# Studies on Assessment of Non Condensable Gases/ Odorous Emissions Level in Wood Based Indian Pulp & Paper Industry

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## INTRODUCTION

The problem of odorous emissions from kraft pulp and paper mills has been existing probably since the inception of the paper industry .The problem was not given much weightage earlier as most of the mills were usually located in remote areas away from cities and towns and the general public was not exposed to foul odor. Over the years with the increase in population , socio –economic factors etc there has been steady growth in public habitat near and around most of the mills. As such increasing cases of public concern / complaints related to foul odorous emission emitted by pulp and paper mills are being reported in recent times.

**Ministry of Environment Forests (MoEF)** too has duly recognized the odor problem as a major environmental concern and has included the issue in recently introduced **Charter on Corporate Responsibility for Environmental Protection** as per which the large pulp & paper mills employing kraft pulping process have to adopt suitable strategies / technology to control the emission of these odorous /non condensable gases by 2007 -08.

**Formation of Odorous Compounds**

The odor problem is basically due to total reduced sulfur (TRS) compounds formed due to reaction of sulfides with methoxyl group ($-OCH_3$) of lignin and are released as air emissions during kraft process which includes mainly **hydrogen sulphide ($H_2S$), methyl mercaptan ($CH_3-SH$) , dimethyl sulphide ($CH_3$-S-$CH_3$) , dimethyl disulphide ($CH_3$-S-S-$CH_3$)** etc. These odorous emissions are perceptible even at lower concentration below the threshold values. **The TRS compounds along with vapours of methanol, turpentine etc are collectively called as non condensable gases (NCGs).** Besides this, the other contributor to the odor problem are non sulfur hydrocarbons associated with extractive components of wood such as terpenes, fatty acids and resins etc. as well as produced due to use of defoamers, pitch control agents, bleach plant chemicals etc in pulp and paper mills. The formation of methylated organo sulphur compounds vary from raw material to raw material and depends upon the nature of lignin and methoxyl group present in concerned fibrous raw material.

It has been observed that many odorous compounds are perceptible at concentrations far below harmful concentration level. For example hydrogen sulphide is perceptible at very low concentration while it is toxic only above a concentration of 10 ppm. In all, the odor threshold concentration of major odorous compounds are :

| Compounds | Odour Threshold (ppb) |
|---|---|
| Hydrogen Sulphide ($H_2S$) | 8-20 |
| Methyl Mercaptan ($CH_3-SH$) | 2.4 |
| Dimethyl Sulphide ($CH_3$-S-$CH_3$) | 1.2 |
| Dimethyl disulphide ($CH_3$-S-S-$CH_3$) | 15.5 |

However it is to be noted that effects as mentioned above could be of concern within pulp and paper mills in rare cases of accidental releases or worker entry into the confined space where the gases have accumulated .Such incidents are thus usually not frequent and this type of exposure is rare and should not be of much concern to the mill workers or the people living in the vicinity. Long term exposure to very low level of reduced sulfur compounds is more common and may cause headache, nasal congestion, fatigue, irritation in eyes and throat. Bad smell & toxicity are not only the negative properties but they are also very explosive & corrosive at certain concentrations when mixed with air. All components of NCG are considered explosive in concentration range of 1 - 45% (by volume)

**Assessment of Level of NCG Emissions in Wood Based Pulp &**

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**Environmental Impact of Odorous Emissions**

The major environmental / health impacts associated with release of NCGs are :

| Compounds | Impact |
|---|---|
| Hydrogen Sulphide | • Reacts vigorously with living tissues<br>• Can paralyze olfactory system<br>• Eye irritation ( 5-10 ppm)<br>• Respiratory tract & eye Irritation ( 50-100 ppm)<br>• Headache, nausea , ENT irritation (above 500 ppm concentration)<br>• Respiratory Arrest ( 900-1000 ppm)<br>• Corrosive to metals and cement |
| Methyl Mercaptan | • Produce effects less toxic but similar to $H_2S$<br>• Respiratory Arrest / Comma (very high concentration)<br>• Affect Central Nervous System<br>• Cause pulmonary edema, convulsions, nausea, eye irritation etc. |
| Dimethyl Sulphide | • Least toxic among other TRS gases<br>• High concentration may cause irritation of mucous membrane |
| Methanol | • May cause developmental , neuro, gastrointestinal or liver disorders |

| Component | Lower Explosive Limit (% V) | Upper Explosive Limit % V) | Auto ignition temperature (°C) |
|---|---|---|---|
| $H_2S$ | 4.3 | 45.0 | 260 |
| M.M. | 3.9 | 21.8 | 340 |
| DMS | 2.2 | 19.7 | 206 |
| DMDS | 1.1 | 8.0 | 300 |

