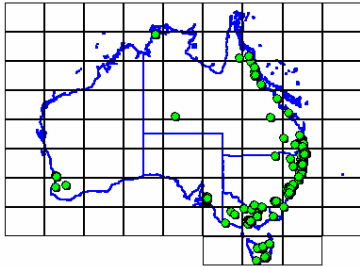


NATIONAL TOXICS NETWORK



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National Toxics Network (NTN) is a NGO (non-government organisation) network working for pollution reduction, protection of environmental health and environmental justice for all. As the Australian focal point for the International POPs Elimination Network (IPEN), NTN hosts the international IPEN working group on community monitoring and body burden and has worked towards the full implementation of the Stockholm Convention on Persistent Organic Pollutants (POPs) 2001 and other relevant international and regional chemical treaties. NTN has a particular focus on children's environmental health

Why is NTN involved ?

The Stockholm Convention obliges countries "to reduce the total releases of the byproducts dioxin and furans from man made sources with the goal of continuing minimization and, where feasible, their ultimate elimination". Article 5 refers to the production of pulp "*using elemental chlorine or chemicals generating elemental chlorine for bleaching*" as a source of dioxin and furans. Best available techniques and best environmental practices are required, while promoting use of *substitute* materials.

Pulp mills may release dioxins and furans (PCDD and PCDF) through:

- Air emissions eg from burning of lignin/black liquor to generate energy
- Water emissions through effluent disposal
- Sludge - incinerated or landfilled
- Emissions in products.

The Stockholm Convention also obliges countries to apply the Precautionary Principle in addressing the problems of POPs.

'Dioxins - Poisons without Passports'

Dioxins are the inevitable unwanted by-products of industrial processes involving chlorine such as in incineration and pulp bleaching. Even at extremely low levels, dioxins are very persistent, semivolatile and mobile, travelling great distances in air and water. They are fat-soluble, bioaccumulating in humans, wildlife and fish, and are transferred from mother to fetus, in utero and through breastmilk.

Dioxins cause cancer, affect the immune system, thyroid, liver and kidney functions and are linked with diabetes. They also disrupt male/female sexual development, cause birth defects and are linked with endometriosis and increased breast cancer rates. The fetus and neonates are the most sensitive groups with prenatal exposure linked with developmental and immune impacts in children.

All Australians already carry dioxin in their bodies through contamination of the food we eat. Australian babies under 3 months already absorb up to 16 times the tolerable monthly intake (70 picograms per kilogram body weight per month.) WHO has recommended that all countries substantially decrease their peoples' exposure.

Misleading Claims ?

NTN is concerned about claims that:

1. Elemental Chlorine Free technology is 'state of the art'- Chlorine dioxide was first used in Sweden 1947 and widely accepted by the 1980s. By the 1990s around a dozen kraft mills were already using Totally Chlorine Free processes.
2. United Nations Environment Programme (UNEP) considered Elemental Chlorine Free (ECF) and the Totally Chlorine Free (TCF) bleaching methods are equivalent with respect to their potential formation of dioxins - UNEP 2003, Dioxin Toolkit (an ongoing work in progress) acknowledges that while ECF results in reduced levels of dioxins, elimination of PCDD/PCDF in ECF bleached effluents and products is dependent of the quality of pulp and the purity of chlorine dioxide. In 2003, the UNEP Expert Group on Best Available Techniques and Best Environmental Practices in their Draft Guidelines on Pulping Processes clearly stated that in "TCF bleaching the formation of dioxins and furans is zero." They also noted that ECF bleaching remained troublesome as some elemental chlorine is both generated in bleaching reactions or may be present in the chlorine dioxide used.

Comparison of Emissions from EFC and TCF

The substitution of 100% chlorine dioxide for chlorine in ECF pulp-making does not prevent the formation of AOX, Absorbable Organic Halogens, the measure of organically bound chlorine. The newer chlorine dioxide generation technologies have reduced the

amount of by-product elemental chlorine to 0.02 metric tons or less per metric ton of chlorine dioxide.

However, in a highly sensitive comparison of the dioxin content of samples of ECF and TCF pulp produced by the same mill showed that while a measurable amount of dioxin (in the form of tetrachlorinated furan) was formed in the ECF bleaching process, there was no evidence of dioxin formation in the TCF process.ⁱ Similarly, in 1995 another study compared ECF and TCF pulp and identified 2,3,7,8-TCDF in chlorine dioxide bleached pulp.ⁱⁱ Chlorinated dioxins and furans have also been detected in air sampling from a Finnish ECF mill,ⁱⁱⁱ and have been reported in sludge from another ECF mill in North Carolina.^{iv}

While, the Government guidelines quote that dioxins and furans are not detectable in modern pulp mill effluent, they fail to acknowledge that while testing for dioxins in the environment is both difficult and expensive, testing for dioxins in fish and wildlife is simple. Analysis of tissue of fish living downstream of mill effluent discharges is one surrogate indicator of the presence of dioxin in mill effluents. One 1994 Australian study cited in the National Dioxin Program reported results for the analysis of carp samples from Lake Coleman which received effluents from a treated pulp and paper mill with concentration in the 4 carp samples between 0.48 – 4 pg I-TE g⁻¹ wwt.^v

