HFC-23 EMISSIONS FROM HCFC-22 PRODUCTION

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ABSTRACT

The compound HFC-23 (Trifluoromethane or CHF_3), a potent greenhouse gas with a 100-year global warming potential of 11,700, is generated as a by-product during the manufacture of HCFC-22 (chlorodifluoromethane or $CHClF_2$). This paper outlines options and issues for good practice guidance in the national inventory management of HFC-23 emissions from HCFC-22 production. The issues presented are organized into three sections: methodological issues, reporting and documentation, and inventory quality.

There are two methodological tiers in the *Revised 1996 IPCC Guidelines for National Greenhouse Gas Inventories* (*IPCC Guidelines)*. Measurement of HFC-23 emissions using a Tier 2 approach is highly accurate because data reflect conditions specific to each plant. Where measurements are impossible, Tier 1 default emissions data must substitute for plant-specific data. The accuracy and precision of Tier 2 HFC-23 emission estimates increase with the number of samples and the frequency of sample collection. If plant processes are relatively static, daily samples at either the process vent, or within the process itself, will produce a very high quality estimate. Most plants already perform regular measurement as a process diagnostic. HCFC-production data are necessary for the Tier 1 methodology, but confidential business information (CBI) concerns may necessitate reporting the data in some type of aggregated form. This may be particularly important given the limited number of HCFC-22 plants.

Reporting has been problematic for this source. Several countries have not reported HFC-23 emissions from HCFC-22 production, and some reports of other Parties have lacked transparency (UNFCCC/SBSTA/1998/7). Currently, HFC-23 emissions are reported under the IPCC category 2E1 (by-product industrial process emissions from the production of halocarbons and sulphur hexafluoride). This table does not have a specific entry for HFC-23, or any other individual species of HFC or PFC. Emissions of different species cannot be summed on a mass basis because there are many different HFCs, with different global warming potentials (GWPs) and different masses.

Ensuring the quality of an inventory also requires that countries implement quality assurance and quality control programmes. The common thread throughout the quality assurance process is the need for thorough documentation and complete transparency. QA/QC (quality assurance/quality control) activities will need to occur at several steps in the process. At the HCFC-22 plant level, key elements should include internal quality control on plant-level measurements, and documentation of data and methods for reviewers. The inventory agency must ensure the accuracy of plant submissions as well as the compiled inventory. It will also be responsible for providing documentation and reporting sufficient information to the UNFCCC Secretariat. One or more different types of external reviews and audits may also be appropriate for HFC-23 inventories, and each will require complete documentation.

1 INTRODUCTION

1.1 Nature, magnitude, and distribution of source

Overview of HCFC-22 Production

Trifluoromethane (HFC-23 or CHF_3) is generated as a by-product during the manufacture of chlorodifluoromethane (HCFC-22 or $CHClF_2$). HCFC-22 is used as a refrigerant in several different applications, as a blend component in foam blowing and as a chemical feedstock for manufacturing synthetic polymers. In developed countries, the scheduled phase out of HCFC-22 consumption will occur by 2020 due to its stratospheric ozone depleting properties. Feedstock production, however, is permitted to continue indefinitely. Consumption in developing countries will be phased out over a longer time period.

HCFC-22 is produced in several developed and developing countries. The U.S. is a major world producer of HCFC-22, with four plants and approximately one-half of all developed country production. Japan is another large producer of HCFC-22, and most other countries are likely to have only a few plants.

Process Description

Chlorodifluoromethane (HCFC-22) is produced by the reaction of chloroform ($CHCl_3$) and hydrogen fluoride (HF) in the presence of antimony pentachloride ($SbCl_5$) catalyst. The antimony pentachloride is the fluorinating agent and achieves a steady-state concentration in the reactor that depends on residence time, composition and concentration of organic compounds in the reactor and temperature. The reaction of the catalyst and HF produces $SbCl_xF_y$ (where x + y =5), which reacts with the chlorinated hydrocarbon to replace chlorine atoms with fluorine.

The stoichiometric relationship for the production of HCFC-22 is:

$$CHCl_3 + 2HF_6 \xrightarrow{SbCl_xF_y} CHClF_2 \text{ (HCFC-22)} + 2HCl.$$

The reaction is carried out in a continuous-flow reactor, usually under high pressure (the range from the literature is 0 to 500 psig) and temperatures on the order of 45 to 200°C. The HF and chloroform are introduced by submerged piping into the reactor, which contains the catalyst in a hydrocarbon mixture of chloroform and partially fluorinated intermediates. Chlorine may also be fed to the reactor to oxidize any unreactive trivalent antimony catalyst back to the more active pentavalent form.

