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Formation of organochlorine by-products in bleached laundry

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HIGHLIGHTS

- ▶ We measure organochlorine and residual hypochlorite in solid-phase fibrous samples.
- ▶ Organochlorine forms in cotton textiles upon laundering with chlorine bleach.
- ▶ Higher wash temperatures favor organochlorine formation in bleached fabrics.
- ▶ Two fractions of organochlorine (labile and stable) appear in bleached fabric.
- ▶ Organochlorine may arise from reactions of hypochlorite with cellulosic materials.

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ABSTRACT

Laundering fabrics with chlorine bleach plays a role in health and hygiene as well as aesthetics. However, laundry bleaching may create chlorinated by-products with potentially adverse human health effects. Studies have shown that toxic chlorinated gases are produced in the headspace of washing machines when hypochlorite-containing bleach is used. Laundry bleaching has also been implicated in contributing dissolved organochlorine to municipal wastewater. However, there have been no reports of organochlorines produced and retained in fabric as a result of laundry bleaching. We have used a chlorine-specific X-ray spectroscopic analysis to demonstrate the formation of organochlorine by-products in cotton fabrics laundered with chlorine bleach under typical household conditions. Organochlorine formation increases at higher wash temperature. At least two pools of organochlorine are produced in bleached fabric: a labile fraction that diminishes over several months of storage time as well as a more stable fraction that persists after more than 1 year. Our results also suggest that residual hypochlorite remains in fabric after laundering with bleach, presenting the possibility of direct and sustained dermal contact with reactive chlorine. This study provides a first step toward identifying a new risk factor for elevated organochlorine body burdens in humans.

1. Introduction

The oxidizing power of reactive chlorine has been responsible for major gains in public health over the last two centuries. However, disinfection with sodium hypochlorite (NaOCl) or gaseous elemental chlorine can generate toxic organochlorine by-products, notably in tap water (Nuckols et al., 2005; Kavcar et al., 2006; Fiss et al., 2007) and swimming pools (Zwiener et al., 2006). Treatment of soiled laundry with hypochlorite, the active ingredient common in household bleach (hereafter referred to as "chlorine bleach") offers aesthetic and microbicidal benefits (Arnold, 1938; Jordan et al., 1969; Walter and Schillinger, 1975; Buford et al., 1977; Belkin, 1998, 2003; Wisniak, 2004; Gerba and Kennedy, 2007). A nonselective oxidant, hypochlorite effectively kills a broad variety of bacteria (Parnes, 1997), and breaks down the unsaturated chromophores that constitute most laundry stains. This reactivity comes with disadvantages, as chlorine bleach can fade fabric dyes and deactivate other components of detergent, such as enzymes and brighteners (Moe, 2000). Another drawback is that hypochlorite may react with organic substrates to create by-products with potential risks to human health.

Previous study of by-product formation during household laundry bleaching focused on volatile organic compounds, such as chloroform and carbon tetrachloride, which are produced in the headspace of washing machines from reactions of hypochlorite with surfactants and other organic chemicals in detergents (Odabasi, 2008). Gaseous by-products pose an inhalation hazard, and, accordingly, the exhaled breath of human test subjects shows appreciable increases in chloroform levels following the act of machine washing with chlorine bleach (Gordon et al., 2006). High chloroform concentrations have also been detected in wash water after application of hypochlorite, implicating household laundry bleaching as a contributor of chloroform to municipal wastewater

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(Shepherd et al., 1996). Overall formation of halogenated by-products in wastewater from household laundry bleaching has been assessed using the adsorbable organohalogen (AOX) sum parameter, with AOX removal used as a major evaluative indicator for water treatment strategies (Ong et al., 1996; Braida et al., 1998).

There have been no definitive reports on the appearance of chlorinated by-products in fabric as a result of laundering with chlorine bleach, an incidence that could pose the risk of direct and continuous dermal and inhalation exposure. Despite the absence of scientific data, this issue has caused public concern (Blanc, 2007) and prompted development of "chlorine-free" alternatives.

To shed light on this question, we laundered an assortment of cotton fabrics with and without chlorine bleach under typical household conditions and analyzed them via X-ray absorption spectroscopy. This synchrotron-based, element-specific technique reveals the bonding environment of chlorine in chemically heterogeneous fibrous samples (Myneni, 2002b), ensuring detection of all chlorine species present, including organochlorine compounds of various molecular size and structure. The method obviates the need for extraction procedures that could result in chemical alterations or incomplete recoveries. Fitting sample spectra with those of chlorine-containing standards establishes the relative proportions of organic and inorganic forms of chlorine in the fabrics (Leri et al., 2006).

In the pulp and paper industry, concerns over organochlorine by-product formation have prompted conversion to "Elemental Chlorine Free" or "Totally Chlorine Free" wood pulp bleaching, yet widespread industrial and household use of chlorine bleach continues. This study unambiguously demonstrates the production of organochlorine in fabrics bleached using common laundering practices, introducing a potential new risk factor for elevated organochlorine body burdens in humans.