**Paper Industry**

CPPRI has been the pioneer to carry out the studies on assessment of level of NCG emissions in pulp & paper industry Today CPPRI has state of art facilities for determination and quantification of NCG emissions. CPPRI has conducted till now NCG determination studies in around 14 mills at various point sources. The main sources of NCG emissions in pulp and paper industry are indicated include :

- Digester ( Digester relief & blow)
- Black liquor storage tank
- Evaporators
- Recovery Boiler
- Smelt dissolving tank
- Lime kiln

## RESULT & DISCUSSIONS

**Level of NCG Emissions :**

## OBSERVATIONS

• NCG emissions can be grouped into two categories:

- **Low Volume & High Concentration ( LVHC)** which consist of relatively high level of TRS ( 10000 ppmv) and low oxygen content. The design philosophy for management of such NCG is to prevent air entry such that the TRS concentration should always remain well above its upper explosive limit. The major sources of LVHC are vents from blow heat recovery, digester blow, evaporator etc.
- **High Volume & Low Concentration ( HVLC)** which consist of relatively low TRS (eg 10 ppmv) and oxygen content equivalent to atmospheric air . Design philosophy for management of such NCG is to dilute the sources with air to ensure that the TRS concentration

**( A ) Mills Using Hardwood**

| Process ppm | MM ppm | DMS+DMDS ppm | MeOH | $H_2S$, ppm |
|---|---|---|---|---|
| Digester relief | 5-125 | 227 -3000 | - | - |
| Digester Blow | 415-500 | 1750-2100 | - | - |
| Black liquor storage tank | BDL -20 | BDL -12 | - | - |
| Evaporators | 23200 -35000 | 11500-15000 | - | 19800- 30,000 |
| Smelt dissolving | 30-90 | 60-48 | 150 -1000 | 10- 200 tank |

**( B) Mills Using Bamboo & Hard Wood**

| Process | MM ppm | DMS+DMDS ppm | MeOH ppm | $H_2S$, ppm |
|---|---|---|---|---|
| Digester relief | 187 –983 | 425- 3000 | 40-100 | BDL -27 |
| Digester Blow | 960- 11500 | 1227-32196 | 658 -10,000 | |
| BDL -800 | | | | |
| Black liquor storage tank | 5-124 | 12-255 | BDL | BDL |
| Evaporators | 1305 -221650 | 1405 -37125 | BDL -19300 | 198 -20,000 |
| Smelt dissolving tank | 10-210 | 18 - 360 | BDL | BDL -200 |

**(C) NCG Emissions : Batch V/s Contiuous Digester**

| Compounds | Batch Digester | Continuous Digester |
|---|---|---|
| MM,ppm | 415-11500 | 141-385 |
| DMS+DMDS,ppm | 1227-32196 | 169-2350 |
| MeOH,ppm | 658-10,000 | 751-900 |
| $H_2S$, ppm | BDL-800 | BDL -27 |

**( D) Level of NCG Emissions (Summery)**

| Process | MM ppm | DMS+DMDS ppm | MeOH ppm | $H_2S$, ppm |
|---|---|---|---|---|
| Digester relief | 75 –983 | 227-4000 | BDL-100 | BDL-27 |
| Digester Blow | 385 -11500 | 1227-32196 | BDL-10000 | BDL-800 |
| Black liquor storage tank | 5-124 | 12-255 | BDL | BDL |
| Evaporators | 1305-221650 | 1405-37125 | BDL-19300 | 198-30000 |
| Smelt dissolving tank | 10-210 | 18-360 | BDL-1000 | BDL-240 |