Although the reaction is exothermic, heat is added to increase the flow of vapours containing the product and other compounds from the reactor. The vapour stream leaving the reactor contains HCFC-22 ($CHClF_2$), HCFC-21 ($CHCl_2F$), HFC-23 (CHF_3), HCl, excess $CHCl_3$ and HF and some entrained catalyst. Subsequent processing of this vapour involves various separation processes to remove/recover by-products and to purify the HCFC-22 product. Generally, unreacted chloroform and under-fluorinated intermediates (HCFC-21) from the vapour stream are condensed and returned directly to the reactor, where they undergo fluorination. Any entrained catalyst is also returned to the reactor. As shown in Table 1, the separation of the hydrocarbon compounds is facilitated by the differences in volatility, which makes it possible to condense the chloroform and HCFC-21 for recycle. As the hydrocarbons (starting with chloroform) are fluorinated, the addition of each fluorine atom results in a significant decrease in the boiling point of the resulting fluorinated compound.

TABLE 1
MAJOR COMPONENTS OF VAPOUR FROM REACTOR

Major compounds leaving the reactor	Boiling point at one atmosphere (ºC)	Fate
$CHCl_3$ (chloroform)	61	Returned to the reactor to produce HCFC-22
HF (hydrofluoric acid)	19	Removed or Recovered
$CHCl_2F$ (HCFC-21)	8.9	Returned to reactor to produce HCFC-22
$CHClF_2$ (HCFC-22)	-41	Recovered as product
CHF_3 (HFC-23)	-82	Separated as a vapour and usually vented to the atmosphere (some is destroyed by incineration and some is captured as a product)
HCl (hydrochloric acid)	-85	Recovered as a by-product (aqueous or anhydrous)

The vapours leaving the condenser consist primarily of HCFC-22, HFC-23, HCl and residual HF. In subsequent processing steps, HCl is recovered as a useful by-product and the HF can be removed by various methods. The HFC-23 is separated as a vapour from the HCFC-22 and generally is vented to the atmosphere as an unwanted by-product, or it may be captured for use in a limited number of applications. The HCFC-22 is purified, typically by caustic and water washing to remove any residual acid and then dried to remove traces of water.

1.2 HFC-23 emission points during HCFC-22 production

The quantity of HFC-23 produced during the production of HCFC-22 depends in part on how the process is operated and the degree of process optimisation that has been performed. For example, research in the US showed that at plants not fully optimised to reduce HFC-23 generation, the upper bound for HFC-23 emissions is on the order of 3 to 4 percent of the HCFC-22 production.[1] However, many plants that are currently operating have implemented process changes in recent years to reduce HFC-23 generation because the generation of more HFC-23 means less valuable product (HCFC-22) is produced. At these plants, the likely range of emissions is about 1.5 to 3 percent of production with 2 percent being a reasonable average estimate.

There are a number of factors that affect halogen exchange of chlorine to fluorine and thus affect the generation of HFC-23 in the reactor. These factors include temperature, pressure, feed rates, catalyst concentration and catalyst deactivation (associated with catalyst life). Another important variable is the reflux rate and the composition of the reflux because this also affects the concentrations of the compounds in the reactor. In general, higher catalyst concentrations and higher pressure will increase the amount of HFC-23 produced. Catalyst life is one of the most important factors affecting the generation of HFC-23 and should be considered in developing a representative sampling programme.

The major emission point for HFC-23 in the HCFC-22 production process is the **condenser vent**, as described above, where it is discharged to the atmosphere after separation from the HCFC-22. It is estimated that 98 to 99 percent of the HFC-23 that is generated is emitted at this point.[2]

There are five additional sources of HFC-23 emissions that are minor at properly-operated and well-maintained plants:

- **Fugitive emissions from leaking compressors, valves and flanges** The process is maintained under relatively high pressures at many plants, which can increase the potential for fugitive emissions from leaking equipment. However, there is a strong incentive to prevent leaks because of the potential for loss of valuable product (HCFC-22), and any leaks can usually be repaired quickly and effectively. Details were available from 2 plants that have a routine programme of leak detection and repair. These plants use an organic vapour analyser to detect any leaking equipment, which is promptly repaired. Fugitive emissions can be estimated from the number and types of equipment components found to be leaking. One plant determined fugitive emissions were less than 340 kg/year compared to less than 400 kg/year at the other plant.[3]
- HFC-23 can also be emitted when it is **removed with the aqueous phases from caustic and water scrubbers** used in the process. Volatile organics in aqueous wastes are readily emitted when the streams are subsequently managed in open systems, such as wastewater treatment processes. HFC-23 concentrations in these aqueous streams are only a few ppm at the most and the quantity of aqueous material is small. Consequently, HFC-23 losses are very small. The process vents on tanks handling these various streams were sampled by one plant, and based on detection limit values, HFC-23 emissions were less than 45 grams/hour.[4]
- Some HFC-23 **is removed with the HCFC-22 product**, and this may be subsequently emitted depending on its fate. Plants have specifications on the concentration of HFC-23 allowed in the product, and these

[1] Based on a review of data at some U.S. plants for 1990 and earlier, discussions with plant technical personnel, and a review of the literature.