2. Materials and methods

2.1. Sample preparation

Five cotton clothing samples purchased from US retailers were sectioned and analyzed unlaundered, after laundering with detergent, and after laundering with detergent and chlorine bleach. One of the textiles tested was labeled "certified organic cotton grown in farming communities without pesticides or synthetic fertilizers;" the remainder were composed of conventional cotton. Laundering was performed in a front-loading high-efficiency residential washing machine with a tap water source using liquid laundry detergent containing nonionic surfactants and no whitening agents. In all cases, laundering with bleach was performed subsequent to laundering without bleach. Commercial chlorine bleach (approximately 4.5% hypochlorite ion solution) from a newly opened bottle was dispensed in the second wash cycle according to the manufacturer's directions, producing an estimated hypochlorite concentration of 100 mg kg^{-1} in the wash water. Washes consisted of ~4.5-kg loads, with a total water volume of 76 L split evenly between one pre-wash cycle, one wash cycle, and two rinse cycles. Water temperatures were 50 °C for the "hot" setting and 20 °C for "cold." Laundered samples were machine-dried on the low-temperature setting, with bleached samples dried separately from and subsequent to the unbleached samples.

To assess the solubility of the by-products, subsectioned bleached fabric samples were agitated in distilled water for 30 min at room temperature (20 °C). To assess the volatility of the by-products, fabrics were baked in an oven at 37 °C for 30 min. All fabrics were stored in the dark at room temperature prior to analysis.

2.2. Lab-based bleaching of cellulose and cotton substrates

Model reactions were performed on cellulose and cotton substrates under simulated laundry bleaching conditions. Chlorine bleach (~4.5% hypochlorite ion) was diluted in distilled water to recommended washing machine standards (a 0.22% bleach solution). Sodium chlorite (Sigma–Aldrich) was tested as an alternative chlorine-containing bleaching agent, using a 1.5% solution buffered at pH 4.0, according to established procedures in the textile industry (Hefti, 1960; Karmakar, 1999).

For each reaction, 0.30 g of raw cotton (Cottonman.com) or powdered cellulose (Sigma–Aldrich) were agitated in 100 mL of hypochlorite or chlorite (cotton only) solution at 20 or 50 °C for 10 min to simulate the wash cycle in a laundry machine (controls contained no bleaching agent). The supernatant was decanted and the solids centrifuged at 2000*g* for 5 min to simulate the spin cycle. Solids were resuspended in 100 mL water and stirred 5 min to simulate the first rinse cycle. After decanting and centrifuging, rinsing was repeated twice more. Solids were allowed to dry completely on watch glasses in a 37 °C oven.

2.3. Cl 1*s* XANES spectroscopy

2.3.1. Qualitative analysis

Fabric samples were analyzed in the solid phase by X-ray absorption near edge structure (XANES) spectroscopy at beamline X19A at the National Synchrotron Light Source in Brookhaven National Laboratory. The peaks in the "near-edge" region of a Cl 1*s* XANES spectrum correspond to the transitions of core electrons in Cl from the 1*s* to empty atomic/molecular orbitals. The spectra are specific to Cl since no two elements have the same energy difference between their 1*s* and outer orbitals. The positions, widths, and relative areas of the peaks in Cl 1*s* XANES spectra vary according to the oxidation state and bonding environment around the Cl

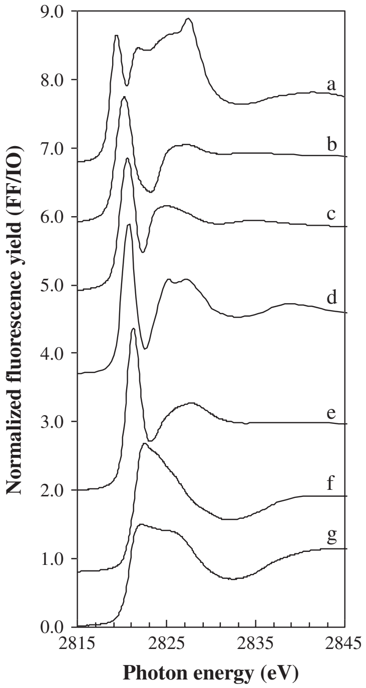

Fig. 1. Normalized Cl 1*s* XANES spectra of model compounds. (a) Sodium hypochlorite (NaOCl) (aq). (b) Trichloroacetic acid. (c) 1-Chlorodecane. (d) 2-Chloro-2-deoxy-D-glucose. (e) Chlorophenol Red sodium salt. (f) Glycine–HCl (s). (g) Sodium chloride (NaCl) (aq). The high-energy features in spectrum a appear obscured by artifacts of oxidation or other reactions, as has been observed previously for aqueous calcium hypochlorite ($Ca(OCl)_2$) (Reina et al., 2004).