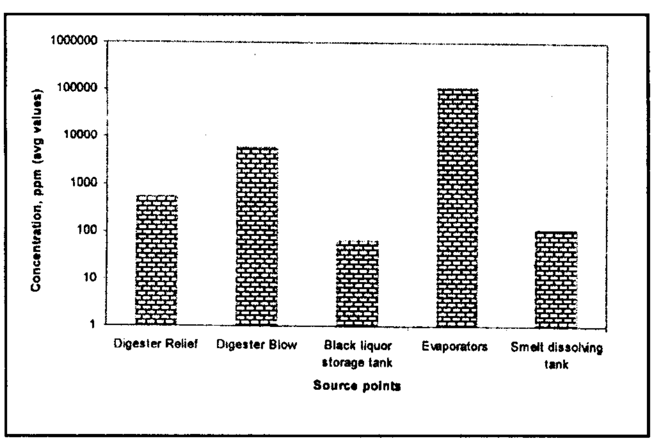
should remain well below its lower explosive limit. The major sources of these dilute NCGs are vents from brown stock washer hoods , liquor storage tanks, smelt dissolving tank etc.

- Level of NCG emissions are influenced by nature of raw material used, process employed, cooking temperature , sulfidity level.

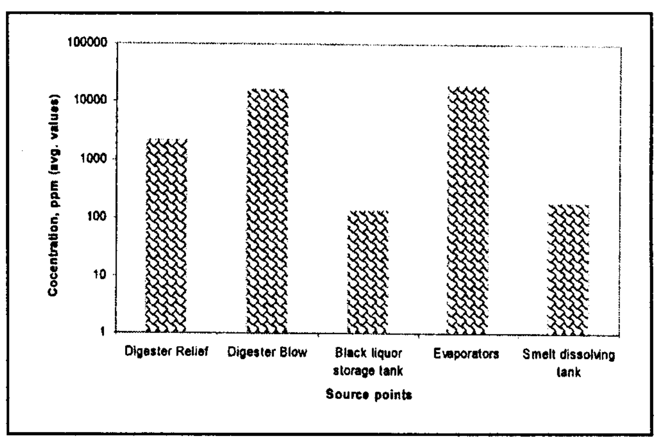
- The order of magnitude of NCG emission observed w.r.t. raw material used is Mixed Hardwood> Bamboo>Bagasse.

- Magnitude of NCG emissions w.r.t source points Evaporator vent> Digester blow > Digester Relief > Smelt Dissolving Tank >Black liquor Storage Tank.

- The profile of NCG emissions is not similar but varies in different blows. Similarly the concentration of NCG emissions does not decrease gradually from blow onset to




**(A) Methyl Mercaptan**




**(B) Dimethyl Sulphide & Di Methyl Di Sulphide**

**The individual advantages of these control methods are summarized below :**

| Incineration Option | Advantages |
|---|---|
| Lime Kiln | • Availability of high temperature & long residence time ensure complete incineration in presence of excess oxygen<br>• Utilization of NCGs heat of combustion in lime kiln leading to possible marginally reduction in fuel consumption.<br>• Control in loss of S as $SO_2$ ( formed during incineration) as it is absorbed in lime and remains within the process |
| Recovery Boiler | • Recovery of NCG is sulfur to green liquor<br>• Calorific Value of NCG is recovered to heat & power<br>• Higher tolerance towards load variations |
| Dedicated Incinerator | • Operation is independent of the process<br>• Some Dilute NCGs can also be used as combustion air in stand alone incinerator |
| Flare | • Standby unit for incineration of concentrated NCG<br>• Require practically no start up time<br>• Less maintenance cost |

**However, individual incineration methods are also associated with certain limitations i.e.:**

| Incineration Option | Limitation |
|---|---|
| Lime Kiln | • Possibility of increased formation of stones and rings in the kiln due to excessive formation of sodium sulphate.<br>• Very small capacity for incineration of dilute NCG.<br>• Due to Feeding of NCG very limited space may be available to combustion air leading to decrease in availability of oxygen in the kiln resulting in incomplete combustion occasionally |
| Recovery Boiler | • Increased Fouling / Slagging<br>• Difficulty in maintaining of $SO_2$ emission level.<br>• Ammonia present in NCG may oxidize on incineration to $NO_x$ and add to the NOx originated from liquor combustion. |
| Bark fired Power Boiler | • Risk of condensation of sulphuric acid and corrosion of air heater , dust collector ,ID fans etc.<br>• Slagging and ash build up |
| Dedicated Incinerator | • High capital investment<br>• May not accommodate all of dilute NCG<br>• High acid dew point of the flue gases from the boiler will only permit a low energy recovery from the incinerator other wise there will be high acid corossion |

completion of the blow but fluctuates through out the profile ( Fig 2).