[2] Final report entitled "The Reduction of HFC-23 Emissions from the Production of HCFC-22," dated July 1996. Prepared for Elizabeth Dutrow, Atmospheric Pollution Prevention Division, U.S. Environmental Protection Agency by Research Triangle Institute. [Investigated the processes and emissions of all U.S. producers, assessed opportunities to reduce emissions.]

[3] "Verification of Emission Estimates of HFC-23 from the Production of HCFC-22: Emissions from 1990 through 1996." Prepared for the Atmospheric Pollution Prevention Division, U.S. Environmental Protection Agency. February 1998.

limits are a fraction of a percent. Consequently, removal with the product also accounts for only a very small portion of the HFC-23 that is generated.

- When plants capture HFC-23, a potential emission source is the **vent from the storage tank where the HFC-23 is recovered** by condensation at high pressures and low temperatures. However, no data were available for these emissions; and they are expected to be relatively low due the use of a refrigerated condenser as an emission control device and infrequent venting of noncondensibles. The plant identified as capturing some of the HFC-23 includes any emissions from the storage tank in their estimate because they measure the quantity of HFC-23 generated in the reactor, subtract what is captured and weighed for shipment and attribute all of the difference to emissions.
- A few plants destroy the HFC-23 by **thermal oxidation**. Emission tests at one plant showed that over 99.996 percent of the HFC-23 was destroyed. Even considering fugitive emissions from leaks, this plant is not a significant source of HFC-23 emissions (less than 0.03 percent of the U.S. total).

1.3 The current state of inventory methodologies

The *IPCC Guidelines* present two broad approaches to estimating HFC-23 emissions from the condenser vent:

- The **Tier 1 methodology** is relatively simple, involving the application of a default emission factor to the quantity of HCFC-22 produced. The Guidelines cite a reference to USEPA that HFC-23 emissions are about 4 percent of HCFC-22 production, assuming no abatement methods (including process optimization).
- The **Tier 2 methodology** is based on measurement of the concentration and flowrate from the process vent at individual plants. The product of HFC-23 concentration multiplied by the volumetric flowrate gives the mass rate of HFC-23 emissions. Many plants monitor HFC-23 generation rates as part of their process control to ensure process optimization.

2 METHODOLOGICAL ISSUES

2.1 Selection of good practice methods

As discussed previously, *IPCC Guidelines* outline two tiers of methodologies for estimating HFC-23 emissions within the condenser vent. For each method, there are different approaches depending on the availability of data. The following discussion describes and evaluates each method.

The Tier 2 methodology is based on measurement of the concentration and flowrate of HFC-23 from the process vent at individual plants. Tier 2 is significantly more accurate than using Tier 1 default estimates because the data reflect conditions specific to each plant. Most HCFC-22 plants perform regular or periodic sampling of the final process vent or within the process itself as part of routine operations. In countries where HCFC-22 plants do not measure or sample, and it is not feasible to implement a sampling programme, the Tier 1 method is the only alternative. When default emission factors are used instead of plant-level data, it is important to establish that the emission factor is representative of the plant's emissions during normal operation. In some cases, where some plants monitor and some do not, the method will be a hybrid of the two tiers, using measurement data where available and default factors to fill in gaps.

There are several measurement options within Tier 2 relating to the location and frequency of the sampling. In general, direct measurements of the final process vent *or within the process* have the highest accuracy. The frequency of measurement must be high enough to represent the variability in the process (e.g., cover the entire life cycle of the catalyst).

The choice of Tier 1, Tier 2, or hybrid will be function of the relative and absolute size of the source within a country, the available sampling practices at plants, the feasibility of implementing new practices at plants and the desired level of accuracy in the inventory estimate.

2.2 Emissions factors

All estimation methods except for continuous emissions monitoring require an estimate (emissions factor) of how HFC-23 emissions vary with the rate of production of HCFC-22. Because this relationship varies with specific plant infrastructure and operating conditions, emissions factors introduce uncertainty. Tier 1 emissions factors represent this relationship by using information from other plants and making assumptions about typical operating conditions. Tier 2 emissions factors provide a significant improvement in accuracy because they represent this relationship based on one or more real data points from the specific plant. The key to minimizing uncertainty is to invest the time and resources for sampling and analysis to determine the appropriate emission factor for a process at each specific plant.

The accuracy and precision of the estimates of annual HFC-23 emissions are directly correlated with the number of samples and the frequency of sample collection. Since production processes are not completely static, the greater the process variability, the more frequently plants need to measure. As a general rule sampling and analysis should be repeated whenever a plant makes any significant process changes. Before choosing a sampling frequency, the plant should set a goal for accuracy and use statistical tools to determine sample size necessary to achieve the goal. For example, a study of HCFC-22 producers notes that sampling once per day is sufficient to achieve an extremely accurate annual estimate.[4] This accuracy goal should then be revised, if necessary, to take into account the available resources.

