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Polychlorinated biphenyl and polybrominated diphenyl ether profiles in serum from cattle, sheep, and goats across California

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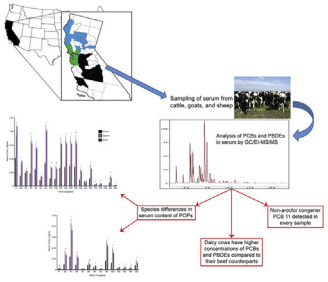
HIGHLIGHTS

- Caprine and ovine sera contain higher levels of PCBs and PBDEs than sera of bovine.
- Dairy cows have higher levels of PCBs and PBDEs than cows used in beef production.
- A non-legacy PCB, PCB 11, was detected at quantifiable levels in all livestock sera.
- There are no significant regional differences in the sum concentration of PCBs and PBDEs in bovine sera in California.

GRAPHICAL ABSTRACT



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ABSTRACT

It has been previously been shown by our lab and others that persistent organic pollutants, such as polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs), are contaminants in milk produced for human consumption. To further this research we determined the concentration of 21 PCB and 14 PBDE congeners in livestock serum, mainly bovine, across California. Congeners were extracted from serum using solid phase extraction (SPE), cleaned up by silica cartridge and quantified using gas chromatography-triple quadruple mass spectrometry. We detected significant differences among species and the production class of cattle (beef or dairy). The sum of all 21 PCB congeners (ΣPCBs) in caprine and ovine sera had a mean value of 9.26 and 9.13 ng/mL, respectively, compared to 3.98 ng/mL in bovine sera. The mean value for the sum of all 14 PBDE congeners (ΣPBDEs) in caprine and ovine sera was 2.82 and 2.39 ng/mL, respectively, compared to 0.91 ng/mL in bovine sera. Mean ΣPCBs in dairy cattle was 5.92 ng/mL compared to 2.70 ng/mL in beef cattle. Mean ΣPBDEs in dairy cattle was 1.33 ng/mL compared to 0.70 ng/mL in beef cattle. There were no regional differences in the ΣPCBs or ΣPBDEs in cattle distributed across California. These results highlight the fact that livestock are still being exposed to these pollutants yet little is known about where this exposure may be coming from.

1. Introduction

Polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs) are synthetic industrial chemicals that have become widespread persistent organic pollutants (POPs) and are resistant to biodegradation leading to their persistence in our environment.

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Both of these classes of POPs contain 209 different congeners with varying degree of halogenation and position of halogen atoms on their aromatic rings. One of the key characteristics shared amongst POPs are their high lipophilicity leading to their ability to accumulate in fatty animal tissue, thus leading to diet being an important source of exposure to these chemicals for humans (Schecter et al., 2010; Chan-Hon-Tong et al., 2013; Cimenci et al., 2013; Ampleman et al., 2015). Human exposure is a point of concern because epidemiologic studies have implicated PCBs and PBDEs in a variety of adverse health effects including immune system dysfunction (Jusko et al., 2012; Kramer et al., 2012), endocrine disruption (Abdelouahab et al., 2011; Silverstone et al., 2012; Valvi et al., 2012), and deficits in neurodevelopment (Schantz et al., 2003; Korrick and Sagiv, 2008; Herbstman et al., 2010; Winneke, 2011; Gascon et al., 2012; Eskenazi et al., 2013). One form of dietary exposure that has a relatively high fat content is milk. Since these toxic compounds are highly lipophilic, milk has been thought to be a prominent source of exposure for humans (Kim et al., 2008; O'Donovan et al., 2011). Many countries have analyzed bovine milk made within its borders for PCB and PBDE content and have found a multitude of congeners at quantifiable amounts (Focant et al., 2003; Durand et al., 2008; Kim et al., 2013; Lake et al., 2013). To date, there has only been one study within the United States (U.S.) looking at a small subset of PCBs in milk samples collected across the country (Schaum et al., 2003), not allowing for any region specific conclusions on PCB content or detection of PBDEs. To expand on this previous study, and since California produces approximately 20% of the total milk supply in the U.S., we analyzed milk samples made in California and discovered PCBs and PBDEs at quantifiable levels (Chen et al., 2017). As a follow up we conducted this current study to pursue these same pollutants in bovine serum, a matrix not yet investigated in the U.S in terms of PCB and PBDE contamination. A previous study from Italy has shown a difference in PCB content between ovine and bovine samples (Benedetto et al., 2016), which led us to expand the scope of this study to include ovine and caprine serum samples for assessing possible species differences.