- NCG Emissions are comparatively less in continuous digesters as compared to batch digesters

### Options/Techniques to Reduce NCG Emissions

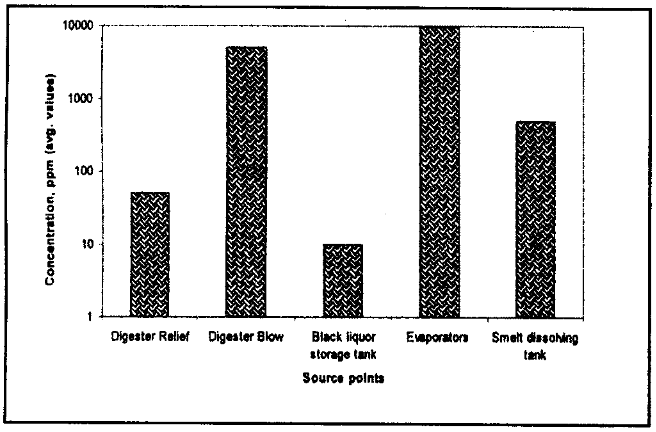
Various options both at source as well as end of pipe have been adopted by the mills globally for reduction / control of odorous emissions . Some of such examples are as under :

#### Scrubbing / adsorption

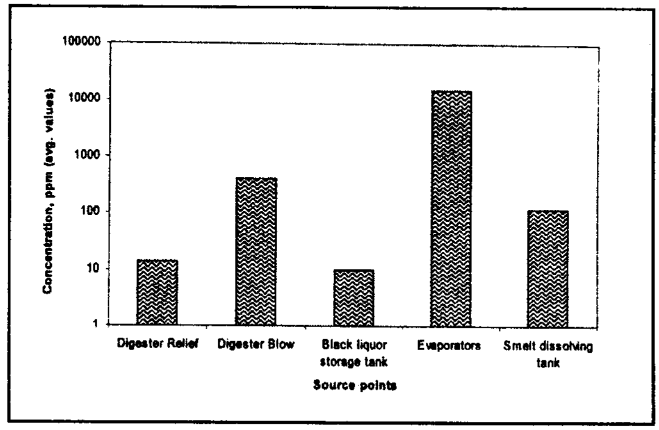
Wet scrubbing of gases to remove odour involve either adsorption or chemical treatment with a suitable solvent/ reagent. Wet scrubbing or adsorption systems can be either ventury systems or packed tower systems. When the odour is caused by the presence of unsaturated organic compounds, it may be necessary to use an oxidizing agent such as chlorine, diluted sulfuric acid and sodium hydroxide to treat odour. Recent development by way of biological scrubbing of $H_2S$ is a revolutionary invention for purification of gaseous emissions containing $H_2S$. The distinguishing feature of the process is that the sulfur is not formed in the scrubber itself but outside the scrubber. The removal efficiency of $H_2S$ in thio scrubbing process is more than 99% and has high operational safety as there is no risk of blockage which is an advantage compared to other conventional methods. The regenerated hydroxide is recycled to the process which reduces the consumption of caustic by 90% compared to conventional process.

#### Chemical treatment

Injecting controlled quantities of chemicals such as chlorine or ozone into process-gas stream can control odor. Similarly, unlike various other "odor control treatments, chlorine dioxide will destroy the odor at source. Chlorine dioxide is several times more effective than chlorine and other




(C) Methanol




(D) Hydrogen Sulphide

commonly used treatments, and will not form hazardous by products, such as chlorinated organics, which can cause more problems than the original odor itself.

**Black Liquor Oxidation**

Black liquor oxidation ( BLOX) is required for those mills operating a cyclone or cascade evaporator to prevent formation of TRS compounds. The process involves oxidation of $Na_2S$ in black liquor to $Na_2S_2O_3$ a stable form of sulphur compound not reacting with $CO_2$ and $H_2O$ present in flue gas from recovery boiler. The additional advantages of BLOX are

- Improved performance of multiple effect evaporators due to reduced scaling.
- Reduced corrosion rates of metal evaporating surface.
- Reduced chemical makeup requirement for $Na_2SO_4$ and CaO.