Some plants use thermal oxidation to destroy the HFC-23, and more plants in the future may use destruction or transformation techniques to reduce HFC-23 emissions. Emission testing should be performed to document the level of destruction and the net reduction in greenhouse gases, and emissions should be determined for any times that the destruction unit is bypassed. Monitoring of process parameters, such as combustion temperature and percent excess oxygen, is typically performed to ensure that the unit is operating properly on a continuous basis. For these plants, annual emissions (E) can be estimated from the quantity generated in the reactor (G), the quantity captured for sale (C), and the fraction that is destroyed or transformed during the year (f):

EQUATION 1

$$E = (G - C) \bullet (1 - f)$$

2.2.1 Continuous emission monitoring of the vent stream

Continuous emission monitoring can be performed using a gas chromatograph with an automated sampling system, appropriate detector (e.g., thermal conductivity or flame ionization), and a device to measure volumetric flowrate. Samples of the vented HFC-23 gas stream can be taken as frequently as every few minutes, and coupled with the volumetric flowrate, provide a direct measure of the mass emission rate.

This approach can be very accurate when quality control and quality assurance (QA/QC) procedures are performed to ensure each device is calibrated and operated properly. It will account for process variability and any other factors that affect emissions. It is also useful as a process monitoring tool to measure the effects of process changes and process optimization.

The major shortcoming of this approach is that it can be expensive in terms of the installed capital cost of the equipment and the operating cost, especially that associated with inspection, QA/QC and maintenance of the equipment. The costs are obviously multiplied if a particular plant has several reactors and multiple process vents that emit the HFC-23. The gains in accuracy in moving from a sampling approach to a continuous monitoring system may not be high enough given the economic costs.

2.2.2 Periodic sampling and analysis of the vent stream

The calculation of a plant-specific emissions factor, which relates the mass rate of HFC-23 to the production rate of HCFC-22 (e.g., tonnes of HFC-23/tonne of HCFC-22), is a highly accurate alternative to continuous monitoring if it is based on periodic sampling. The sampling must be performed under process conditions that are representative of routine operation. If process changes are subsequently made that will affect the generation rate of HFC-23, the sampling should be performed again to quantify emissions under the new conditions. Otherwise, scaling an emissions factor based on non-representative sampling over the period of a year will introduce error.

Samples of the vent stream are taken in an appropriate container, such as glass flasks, flexible bag, or stainless steel canister, and transported to the laboratory for analysis of HFC-23 concentration. At the time the sample is taken, the volumetric flowrate is determined using an appropriate measuring device, such as a gas volume meter, pitot tube, orifice plate, rotameter, etc. The concentration multiplied by the flowrate provides a measure of the mass rate of HFC-23, which can be applied to the rate of production of HCFC-22 for the whole year.

[4] RTI, Cadmus, "Performance Standards for Determining Emissions of HFC-23 from the Production of HCFC-22", draft final report prepared for USEPA, February, 1998. Analysis of data received from the manufacturers of HCFC-22 showed that between 21 and 29 samples per month are required to calculate annual HFC-23 emissions with an expected 1% error rate, 95% confidence.

2.2.3 Process sampling and measurements

A variation of continuous monitoring and periodic sampling is to base the emissions estimate on the quantity of HFC-23 generated in the reactor. This method can be as accurate as the two described earlier, and depending on where the measurements are made, can include estimates of the minor HFC-23 emissions that occur other than from the process vent (such as equipment leaks, direct contact with aqueous streams). Some facilities in the US have been using these procedures for years to monitor and control the production process because the generation of excess HFC-23 directly affects the process economics. Annex 1 describes procedures developed by two U.S. plants.

2.2.4 Literature values and default emission factors

In the absence of site-specific measurements, the alternative is to rely on measurements made at other plants and to assume they are representative for the plant of interest. A larger database of emissions factors from plants around the world, perhaps as a function of typical process conditions or some other relevant considerations, would minimize the bias introduced by the "borrowing" of emissions factors from other plants.

Studies done on several plants show that the ratio of HFC-23 to HCFC-22 has historically been in the range of 2 to 4 percent. Some plants have implemented process changes in recent years, and a range of 1.5 to 3 percent (typically on the order of 2 percent) is probably more representative of current operations. However, plants that do not have actual measurements are unlikely to have optimized their process with respect to the generation of HCFC-23. Consequently, an emission factor closer to 3 to 4 percent might be more accurate.

2.3 Activity data

Generally, annual HCFC-22 production data are necessary for the Tier 1 methodology. Even with the Tier 2 methodology, plant and/or national level HCFC-22 production data should be collected to allow for a point of comparison, and to back-calculate emissions factors from measurement data. Countries should obtain plant-level data if at all possible, so that they can use plant-level emission factors. Since producers may consider chemical production data proprietary, it may be necessary to ensure that it is not released to the public, or to publish it in such a way so that individual plants are not identified. Reporting aggregated national level production data through a national or international producer organisation is an alternative. The submission of HCFC-22 production data is already required under the Montreal Protocol.

