) Regulations 1996 (GSMR) and in the Network Entry Agreements (NEA). These are:

- Total Sulphur: less than or equal to 50 mg m^{-3};
- Hydrogen Sulphide: less than or equal to 5 mg m^{-3}.

As the limits within the GSMR and NEA are lower than the limits indicated by the revised risk assessment, compliance with the GSMR limits would guarantee compliance with these limits, with the specific sulphur organic compounds being subsumed within the "Total Sulphur" limit category. All sulphur-containing containing compounds in the biomethane would be measured by the analytical procedure applied and, therefore, the "total sulphur" category would encompass the range of individual compounds originally considered. A review of limits set by other European countries and advice from the Technical Advisory Group on the limit being considered for the forthcoming CEN Standard were also considered.

To be consistent for all uses, including compatibility with limits presently under consideration for the forthcoming CEN Standard, we therefore, propose to set the following limits for BtG and BfA:

- Total Sulphur = 30 mg m^{-3};
- Hydrogen Sulphide = 5 mg m^{-3}.

Inorganic Gases

Within the draft Quality Protocol produced for the 2012 national consultation we proposed limits for the following inorganic gases:

- Ammonia (1,455 mg m^{-3} for BtG and BfT);
- Total Chlorine (40.9 mg m^{-3} for BtG and BfT);
- Total Fluorine (1.68 mg m^{-3} for BtG and BfT).

Ammonia appeared as a substance of particular concern within the biomethane gas part of the risk assessment. Hydrogen Chloride and Hydrogen Fluoride were identified as substances of particular concern in the combustion gas risk assessment.

In revised risk assessment calculations, we have confirmed that we still need to set limits for these substances; however, the limits have been revised, taking account of the double inclusion of the 'upgrade factor'. The revised maximum levels are:

- Ammonia = 5,800 mg m^{-3};
- Hydrogen Chloride = 520 mg m^{-3};
- Hydrogen Fluoride =110 mg m^{-3}.

Based upon our review of limits set in other EU Member States for these compounds, which are all significantly lower than our limits calculated from the environmental risk assessment, we have harmonised our proposed limits, also taking into account the likely levels in biomethane after upgrading. The proposed limits in the Quality Protocol for both BtG and BfA are, therefore:

- Ammonia = 20 mg m^{-3};
- Hydrogen Chloride = 1.5 mg m^{-3};
- Hydrogen Fluoride =5 mg m^{-3}.

Halogenated Hydrocarbons

Within the draft Quality Protocol produced for the 2012 national consultation we proposed limits for the following halogenated hydrocarbons:

- 1,2-Dichloroethane (0.24 mg m^{-3} for BtG and BfT);
- Total Halogenated Hydrocarbons (1.5 mg m^{-3} for BtG and BfT).

In the case of Biomethane to Grid, the gas provider is required to comply with a limit for organohalides of 1.5 mg m^{-3}. This specification is contained within the unified code for network entry agreements. This limit is more stringent than the calculated limits for each of these substances in the original assessment with the sole exception of 1,2-Dichloroethane.

The results of the revised risk assessment indicate that we only need to set limits for Chlorobenzene and Chloroethene. As the acceptable concentrations for these substances are above the organohalide limit within the unified code for network entry agreements, for the Biomethane to Grid application, we can rely on a total Halogenated Hydrocarbons limit of 1.5 mg m^{-3} for this application.

To be consistent for all uses, we therefore propose to set the same limit for both BtG and BfA of total Halogenated Hydrocarbons - 1.5 mg m^{-3}. This then removes the need to set specific limits for BfA which had been proposed for Chlorobenzene (3,260 mg m^{-3}) and Chloroethene (57 mg m^{-3}).

Aromatic Hydrocarbons

Within the draft Quality Protocol produced for the 2012 national consultation we proposed limits for the following aromatic hydrocarbons:

- Benzene (1.09 mg m^{-3} for BtG and BfT);
- Toluene (27.4 mg m^{-3} for BtG and BfT);
- Xylene - all Isomers (3,495 mg m^{-3} for BtG and BfT).

All of these substances were identified as being of concern as a result of the original biomethane gas risk assessment.