Dioxins are not the only compounds of concern in effluent. A 1999 published study^{vi} in the Journal of Environmental Toxicology and Chemistry looked at toxicity of nine effluents from Swedish kraft-pulp mills using either ECF or TCF bleaching processes. In a comparison of effluents, which had not undergone secondary treatment, using the Microtox® test (utilised by State Water departments in Australia) conventional ECF effluent was the most toxic and TCF effluents were clearly the least toxic. These findings were supported by other studies demonstrating effluent from ECF mills had higher toxicity than that of TCF mills, with secondary TCF effluent being the least toxic.^{vii} Evidence of toxicity to fish was demonstrated in a 1997 Canadian study which showed genetic damage to juvenile salmon from the diluted effluent from a ECF mill.^{viii}

In regards to air emissions, side reactions during chlorine dioxide bleaching lead to the formation of chloroform, chlorinated phenolics and other chlorinated organics, as well as phenol and methanol. Chloroform, dichloroacetic acid methyl ester and other volatile organochlorine compounds have been found in the vent gases of mills using 100% chlorine dioxide substitution. These compounds have also been found to volatilise from the treatment ponds of these mills, but were almost non-existent when investigated in a TCF mill.^{ix} The precursors for the chlorinated organic chemicals are not present in TCF bleach plants

The issue of the disposal of ECF sludge is also problematic. A range of studies have shown that many chemicals are found in the sludge from ECF mills, including phenols, phthalates, terpenes, benzene and chlorinated alcohols. This means it is not fit for land distribution and burning this material has its own problems. Incineration of any organochlorine wastes will result in a wide range of chlorinated substances being emitted including dioxins and furans to air and also deposited in the ash. This has been verified

by a wide range of studies. Similar concerns apply to the treatment of ECF waste streams through the use of recovery boilers. However, the sludge of TCF also requires further study and careful management, due to the metal chelating agents used in the process.

Conclusion – TCF is the safer choice

Even with a preliminary review of the published literature, it is clear that many problems are associated with the formation of chlorinated compounds in the emissions from ECF mills and that TCF is clearly a safer and more precautionary choice. The benefits of low-effluent or closed-loop mills using Totally Chlorine Free kraft bleaching are many and include the elimination of production of dioxins and furans and other toxic organochlorines in mill waste. Oxygen based bleaching chemicals significantly reduce threats to workers, as ozone is made and used immediately in the exact quantities needed, ie no on-site storage of highly oxidative chemicals. Hazardous chlorinated air pollutants (including chloroform) are eliminated and sludge is not contaminated by persistent organochlorine wastes. TCF effluents may be easier to treat while current TCF technologies allow almost full closure of the bleach plant, reducing solid waste significantly and allowing nearly full recovery of bleaching wastewater. Importantly, no costly monitoring and reporting of chlorinated compounds is required.

Endnotes

ⁱ Barry Commoner, Mark Cohen, Paul Woods Bartlett, Alan Dickar, Holger Eisl, Catherine Hill, Joyce Rosenthal (June 1996) DIOXIN FALLOUT IN THE GREAT LAKES, Where It Comes From; How to Prevent It; At What Cost, Center For The Biology Of Natural Systems, Queens College, Cuny, Flushing, New York. Available at <<http://www.qc.edu/CBNS/dxnsun.html>>

ⁱⁱ Rappe, C. and Wagman, N., (1995) Trace Analysis of PCDDs and PCDFs in unbleached and bleached pulp samples. *Organohalogen Compounds* 23: 377-382

ⁱⁱⁱ Rodenberg, C., Kontstas, H., Jappinen, P., Tornaesus, J., Hesso, A., & Vainio, H (1994) Airborned chlorinated dioxins and furans in pulp and paper mill. *Chemosphere* 29 (9-11): 1971-1978

^{iv} Gleadow, P., Vice, K., Johnson, A., Sorenson, D., & Hastings, C., (1996) Mill application of closed cycle technology. *Proceedings 1996 Non Chlorine Bleaching Conference, Orlando Fl. March 1996*

^v (Ahokas J, Holdway D, Brennan S, Goudey R, and Bibrowska H 1994, 'MFO activity in carp (*Cyprinus carpio*) exposed to treated pulp and paper mill effluent in Lake Coleman, Victoria, Australia, in relation to AOX, EOX, and muscle PCDD/PCDF', *Environmental Toxicology and Chemistry*, vol. 13, pp. 41-50.)

^{vi} Maria Tarkpea, Britta Eklund, Margareta Linde, and Bengt-Erik Bengtsson, Toxicity Of Conventional, Elemental Chlorine-Free, And Totally Chlorine-Free Kraft-Pulp Bleaching Effluents Assessed By Short-Term Lethal And Sublethal Bioassays (1999) *Environmental Toxicology and Chemistry: Vol. 18, No. 11, pp. 2487-2496.*

^{vii} Kovacs et al, "A Comparison of the Environmental Quality of ECF and TCF Bleached Plant Effluent". *Proceedings of the Annual International Non-Chlorine Bleaching Conference (1995)*

^{viii} Easton, et al. "Genetic Toxicity of Pulp Mill Effluent on Juvenile Chinook Salmon (*Onchorhynchus Tshawytscha*) Using Flow Cytometry." *Water, Science, & Technology*. 35,2-3 (1997).

^{ix} Juuti, S. et al. "Volatile Organochlorine Compounds Formed in the Bleaching of Pulp." *Chemosphere*. 33,3 (1996).