At a plant-level, production data should be obtained directly from producers. There are several ways producers may determine their production levels, including shipment weights, measuring volume time density, using flow meters, etc. This data should account for all HCFC-22 production for the year, whether for sale or for use internally as feedstock, and the plant should describe how the HCFC-22 production rate is determined (weighing all shipments, measuring volume times density, flow meters, etc.). In some circumstances, producers may consider plant production data to be confidential.

2.4 Uncertainty

Parallel to the IPCC sector-specific workshops on *good practice guidance*, the IPCC is completing a programme of work on emissions inventory uncertainty. This work resulted in recommendations to the IPCC on approaches to assessing and managing uncertainty. During the sector workshop held in Washington, DC in January 1999, estimates of uncertainty were developed. Based on expert judgment, the Tier 1 approach using an emission factor of 4 percent was assigned an uncertainty of 50 percent. The Tier 2 methodology can generate an empirical or statistical estimate of uncertainty based on sampling frequency, accuracy of the measurements, and the variability associated with both the process and the measurements. One empirical study based on many plant measurements over three months and the use of analytical standards to determine accuracy concluded that sampling once per day for this plant could result in an accuracy of 1 to 2 percent.

2.5 Completeness

Given the discrete nature and small number of sources, complete reporting of this source should not pose significant resource challenges. Complete reporting should include all HCFC-22 producers and provide at least qualitative information on all plants and all sources. The Alternative Fluorocarbons Environmental Acceptability Study (AFEAS), a programme set up by 17 of the world's chemical companies to test alternatives to CFCs for their environmental health and safety characteristics, published a list of major producers in its "Production, Sales and Atmospheric Release of Fluorocarbons Through 1995." While this list does not represent 100% of global HCFC-22 production, every country represented on this list should report HFC-23 emission estimates.

A small amount of HFC-23 is currently captured by plants and sold for use as a fire extinguishant. Because this is an end-use of HFC-23, these emissions are not considered to come directly from HCFC-22 production. Instead, these emissions are to be included in the source categories associated with that end use.

Historically, some HFC-23 was captured and brominated to produce CBrF3 (Halon 1301), which was also used in fire extinguishers. Although this use has been phased out and is not relevant to determinations of future HFC-23 emissions, the practice could be important in determining pre-phase-out emissions (i.e. early baselines). Captured HFC-23 converted to Halon 1301 in the past should not be included as emissions from HCFC-22 production.

2.6 Other important issues

2.6.1 Baseline

If measurements and sampling of HFC-23 emissions are not available for previous years, there will be a consistency problem in an emissions time series. This will inevitably be the case, for example, if a plant emits during a baseline year but shuts down before a rigourous inventory measurement programme is implemented. The only alternative in this case is to apply emissions factors developed from other plants to available historical production data, or production estimates based on operating capacity. It is important that the emissions factors represent operating conditions in the baseline year as closely as possible. Nevertheless, emissions estimates for these plants in these years will be highly uncertain and little documentation will be available for verification.

2.6.2 HFC-23 destruction (including transformation)

Some plants use thermal oxidation or incineration to destroy HFC-23 before it is emitted, and other plants are actively investigating transformation techniques. If operating properly, these plants have a very low emission potential and may not need to measure as frequently as plants that do not destroy HFC-23. Plants that use thermal oxidation to destroy HFC-23 (currently or in the future) should document the level of emissions by conducting a representative emission test under normal process conditions to measure the quantity of HFC-23 emitted from the oxidiser. The oxidiser should be monitored (e.g., for combustion temperature and excess oxygen) to ensure that it is operating properly on a continuing basis. An annual reporting form should be submitted that identifies any time periods when the oxidiser is bypassed or not operating normally along with a determination of the HFC-23 emissions during the events. The annual emissions from such events, should they occur, can be determined from measurement of the flow rate and concentration of HFC-23 (to get mass rate in units such as kg/hr) times the total time during the year that the unit was bypassed.

3 REPORTING AND DOCUMENTATION

A recent report from the UNFCCC (United Nations Framework Convention on Climate Change) Secretariat "Methodological Issues Identified While Processing Second National Communications"[5] noted that reporting has been problematic for this source. Several countries did not report HFC-23 emissions from HCFC-22 production, and some reports from other Parties lacked transparency. This section provides information on the current *IPCC Guidelines* and outlines some options for improved reporting transparency.

3.1 Current IPCC *Reporting Guidelines*

The *IPCC Guidelines* are used to guide countries in the preparation and submissions of *annual* greenhouse gas emissions inventories to the UNFCCC Secretariat. The Guidelines establish:

- Standard tables, definitions, units and time intervals for reporting all types of emissions;
- The necessary documentation to enable comparison of national inventories, including worksheets, major assumptions, methodological descriptions and enough data to allow a third party to reconstruct the inventory from national activity data and assumptions, and
- An uncertainty assessment.