In our revised risk assessment calculations, we conclude that Benzene could be present in the biomethane (up to 73 mg m^{-3}) at a level which is lower than the concentration in natural gas provided by the National Grid in their material safety data sheet (487 mg m^{-3}). Hence, we conclude that Benzene does not need to be controlled in the Quality Protocol.

Toluene is now predicted to be below the relevant health criteria values and is therefore also omitted.

For Xylene, our revised calculations indicate a revised limit of 13,900 mg m^{-3}. However, a limit proposed in the Netherlands of 500 ppm for Benzene, toluene & Xylene is equivalent to 2,500 mg m^{-3} as Xylene. Operational data indicated Xylene should never reach these levels, so a level of 100 mg m^{-3} was selected and it is therefore proposed to adopt this limit for both BtG and BfA.

Metals

Our revised risk assessment concludes that Mercury could only be found below the health criteria value in all of the assessments. Therefore, we propose to remove the limit from the draft Quality Protocol. For Arsenic, we have calculated a revised limit of 0.37 mg m^{-3} in the revised risk assessment but operational data indicates that this level would never be reached, so a limit of 0.1 mg m^{-3} has been set for the Quality Protocol.

The revised limits for substances in biomethane are summarised below in Table 3.

Table 3 – Revised limits in the revised draft Quality Protocol for biomethane

Trace Gas	Limit indicated in risk assessment (mg m^{-3})	Quality Protocol Limit (mg m^{-3})
Total Sulphur	405	30
Hydrogen Sulphide	319	5
Ammonia	5,824	20
Hydrogen Chloride	527	1.5
Hydrogen Fluoride	113	5
Halogenated Hydrocarbons	1.5	1.5
Xylene	13,932	100
Arsenic	0.37	0.1

5.0 Monitoring

For the limits are set in the Quality Protocol, monitoring will need to consider:

- The reference conditions for the limit;
- The monitoring method with an appropriate limit of detection.

To ensure that the analytical report reflects the conditions that were considered within the risk assessment it is proposed that the following reference conditions are used:

- Standard temperature and pressure of 288 K and 101.3 kPa; and
- Oxygen concentration of 5%, dry gas.

It is proposed in the Quality Protocol that techniques for the sampling and analysis of biomethane should accord with the Guidance for Monitoring of Trace Components in Landfill Gas[3].

For Biomethane to Grid, the risk assessment methodology developed by National Grid (GQ8) will also provide a suitable method to determine monitoring frequencies for the Quality Protocol. This has the following benefits:

- This would identify the substances within the biomethane that have a potential to breach a limit and therefore require a high frequency of monitoring ;
- This approach is reviewed and validated on a case-by-case basis by the gas transporter during the completion of the Network Entry Agreement;
- The monitoring frequencies are reviewed in the event that the composition of a gas is likely to change.

[3] Environment Agency (2010) Guidance for monitoring trace components in landfill gas. LFTGN04 v3.0.

Appendix 1 – Membership of the Technical Advisory Group (TAG)

TAG Member	Organisation
Martyn Cheesbrough (Chair)	Environment Agency
Jane Salter	Agricultural Industry Confederation
Matt Hindle	ADBA
Chris Phillips	ABDA/Biogroup
Chris Parry	Biffa Group Ltd
Steve McCulloch	Chesterfield Biogas Ltd
Glenn Mercer	Chesterfield Biogas Ltd
Nick Blake	Daimler
Dave Lander	Dave Lander Consulting
Sean Ryan	Department for the Environment, Food and Rural affairs (Defra)
Patrick Leahy	Department for Transport (DfT) (Biofuels Strategy and Research)
John Baldwin	CNG Services Ltd
Howard Leberman	Environment Agency
Satish Kler	Gasrec Ltd
Rick Twomey	Gasrec Ltd
Jim Stancliffe	HSE
Stuart Gibbons	National Grid
Chris Maltin	Organic Power Holdings Ltd
David Collins	Renewable Energy Association
Richard Lowes	Scotia Gas Networks (SGN)
Colin Small	SGN
Colin Thomson	SGN
Simon Farris	Severn Trent Water Plc
Alex Forrest	SKM
Alun McIntyre	SKM
Ian Bacon	Society of Motor Manufacturers and Traders (SMMT)
Rob Walker	SMMT
Ian Morrish	Viridor Waste Management Ltd
Nina Sweet	WRAP

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