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Formaldehyde In Fish and Shellfish: Formation and Toxicity

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Fish is a rich source of protein, healthy fats (omega-3 and omega-6), essential vitamins (B and D), and minerals, promoting benefits like reduced blood pressure and lower risks of heart disease. However, some countries face issues with the illegal use of formaldehyde (FA) to extend fish shelf life. FA, a Group 1 carcinogen, also forms naturally in fish. This popular article covers FA levels in fish since 2000, examining its formation pathways, health risks, regulations, and detection methods. Reported FA levels often exceed the safety limit set by regulatory agencies (any), emphasizing the need to monitor natural versus illicit FA, strengthen regulations, and prevent illegal FA addition

INTRODUCTION

Formaldehyde (FA), discovered in 1859, stands as the simplest aldehyde in terms of chemical structure. This colourless gas, with its distinctive irritating smell, is Known as CH2O at ambient temperature. In its liquid form, FA, often referred to as "formalin," serves various purposes in the agricultural sector, acting as a cost-effective preservative and disinfectant (Jinadasa et al., 2022). Notably, it finds usage in inhibiting bacterial growth during juice production in the sugar industry and as a bacteriostatic agent in select varieties of Italian cheese. FA holds significant importance across diverse industries globally, including construction (in wood processing, furniture, textiles, and carpeting) and consumable household products (such as antiseptics, medicines, cosmetics, dishwashing liquids, glues, and lacquers). However, one of the major challenges arises from its illegal addition to various food items, including fish and seafood, fruits and vegetables, fruit juice, mushrooms, and milk, aimed at extending shelf life (Veríssimo et al., 2020). In the degradation pathway of trimethylamine oxide (TMAO) in fish muscle, intrinsic and extrinsic factors, including post-harvest practices, contribute to the production of FA. Factors such as fish dimensions, feeding quality, fishing zones, preservation methods, handling techniques, and storage conditions all play significant roles in determining FA variability (Li et al., 2023; Kim et al., 2011).

TOXICITY OF FORMALDEHYDE

Formaldehyde serves as a natural intermediate metabolic product within the human body, generated during amino acid metabolism. However, heightened exposure to high doses can lead to acute toxicity, while prolonged exposure may result in chronic toxicity and an increased risk of cancer (Veríssimo et al., 2020). Notably, formaldehyde is classified as a Group 1 carcinogen by the International Agency for Research on Cancer (IARC) in its monograph (ROC, 2020), with the United States Department of Health and Human Services (DHHS), National Toxicology Program (NTP), listing it in their report on carcinogens (ROC). Specifically, elevated exposure to formaldehyde has been linked to nasopharyngeal cancer, sinonasal cancer, and lymphohematopoietic cancer, notably myeloid leukemia. Formaldehyde exists in the environment through various routes, including natural sources like forest fires and anthropogenic activities such as smoking tobacco and wood burning (Kim et al., 2011). Its environmental concentration is contingent upon atmospheric conditions like temperature, humidity, and wind.

Human exposure to formaldehyde occurs through inhalation (both outdoor and indoor) and ingestion. Additionally, formaldehyde is a natural metabolic product, particularly arising from the breakdown of folate derivatives, proteins, and nucleic acids in the human body. Adverse effects of formaldehyde exposure include acute mucous membrane irritation (nose, eyes, throat), gastrointestinal burns and ulceration, chest or abdominal pain, nausea, vomiting, diarrhea, and gastrointestinal bleeding. Long-term exposure may lead to severe and chronic health complications such as neurotoxicity, pulmonary function impairment, reproductive toxicity, genotoxicity, and carcinogenesis. Studies have indicated a potential association between formaldehyde and Alzheimer's disease, with higher formaldehyde levels observed in the urine of sufferers compared to controls (Li et al., 2023). However, the European Food Safety Authority (EFSA) concluded that there's no evidence suggesting formaldehyde acts as a carcinogen through oral exposure in laboratory animals (EFSA, 2006).