HFC-23 emissions are reported under the IPCC category 2E1, which fits into the following classification scheme:

2 : Industrial processes

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[5] (UNFCCC/SBSTA/1998/7)

2E : Production of Halocarbons and Sulphur Hexafluoride

2E1 : By-Product Emissions.

As one of the significant sources of HFC emissions, HCFC-22 production could be listed as its own category under halocarbon production.

HFC-23 emissions from HCFC-22 production are reported in IPCC Table 2: Sectoral Report for Industrial Processes, which calls for emissions data from each source of carbon dioxide, methane, nitrous oxide, precursor gases (NOX, CO, NMVOC, SO2), HFCs, PFCs, and SF6. Currently, the table does not have a specific entry for HFC-23, or any other individual species of HFC or PFC. Emissions of different species cannot be added on a mass basis because there are many different HFCs, with different global warming potentials (GWPs) and different masses. They can be aggregated on a carbon equivalent basis, but this does not allow for reconstruction of the inventory since a third party will not know the relative share of each gas in the total.

In addition to the lack of transparency in the reporting of emissions estimates, there is also a lack of clear information on how estimates were calculated. Issues to consider in order to address this shortcoming include:

- Reporting of the estimation methodology;
- Reporting of the source and nature of activity data and emissions factors, and
- Reporting on QA/QC procedures.

3.2 Confidential business information

Most plant operators consider HCFC-22 production data to be sensitive and therefore confidential. The use of the Tier 1 methodology would enable the national production of HCFC-22 to be back-calculated from published emissions of HFC-23. In cases where there are a small number of plants, confidential plant-level production data could be determined from national statistics. Countries may need to establish a confidential data tracking and reporting system similar to that used for the ozone-depleting substances to ensure the accuracy of HCFC-22 production data. In these cases, HFC-23 emissions from HCFC-22 production may have to be aggregated into other HFC emissions to avoid releasing proprietary information. This type of aggregation should also be documented.

The use of the Tier 2 methodology allows emissions of HFC-23 to be reported separately from HCFC-22 production. By de-coupling the HFC-23 emissions and HCFC-22 production data, national estimates cannot be considered to be of commercial confidence. It is impossible to determine HCFC-22 production from a measured emissions estimate without detailed and confidential knowledge of the individual manufacturing facility.

4 INVENTORY QUALITY

4.1 Introduction

Inventory quality assurance QA/QC (quality assurance/quality control) is a process that encompasses the whole range of activities and intermediate steps in creating an inventory. Figure 1 describes this general process in more detail. A well-developed and well-implemented quality assurance programme fosters confidence in the final inventory results regardless of the purpose and goal of the inventory. The common thread throughout the quality assurance process is the need for thorough **documentation** and complete **transparency**. For example, a government agency responsible for compiling the national HFC-23 inventory needs to receive full documentation of plant-level data and calculations in order to perform its own QA. It also needs to document the national compilation process and the QC performed on plant data so that it is transparent to external reviewers and the UNFCCC. In short, each group should have the necessary information with which to fulfill its function. Figure 1 outlines the flow of information and the inventory quality process at each step.

Some plants are sensitive to the release of information that may affect their competitive position, but this information may be important to verify emissions. For example, some countries do not release information on the production of HCFC-22 for individual companies. Emissions of HFC-23 and the production of HFC-23 as a percentage of HCFC-22 are also not released because capacity and production can be inferred from the information. In the past, however, some producers have agreed to release the numbers when aggregated for all companies, and in addition, allow the review of individual company numbers by a third party if the company-specific information is protected as confidential information.

Figure 1 Key steps in the inventory QA/QC process

	HCFC-22 Plant
Internal QC:	Plant-level measurement and calculations
Documentation:	Plant-level information provided to the government agency, and results of internal QC
	⇓
	Government Agency
Review/QA:	Plant-level inputs
Internal QC:	Compilation of national inventory from plant-level data.
Documentation:	Results of compilation and results of QA/QC
Reporting:	Official submission to UNFCCC
	⇓
	External Review
External Review:	External audit; stakeholders, peer & public review of inventory results; external verification against other data etc.
Documentation:	Results of external review.
	⇓
	UNFCCC Secretariat
External Review:	Requires standard format and transparency ensure consistency with other inventories and external data

4.2 International inventory QA/QC systems

4.2.1 Plant-level activities

Plant-Level Measurement and Sampling QC

The inventory QC procedures used at the HCFC-22 plant level will be determined, in large part, by plant personnel. There are, however, certain procedures common to monitoring programmes that should be specified:

- Sample collection and containers;
- Sample stability (prior to analysis);
- Sampling frequency;
- Written standard operating procedures for sampling and analysis;
- Calibration procedures (number, frequency, acceptance criteria);
- Limits for accuracy and precision;
- Flagging suspect data, and
- Maintenance of records.