PCBs are categorized into dioxin-like (DL) and non-dioxin-like (NDL) compounds. DL PCBs are potent activators of the aryl hydrocarbon receptor (Vondracek et al., 2005). Previous assessment of POP contamination of dairy products have primarily evaluated DL-compounds (Focant et al., 2003; Durand et al., 2008; Pizarro-Aranguiz et al., 2015) because, in the past, these compounds were considered to be the most toxic. However, NDL-PCBs dominate over DL-PCBs in biological and environmental samples (DeCaprio et al., 2005), and specifically multiple NDL-PCBs have been shown to be potent neurodevelopmental toxicants (Schantz et al., 1997; Howard et al., 2003; Yang et al., 2009; Yang and Lein, 2010; Wayman et al., 2012; Lesiak et al., 2014; Yang et al., 2014). Many of the previous studies with focus on DL-compounds also do not include assessment of PBDEs leaving out an entire class of compounds implicated as neurodevelopmental toxicants (Chen et al., 2012; Bradner et al., 2013; Behl et al., 2015; Jarema et al., 2015). PBDEs have been used extensively in products in California until their proposed ban in 2003. Following the ban in 2004, two commercial formulations, penta-BDE and octa-BDE, were phased out of production in some U.S. states after a voluntary agreement between the U.S. EPA and the sole manufacturer of these products (Dodson et al., 2012a). Despite the phase out of many PBDEs used in industry, these compounds persist in our environment due to their resistance to biodegradation (Dodson et al., 2012b; Bradman et al., 2014; Whitehead et al., 2015). Thus, we focused our study on mainly NDL-PCBs and PBDEs with potential neurodevelopmental toxicity as this is a highly sensitive endpoint of concern for these POPs. In addition, previous work assessing PBDEs and PCBs in bovine milk for human consumption detected a non-legacy PCB, or a PCB that was never intentionally synthesized for industrial purposes, PCB 11, at quantifiable levels (Chen et al., 2017). PCB 11 has recently emerged as a global pollutant and is currently produced as an unintentional byproduct of paint pigment synthesis (Choi et al., 2008; Du et al., 2008; Hu et al., 2008; Basu et al., 2009; Du et al., 2009; Hu and Hornbuckle, 2010; Heo et al., 2014); thus, we included PCB 11 in the analysis of serum samples collected in this study.

This study was performed to 1) evaluate the presence of PCBs and PBDEs in bovine, caprine and ovine sera and to 2) assess differences in pollutant profiles based on species or cattle production class (beef or dairy).

2. Materials and methods

2.1. Materials

All organic solvents used were of HPLC grade and obtained from Fisher Scientific (Fair Lawn, NJ, USA). The PCB standards (PCB-11, 28, 52, 77, 84, 91, 95, 101, 118, 131, 132, 135, 136, 138, 149, 153, 174, 175, 176, 180, 196) and PBDE standards (BDE-17, 28, 47, 49, 52, 66, 85, 95, 99, 100, 136, 153, 154, 183) were purchased from AccuStandard Inc. (New Haven, CT, USA). The ^{13}C12 labeled 2,2′,3′,4,5-pentachlorobiphenyl (^{13}C12-PCB-97) and ^{13}C12 labeled 2,3′,4,4′,5-pentabromodiphenyl ether (^{13}C12-BDE-118) were purchased from Cambridge Isotope Laboratories (Tewksbury, MA, USA). Control human serum was purchased from Golden West Biologicals (Temecula, CA, USA). Mirex was purchased from Sigma Aldrich (St. Louis, MO, USA). Solutions were diluted with isooctane to appropriate concentrations.

2.2. Sample collection

Samples were collected from August 2012 to September 2015 from locations depicted in Fig. 1. Counties were grouped into three different areas to identify any regional differences: Northern, Bay Area and Central California. All ovine and caprine serum samples were collected during appointments at the Veterinary Medical Teaching Hospital (VMTH), School of Veterinary Medicine, University of California Davis. Bovine samples were from cattle presented to the VMTH for appointments, and to the California Animal Health and Food Safety Laboratory, University of California Davis for diagnostic work-up. Additional bovine serum samples were collected in the Bay Area region under the supervision of a licensed large animal veterinarian. All samples were stored at −80 °C prior to analysis. In total, 172 serum samples were included in this study (Bovine n = 145, Caprine n = 17, Ovine n = 10). Information on location and production class was also noted when available. Location was designated by county and the various counties sampled were grouped into three regions of California based on geography and anthropogenic activities within the region. Only bovine serum samples were used in regional comparisons (Northern n = 51, Bay Area n = 46, or Central n = 53). Caprine and ovine samples were collected in the northern and bay area regions and were thus excluded from regional analyses since there was uneven regional distribution. The Bay Area was defined by any county touching the San Francisco bay and counties north of the bay were considered to be in the Northern region. All other counties were grouped into the Central region (See Table 1).

2.3. Sample processing and analysis

The serum sample extraction protocol was adapted from our previously published method (Lin et al., 2013). Samples were thawed and briefly vortexed. Aliquots of 0.5 mL of serum were