Key aspects of AOX and dioxin formation in chlorine and chlorine dioxide bleaching

2023-02-21, Folke Österberg and Per Engstrand

Organically bound chlorine, determined as AOX (adsorbable organic halogen), in bleaching effluents has spearheaded the attacks of the environmental movements during the 80-ies on the forest industry and in specific bleached pulp production. A reason for this focus on AOX was that such material was believed to be of only anthropogenic (human-caused) origin. However, a considerable amount of organically bound chlorine has been proven to be formed naturally (1 and references therein). Obviously, nature should be adapted to many chlorinated compounds, both naturally formed and anthropogenic of the same or similar type.
An increasing number of investigations on the effluents from pulp mills show that biological effects are not correlated to AOX (2-8). This is to be expected as AOX stands for the material of high and low molecular mass matter with a majority of high molecular mass matter.
The high molecular mass matter of M>1000 cannot easily penetrate cell membranes and thereby not possible to accumulate in living organisms.
Furthermore, the lipophilic (attractive to fat) part (determined as extractable with organic solvents, EOCL) in the low molecular mass material is low at both chlorine and chlorine dioxide bleaching (9-11) and decreases rapidly with AOX decrease, see figure 1 (12, 13). For softwood pulps the EOCL becomes very low at AOX about 1 kg ptp (per ton pulp), using chlorine dioxide reduces the EOCL value to a very low value.

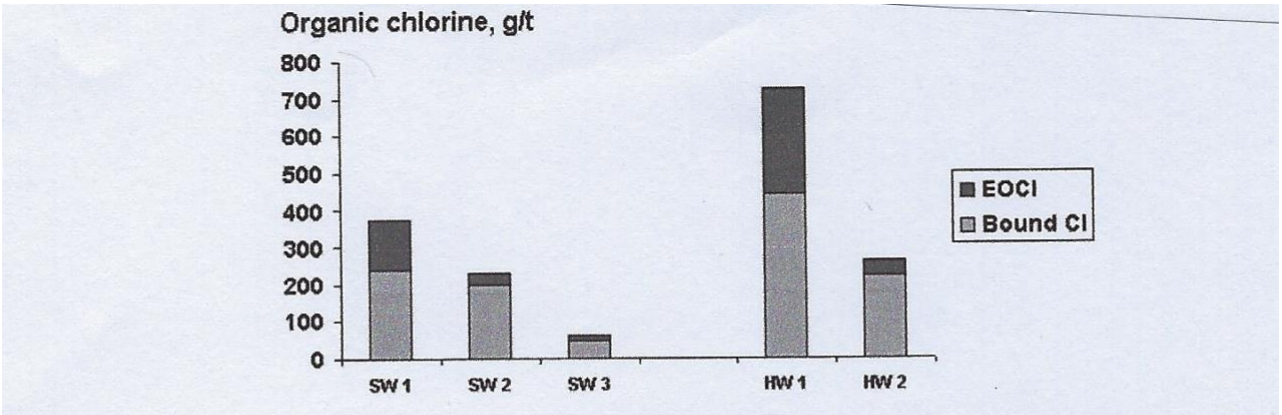

Figure 9.39 **Totally bound organic chlorine (Bound Cl) and extractable organic chlorine (EOCl) in softwood and hardwood (birch) kraft pulps.** Bleaching sequences: SW 1 = (C85+D15)EDED, SW 2 = O(C85+D15)(E+P)DED, SW 3 = OZEDP, HW 1 = O(C85+D15)(E+P)DD, HW 2 = OD(E+P)DD (Björklund Jansson et al, 1991)

Figure 1. EOCL and AOX in effluents at different bleaching sequences (ref 12,13).

In 1996 AET (14) stated that the complete replacement of elemental chlorine with chlorine dioxide results in the virtual elimination of the most common dioxins (2,3,7,8-

Tetrachlorodibenzo-p-Dioxin (2,3,7,8-TCDD) and that 2,3,7,8-Tetrachlorodibenzofuran (2,3,7,8-TCDF)) cannot be detected if the level of dibenzofuran in the pulp does not exceed 10 ppb. Concerns regarding dioxins in coastal fish in the Bottnia Lake were raised in 2005 by the Swedish EPA, SEPA, and the role of ECF bleaching was discussed (15).
Innventia carried out screening laboratory studies to clarify if modern chlorine dioxide bleaching can contribute to the formation of chlorinated dioxins and furans.