For those plants taking direct measurements, multiple tests or samples are preferred because they can provide insight into variability. Information on variability can in turn be used to establish a reasonable sampling frequency that improves the confidence in estimates of annual emissions based on a few tests.

Plant-Level Production Data QC

In most cases, annual plant emissions are based on an estimate of annual HCFC-22 production. Production data should be cross-checked periodically to compare what is placed in storage (by the change in volume, weight, cumulative flow meter etc.) with what is shipped.

Plant-Level Documentation

As discussed above, inventory quality cannot be assured without adequate documentation and transparency. In this case, HCFC-22 producers are likely to report emissions information to the agency responsible for preparing the national inventory. This agency will conduct a quality assessment (QA) on plant-level data. For plant-level data, the type of information needed to provide transparency depends on the type of monitoring method used. For plants using **direct emission measurements**, either continuous or periodic sampling and analysis, examples include:

- Description of the methods for sampling and analysis (or a reference to standard methods);
- A description of QA/QC procedures for the measurement of volumetric flowrate and concentration (including the results of any determinations of accuracy and precision for the measurements);
- Details on the testing procedure (such as the number of samples, period of time sampled, whether sampling is instantaneous or composited over time, etc.);
- Results of the sampling (volumetric flowrate, concentration) in consistent units of measure, and
- A discussion of the process operating conditions at the time of the test and certification that they were representative of normal operation.

A standardized reporting form, certified by a responsible plant official, would facilitate review and verification of the emission determinations. It would provide the transparency necessary to understand exactly how the emissions were determined, reproduce the basic calculations, identify the level of uncertainty and establish the credibility of the estimate. If plants reduce their HFC-23 emissions by optimizing the HCFC-22 process or by installing an abatement system such as thermal oxidation, the actions taken and the effect on emissions must be documented to ensure that reductions are not an artefact of the procedures used to determine emissions.

Several plants use a combination of process measurements other than direct emission measurements to determine HFC-23 emissions, often in association with a material balance approach. Because some of the calculation procedures can appear to be quite complex, it is important that their derivation be clearly explained and any underlying assumptions identified. The description of the methodology should address the validity of the major assumptions and identify the magnitude of any biases that might be introduced. Techniques used to measure concentration and quantities should be included, along with a description of procedures used to assess accuracy and precision of measurements.

4.2.2 Inventory agency level activities

Inventory Agency Review (QA) of Plant-Level Information

Before accepting plant-level emissions data, the inventory agency should carry out an assessment of data quality and sampling procedures. This type of review requires close co-operation with plant owners to obtain enough information to verify the reported emissions, as discussed above. The assessment should include sample recalculations, an examination of the representativeness of the data and operating conditions and an identification of potential bias in the methodology and recommendations for improvement.

Inventory Agency QC on Compiling National Emissions

In addition to a thorough quality of assessment of plant-level data discussed above, the inventory agency should ensure that the process of aggregating plant data to develop the national inventory undergoes quality control. This should include, among other things:

- Cross-referencing aggregated HCFC-22 production statistics with national totals;
- Back-calculating national emissions factors from aggregated emissions and production data, and
- Ensuring that all plants are included and comparison with industry trends to identify anomalies and patterns.

Inventory Agency Documentation on Compiling National Emissions

For the HFC-23 inventories, a QA/QC management plan should address the specific items needed to perform audits and reviews. When the estimates are provided by each plant, the details should be documented at the plant level to account for differences in the procedures among plants. Examples of the types of information needed for documentation and external audit include:

- A detailed description of the inventory methodology;
- Identification of the input parameters that are needed;
- How the input parameters are obtained (measured or estimated);

- Frequency of the measurements;
- Results of determinations of accuracy and precision for the measurements;
- An estimate or discussion of uncertainty and variability for input parameters that are estimated instead of measured;
- Enough data for the input parameters to reproduce the calculations, and
- Back-calculated emissions factors from continuous monitoring for comparison.

When **simple emission factors** are used to estimate HFC-23 emissions, the uncertainty can increase dramatically. Countries using the emission factor approach should provide information on the origin and basis of the factor, compare it to other published emission factors and explain any significant differences, and attempt to place bounds on the uncertainty. In addition, the country should address how the quantity of HCFC-22 produced is determined and ensure that all production is accounted for (including HCFC-22 used internally for feedstock).

4.3 External inventory QA/QC systems

Several types of external reviews, or audits, may be appropriate for HFC-23 inventories. The most appropriate type of audit should consider that there are a limited number of plants (i.e., the effort is manageable), and that the nature of the source creates the potential for highly accurate determinations of emissions.