**Addition of Pulping Aid**

The pulping aids like anthraquinone isusually used during pulping process to enhance the removal of lignin .Use of anthraquinone helps in reducing the chemical requirement for pulping without compromising the product quality which ultimately results in reduction of NCG emissions

**Addition of Additives into Black Liquor**

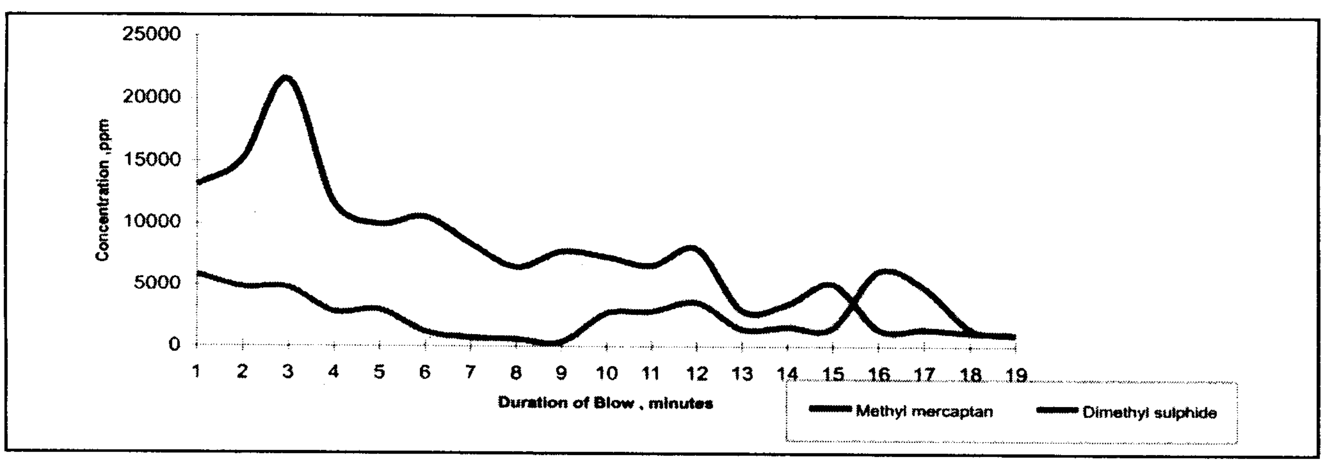
Recently some companies have claimed to developed additives which when added to the black liquor before being subjected to chemical recovery system substantially reduces the odorous emissions from evaporator vent.

**Incineration**

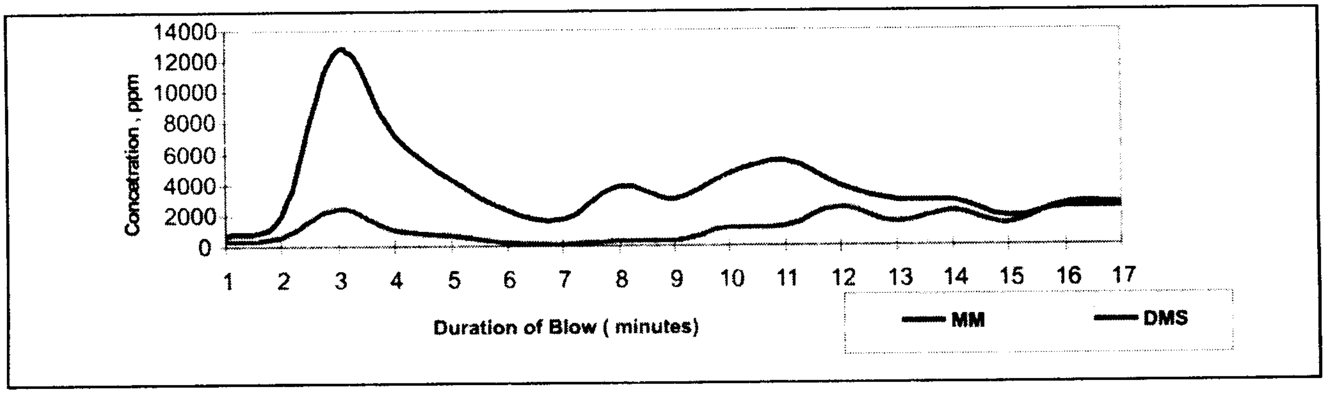
The common and widely practiced method for NCG control is incineration in lime kiln, boiler or dedicated incinerator .