In modern pulp bleaching ECF (elemental chlorine free) bleaching with chlorine dioxide combined with oxygen delignification and Q(PO) bleached pulp the PCDD/Fs are in the same magnitude as blank samples. The purity of the chlorine dioxide solution, on the other hand, is a prerequisite for dioxin-free bleaching (16-17). When the content of chlorine in the chlorine dioxide solution increased above 5% (as active chlorine) levels of PCDD/F could be observed. A chlorine impurity level of 5% is far above the level of modern chlorine dioxide generators, i.e., a content less than 0.8 % is possible to obtain.
An overall conclusion from these studies is that in modern Elementary Chlorine Free (ECF) bleaching technology, there is no formation of dioxins during the bleaching of industrially produced kraft pulps.

As the kraft pulp bleaching production lines stopped using elementary chlorine during the 1980-ies and developed lignin-dissolving bleaching technologies involving oxygen, ozone, chlorine dioxide, and peroxide the AOX level has gone down from 8 kg/tonne to some g/tonne (18). As ECF bleaching results in a somewhat higher yield and somewhat better final product properties than TCF (totally chlorine-free) bleaching research is still performed to minimize AOX in spite of the fact that this AOX doesn't contain hazardous chlorinated compounds (19).

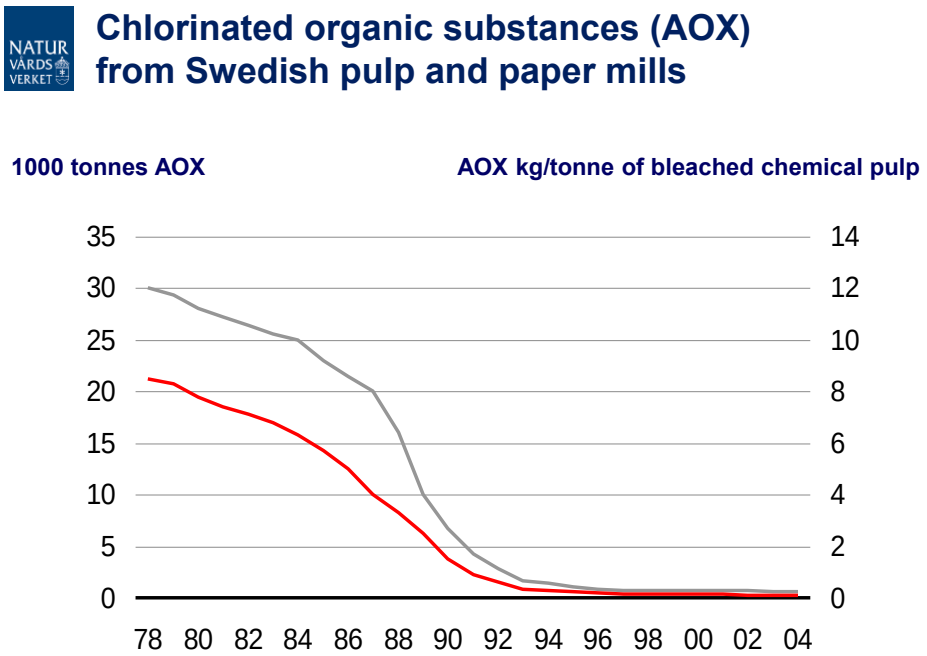

Figure 2. AOX reduction in Swedish pulp and paper mills during the 1980-ies.

From the recently built bleached kraft pulp production lines and in production lines with recent permissions to increase capacity in Sweden are allowed by the Environmental Protection Agency a level of AOX of 0,15 kg/tonne when a mill producing 250 000 tonnes per year situated at the lake Vänern in Sweden (20). This is due to that it has been clarified as explained above that ECF bleaching resulting in this level of AOX does not give rise to any risks for marine life. It is worth mentioning that any intentional dilution of wastewater going to recipient is not taking place as there are regulations of how much water is going to the recipient.

Concluding remarks

It is a fact that the AOX (adsorbable organic halogen) formed by ECF bleaching doesn't affect the marine life at all as there will be no dioxin formation. The background level of naturally occurring AOX in the Baltic Sea is most probably on a level where it will be impossible to see any measurable difference when adding effluent from a mill producing 500 000 tonnes per annum of bleached kraft pulp. Moreover. The natural adsorbable organic halogens have important known and unknown functions in fungi and plant.

References

1.Holm, G., Wennberg, L., & Enell, M. (1990). *Naturlig produktion av halogenerade organiska föreningar. En litteratursammanställning*. IVL Svenska Miljöinstitutet. (https://www.ivl.se/english/ivl.html) *Natural production of halogenated organic compounds. A literature review https://www.ivl.se/publikationer/publikationer/naturlig-produktion-av-halogenerade-organiska-foreningar.-en-litteratursammanstallning..html)*

2. Strömberg LM, Lehtinen K-J and Annergren G.E, 24 th EUCEPAconference Stockholm , May 8-11 1990

3.Axegård, P., Dahlman, O., Haglind, I., Jacobson, B., Morck, R., & Stromberg, L. (1993). Pulp bleaching and the environment-the situation 1993. *Nordic Pulp & Paper Research Journal*, *8*(4), 365-378.