Third party audit by an accredited organization, expert, independent third party

An audit of the documentation and calculations ensures that each number is traceable to its origin. Given that much of the information used in developing HFC-23 emission estimates may be proprietary, a third party audit that protects confidentiality may be a necessary type of review.

Expert (peer) review

A detailed peer review would be appropriate when a procedure for determining HFC-23 emissions is first adopted or revised; it would not be needed on an annual basis. Such a review is designed to ensure that the methodology accurately represents the plant's particular situation, is as rigorous as possible, and that the data and assumptions used reflect the best available information.

Stakeholder review

Review by HCFC-22 producing companies, industrial organizations, and air pollution consultants can provide a forum for review of the methods used. This type of review would be of most value early in the inventory process when plant-specific details are shared, which can lead to ways for some companies to improve their methods to the levels achieved by the plants with the best methodology.

Public review

Some countries make their entire inventory available for public review and comment. This process may result in a range of comments and issues broader than those from other review processes.

Confidential Business Information Issues

In most cases, detailed descriptions of how HCFC-22 producers determine HFC-23 emissions can be evaluated based on knowledge of the process chemistry; however, validation of the actual calculations requires access to confidential business information. For example, some producers have indicated that the following information is considered as CBI at the company level, but not when aggregated for all companies:

- HCFC-22 production rate;
- HFC-23 emissions;
- Ratio of HFC-23 to HCFC-22, and
- Values of the individual measurements that are used as inputs for the estimation methodology.

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ANNEX 1 EXAMPLES OF MEASUREMENT SYSTEMS

Plant A: Plant A measures the concentration of HFC-23 and HCFC-22 in the crude gas stream as it leaves the reactor twice per day.[6] The quantity of HCFC-22 produced is measured two ways and has shown close agreement: the quantity added to the storage tanks each day is measured (change in volume times the density) and the quantity that is packaged and shipped is weighed. The ratio of concentration of HFC-23 to HCFC-22 times the quantity of HCFC-22 provides a measure of the quantity of HFC-23 produced each day. The HFC-23 generation rate is the same as the emission rate because all of the HFC-23 that is produced is emitted. This plant, in effect, generates its own daily emission factor (kg HFC-23/kg HCFC-22) by direct measurement of the concentrations of the two compounds.

As an example calculation, assume that the ratio of HFC-23:HCFC-22 for the day was 0.02 and that 40,000 kg of HCFC-22 was produced. Then the HFC-23 emissions for the day would be 800 kg (0.02 ● 40,000).

A potential small source of bias is the loss of HCFC-22 during subsequent processing. All plants stated that these losses were less than 1 to 2 percent. If the losses were as high as 2 percent, the emission estimate would have a small negative bias (for the example, 816 kg emitted instead of 800 kg).

Plant B: The HFC-23 emission determination for Plant B will be based on measurements of the quantity of HCl byproduct produced and the concentrations of HFC-23 and HCl in the byproduct stream after the HCFC-22 has been removed and recovered. The quantity of HCl generated will be measured continuously by a flow meter, and the stream concentrations are determined several times per hour by an automatic sampler and gas chromatograph. The data are stored in a computer and several calculations per hour give a determination of the quantity of HFC-23 generated. The results are summed each day to provide a daily determination of the HFC-23 that is generated.

Some HFC-23 is recovered at this plant for various uses. The quantity of HFC-23 that is recovered is carefully and accurately measured in the packaging/shipping process. The amount generated in the reactor minus the quantity recovered is used as an estimate of the quantity that is emitted and accounts for emissions from various sources (e.g., fugitive losses, emissions from direct contact streams, the process vent, and storage tank). In other words, any HFC-23 that was generated and not captured was assumed to be emitted, either by venting from the process, loss from storage tank venting, or removal with other process streams.

CALCULATION EXAMPLE

Let x = the measured mass fraction of HFC-23 in the HCl/HFC-23 stream. Then, 1-x is the mass fraction of HCl in the HCl/HFC-23 stream. Let Q_{HCL} be the quantity of HCl produced as measured by the flow meter.

Then the quantity of HFC-23 generated in the reactor would be calculated from:

$$\text{HFC-23 generated} = (Q_{HCl})(x)/(1-x)$$

For example, assume that 180,000 kg of HCL are measured as the production for the month and the measured concentration of HFC-23 in the stream containing HCl/HFC-23 is 10 percent by mass (mass fraction of 0.10). Then the quantity of HFC-23 generated in the reactor would be:

$$\text{HFC-23 generated} = (Q_{HCL})(x)/(1-x) = (180{,}000)\ (0.1)/(1 - 0.1) = 20{,}000 \text{ kg.}$$

If 10,000 kg of HFC-23 were captured, weighed, and shipped, the HFC-23 emissions are:

$$20{,}000 – 10{,}000 = 10{,}000 \text{ kg.}$$

[6] At the time of the study, the plant was in the process of installing an automated in-line sampler that would give several anaylses per hour.