Despite its potential health risks, formaldehyde remains widely used as a disinfectant in aquaculture to maintain fish health and water quality. It is particularly effective in treating parasitic infections like protozoa and monogeneans on fish's external surfaces such as skin, fins, and gills. Nonetheless, its use may result in negative health impacts such as gill damage and alterations in mucous cells in fish. The body detoxifies formaldehyde enzymatically through one-carbon metabolism, which encompasses the one-carbon cycle, methionine cycle, and transsulfuration pathway describing the formaldehyde cycle and detoxification process. In mammals, formaldehyde toxicity is mitigated primarily through an enzymatic detoxification pathway that oxidizes formaldehyde, ultimately producing formate (Kim et al., 2011). Recent advancements in research on metabolic methanol, a more stable formaldehyde precursor, have shed light on mechanisms maintaining low levels of formaldehyde in human plasma.

FORMALDEHYDE FORMATION IN FISH/SHELLFISH

FA presence in fish and seafood can arise through natural processes or illegal additions aimed at extending shelf life (Jindasa et al., 2022). Detecting illegally added formaldehyde amidst naturally occurring levels presents a challenge, but advanced technologies such as stable isotope FA exposure measurement via nano-ultra performance liquid chromatography-tandem mass spectrometry offer promising solutions, providing insights into DNA-protein crosslinks and distinguishing between exogenous and endogenous formaldehyde levels (Nakamura et al., 2014). The enzymatic pathway and thermal processes have been identified as the primary means of formaldehyde formation in aquatic products (Zhang, 2015).Fish typically contain small amounts of carbohydrates and high levels of free amino acids. Trimethylamine oxide (TMAO) serves as an osmolyte aiding in osmoregulation, with higher concentrations found in marine fish compared to freshwater counterparts (Summers et al., 2017). Post mortem degradation of TMAO leads to the production of trimethylamine (TMA), dimethylamine (DMA), and formaldehyde, catalyzed by endogenous enzymes such asTrimethylamine-N-oxide demethylase (TMAOase) (Li et al., 2023). TMAOase is primarily concentrated in internal organs, red muscles, and the liver. During frozen storage, TMAO breaks down via TMAO demethylase, generating equal amounts of DMA and formaldehyde (Summers et al., 2017). Freshly caught fish typically exhibit low DMA levels, serving as an indicator of freshness for various fish species. The cumulative levels of TMA, DMA, and formaldehyde, referred to as total volatile base (TVB), contribute to fish quality deterioration and serve as spoilage indicators. Deepwater fish, particularly elasmobranchs, exhibit the highest levels of TMAO.

Thermal processing can significantly elevate formaldehyde levels in fish and seafood (Fu et al., 2007). Few authors studied the impact of processing steps on the physiochemical properties of dried squid, noting a gradual decrease in TMAO levels and a simultaneous increase in TMA, DMA, and formaldehyde levels, especially during boiling. Boiling temperature critically influences formaldehyde levels, although subsequent cooling processes such as washing with water or altering roasting practices can mitigate this effect. Sanyal et al. (2017) observed a decrease in formaldehyde levels in ice-stored fish (mrigal carp) due to formaldehyde leaching into melted ice, although complete removal from the sample did not occur. Similar significant decreases in formaldehyde levels during ice storage were reported by Laly et al. (2017) for formaldehyde-treated Indian mackerel. However, Yeasmin et al. (2010) noted reduced protein solubility and gel-forming ability in formaldehyde-treated fish muscle, leading to poor palatability, alongside low levels of non-protein nitrogen, possibly due to reduced bacterial loads.

CONCLUSION

Illegal addition and naturally high levels of formaldehyde (FA) in fish and seafood pose significant health concerns. Distinguishing between natural and illicit FA remains challenging, as some species naturally contain high FA levels—up to 200 mg/kg in species like haddock, mullet, and cod, with deep-frozen hake reaching 232–293 mg/kg (EFSA, 2014). Deep-sea species also have high trimethylamine oxide (TMAO) levels, which can convert to FA after death. FA content varies by species, handling, and processing techniques. Effective FA detection methods have been developed for routine monitoring, but comprehensive studies on natural FA levels across fish species are essential for enforcing regulations. To reduce FA exposure, consumers should wash fish thoroughly and cook it to at least 70°C. Clear consumer guidance on FA risks is crucial to avoid unnecessary alarm.

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