In India only one mill i.e. APPM has so far installed a full fledge NCG incineration system. With odor being included as an agenda in CREP Charter other mills are also in process of process modification / selecting suitable control system to reduce odour.

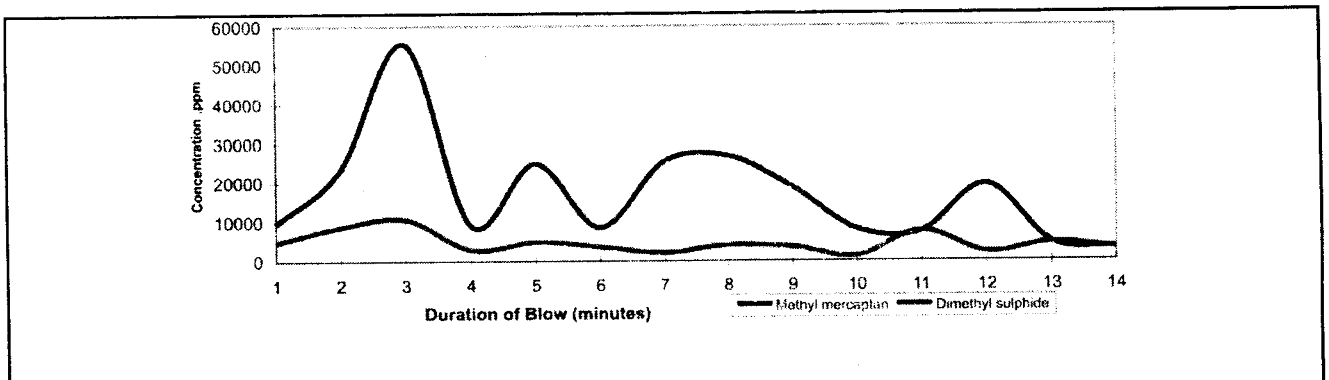
The major limitation in installation of odor control equipment is the cost factor as the NCG collection and incineration system is reported to cost between 5-9 million US dollars for mills in developed countries and of production capacity around 1500 tpd. In Indian perspective, it comes to




Blow - I




**Blow - II**




**Blow - III**

around Rs 2.5 -4.5 crores of investment .

## CONCLUSIONS

With the inclusion of odor control as one of the agenda in CREP as wellas public concern due to bad smell adoption of appropriate technology or modification of pulping process to reduce the NCG emissions will be a priority area for wood based large scale pulp and paper mills in coming years. However , the starting step will be to assess the level of NCG emissions for deciding about the selection of appropriate technology /options for management of these organo sulphur compounds . Mills can avail technical assistance from CPPRI which has now facilities & expertise to assess the level of NCG emissions Further efforts are required for a synergy among industry , R&D organizations like CPPRI & technology suppliers to develop indigenous techniques / technologies so as to address the odor issue in a cost effective manner.

## ACKNOWLEDGEMENT

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## REFERENCES


- Industrial Environmental Control –Pulp &Paper Industry III Edition, Allan M.Springer, TAPPI Press.
- Papermaking Science &Technology Series Book 19 - Environmental Control, TAPPI Press.
- All About Paper , Green Rating Project 2004, Centre for Science & Environment.
- Odorous Emissions –An Emerging Environmental Issue in Indian Paper Industry S.Panwar, N. Endlay, A. Pandey, B. Sarangaraja, R. M. Mathur, A.G.Kulkarni, Proceedings of International Conference on Pulp &Paper Industry, 2005.
- Burgess T., "Collecting and Burning of Non condensable Gases" Tappi Kraft Recovery Short Course 1999,Orlando FL , 1999
- Barynin, J.A, Berg L. & Lee,B. "Recent Trends in NCG Disposal Design", Pulp & Paper Canada T409-413,94:12(1993)
- Urbanski,R., Lister ,S.& Raoul , D."Development of an Effective TRS & Odor Reduction Programme" Pulp & Paper Canada T278- 281,99:8 (1998)
- Connor,Brian , Phaneul, Dominique & Dunn,Terry "Reduction of Total Reduced Sulphur (TRS) from Kraft Emission Vents Using Bleach Plant Chlorine Dioxide",891-898, International Environment Conference (1999) TAPPI Proceedings