4.Lehtinen, K. J., Axelsson, B., Kringstad, K., & Stromberg, L. (1991). Characterization of pulp mill effluents by the model ecosystem technique. *Nordic Pulp & Paper Research Journal*, *6*(2), 81-88.

5. NCASI Spec report No 90-11 September 1990 A Review of Recent Scandinavian Research on the Aquatic Effects of Bleached Pulp Mill Effluents. https://www.ncasi.org/resource/special-report-no-90-11-a-review-of-recent-scandinavian-research-on-the-aquatic-effects-of-bleached-pulp-mill-effluents/

6. First progress report NCASI Spec report no 90-07 July 1990. An Examination of the Relationship between the Adsorbable Organic Halide Content of Paper Industry Wastewaters and Potential Aquatic Biological Effects.
https://www.ncasi.org/resource/special-report-no-90-07-an-examination-of-the-relationship-between-the-adsorbable-organic-halide-content-of-paper-industry-wastewaters-and-potential-aquatic-biological-effects/

7. Craig, G. R., Orr, P. L., Robertson, J. L., & Vrooman, W. M. (1990). Toxicity and bioaccumulation of AOX and EOX. *Pulp & Paper Canada*. 91 (1990) : 9, 39

8. Earl P. F. And Reeve D. W Chlorinated organic matter in bleached chemical pulp production: The effect of chlorination-stage variables on chlorinated organic matter in effluent, TAPPI JOURNAL October 1989 Tappi J. 72 (1989): 10,183

9. Österberg F. Klororganiskt material i blekeriavlopp (short summary of doctoral thesis) Nordic Cellulosa 1985: 3, 65

10. Lindström K. And Österberg F. Holzforschung: 38(1984) 201
Lindström, K., & Österberg, F. (1984). Characterization of the High Molecular Mass Chlorinated Matter in Spent Bleach Liquors (SBL)-Part 1. Alkaline SBL Holzforschung: 38(1984) 201.

11. Österberg F. And Lindström K Holzforschung: 39 (1985) 149
Osterberg, F., & Lindstrom, K. (1985 Characterization of the High Molecular Mass Chlorinated Matter in Spent Bleach Liquors (SBL). 2. Acidic SBL. *Holzforschung*, *39*(3), 149-158.

12. Gellerstedt, G. Environmental Effects on Bleaching with Chlorine, and Chlorine Dioxide in chapter 9.5.7 in Ljungberg textbook 2006

13. Björklund Jansson, M., Dahlman, O., Månsson, K., Rutquist, A., & Wickholm, J. (1991). On the nature of chlorinated organic matter in bleached kraft pulp. In *International Pulp Bleaching Conference, Stockholm. Proceedings* (Vol. 1, pp. 123-136).

14. Neeta P. Thacker*, Vaishali C. Nitnaware, Swapnesh K. Das and Sukumar Devotta
Environmental Science and Pollution Research 14(4):225-6
Thacker, N. P., Nitnaware, V. C., Das, S. K., & Devotta, S. (2007). Dioxin formation in pulp and paper mills of India. *Environmental Science and Pollution Research-International*, *14(4)*, 225-226.

15. Stephen E. Swanson, Christoffer Rappe, Jan Malmström, Knut P. Kringstad Emissions of PCDDs and PCDFs from the pulp industry
Chemosphere Volume 17, Issue 4, 1988, Pages 681-691

16. Environmental performance of modern ECF bleaching Axegård P and Bergnor E International pulp bleaching conference 2011 p 119-149
Axegård, P., & Bergnor, E. (2011). Environmental performance of modern ECF bleaching. In *Proceedings Tappi International Pulp Bleaching Conference 2011* (pp. 119-127).

17. Axegård P. Chemosphere 236 (2019) 124386
Axegård, P. (2019). The effect of the transition from elemental chlorine bleaching to chlorine dioxide bleaching in the pulp industry on the formation of PCDD/Fs. *Chemosphere*, *236*, 124386.

18. Almgren, R. and Jansson, B., Best Available Techniques (BAT) in the Pulp & Paper sector for the continual environmental improvement – Lessons learnt in Sweden Naturvårdsverket | Swedish Environmental Protection Agency 2018-06-06
http://burondt.ru/docs/conference/dayone/en/10-final_jansson_almgren_bat_eng.pdf

19. Starrsjö, S. (2021). *On the Process Development of an ECF Light Bleaching Sequence for the Production of High Quality Softwood Kraft Pulp and Low AOX Formation* (Doctoral dissertation, Mid Sweden University).

20.https://www.naturvardsverket.se/contentassets/e5e688398ba64c0fbc1b65b4a8d709be/2018-10-15-mmd-vanersborg.pdf