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BIOMONITORING OF SOME PERSISTENT ORGANOCHLORINE CONTAMINANTS IN THE MILK OF ANATOLIAN WATER BUFFALOES

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ABSTRACT
In this study, 50 raw milk samples of Anatolian water buffalo (*Bubalus bubalis*, Linneaus, 1758) belonging to different dairy farmers in the Kızılırmak Delta in Samsun, Turkey, were investigated for contamination by 9 organochlorine pesticides (OCPs) and 16 polychlorinated biphenyls (PCBs). The contaminants were extracted cryogenically from the milk fat and their concentrations were determined with a gas chromatography-electron capture detector (GC-ECD). The mean level of alpha-hexachlorocyclohexane (HCH) in the milk samples was 6.34 ng/g/fat, beta-HCH was 20.41 ng/g/fat, gamma-HCH was 9.77 ng/g/fat, ∑DDTs was 18.11 ng/g/fat and ∑Indicator-PCBs was 127.27 ng/g/fat. The mean values, except for aldrin and ∑DDTs, were above the maximum residue limits (MRLs) stated in the European Commission (EC) Regulations and Turkish Food Codex (TFC). Regular monitoring and reporting of the levels of persistent organochlorines in the meat, milk and processed products of water buffaloes is essential for the assessment of human, animal and environmental health.
Keywords: Biomonitoring, organochlorine pesticides, polychlorinated biphenyls, water buffalo milk.

ANADOLU MANDASI SÜTLERİNDE BAZI KALICI ORGANİK KLORLU KİRLETİCİLERİN BİYOİZLENMESİ

ÖZ
Bu çalışmada, Samsun Kızılırmak deltasındaki farklı yetiştiricilere ait mandalardan (*Bubalus bubalis*, Linneaus, 1758) toplanan 50 çiğ süt örneğinde, çevresel kontaminasyonu belirlemek için 9 organik klorlu pestisit ve 16 poliklorlu bifenil bileşik kalıntısı araştırıldı. Süt yağından kriyojenik yöntemle ekstrakte edilen analitlerin düzeyleri elektron yakalama detektörlü gaz kromatografi (GC-ECD) ile ölçüldü. Süt örneklerinde ortalama alfa-HCH düzeyi 6.34 ng/g/yağ, ortalama beta-HCH 20.41 ng/g yağ, ortalama gamma-HCH 9.77 ng/g/yağ, ortalama ∑DDT 18.11 ng/g/yağ ve ortalama ∑İndikatör-PCB 127.27 ng/g/yağ olarak tespit edildi. Aldrin ve ∑DDT dışındaki miktarlar Avrupa Birliği Yönetmelikleri ve Türk Gıda Kodeksi'nde belirtilen değerlerin üzerinde bulundu. Çevrede uzun yıllar etkinliklerini koruyabilen kalıcı organik klorlu bileşiklerin mandalardan elde edilen et, süt ve işlenmiş hayvansal ürünlerde düzenli aralıklarla izlenmesi ve bildirilmesi insan, hayvan ve çevre sağlığının değerlendirilmesi açısından önemlidir.
Anahtar kelimeler: Biyoizleme, organik klorlu pestisitler, poliklorlu bifeniller, manda sütü.

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INTRODUCTION

Organochlorine contaminants (OCs) like hexachlorobenzene (HCB), the insecticide dichlorodiphenyltrichloroethane (DDT) or its persistent metabolite p,p'-dichlorodiphenyldichloroethylene (DDE) as well as the polychlorinated biphenyls (PCB) are substances that are characterised by their high lipophilicity and high bioaccumulative potential (Schettgen et al., 2015) .They enter the atmosphere in numerous ways such as urban runoff, municipal sewage, industrial waste, outflow from agricultural area, chemical spill and transport (El-Shahawi et al., 2010; Hong et al., 2003). Once released in the environment they resist for physical, biological, chemical and photochemical breakdown processes and thus persist in the environment (Mrema et al., 2013). The persistency of the compounds allows them to accumulate in animals, particularly in the fat cells (El-Shahawi et al., 2010). These substances are still of environmental concern despite the worldwide ban on their production and use in the framework of the Stockholm Convention (StockholmConvention, 2001). Exposure to these persistent chemicals has been associated with various disorders including cancer (Medrado-Faria et al., 2000; Muscat et al., 2003), reproductive diseases (Porpora et al., 2009) and neurobehavioral effects (Colosio et al., 2003). It has been reported that these effects are related to their ability to disrupt the functions of certain hormones, enzymes, growth factors and neurotransmitters in the organism (Mrema et al., 2013).

The human population is exposed to OCPs and PCBs through several ways, food being the major route of exposure (Mrema et al., 2013). Buffalo milk is a preferential food source in different parts of the world and the second most consumed milk in the worldwide and in Europe. Italy, Turkey, Bulgaria and Greece are the countries where the largest amounts of buffalo milk being produced (Pasquini et al., 2018).

Fat content is higher in buffalo milk than in cow milk (Ménard et al., 2010) and the fat ratio of Anatolian water buffalo milk ranged from 5.91% to 8.15% with an average of 7.09% (Yilmaz et al., 2017). The high fat content of buffalo milk makes it highly suitable to accumulate persistent organochlorinated chemicals due to their lipophilicity. Although there is a public concern on the use of pesticides, yet studies on residual levels in water buffalo milk and their effects are limited (Abbassy, 2017; Aslam et al., 2013; Barman and Mishra, 2015; Bulut et al., 2011; John et al., 2001; Makadiya and Pandey, 2017; Sajid et al., 2016; Shaker and Elsharkawy, 2015), even there is no data in the national summary reports on pesticide residue analysis in food performed by European Food Safety Authority (EFSA) (EFSA, 2018). Therefore, monitoring of residues of pesticides and organochlorine contaminants in water buffaloes milk can provide data about the types and quantities of these hazardous compounds in the environment as well as in the milk. In this study, milk of Anatolian water buffaloes has been examined because the Kızılırmak Delta is one of the most important regions in Turkey for the breeding of Anatolian water buffaloes and the production of milk and milk products. Therefore, urgent efforts should be undertaken to determine the sources of the contaminants and then apply practical measures to reduce the levels of all the contaminants in the milk fat below the stated MRLs.

MATERIALS AND METHODS

A total of 50 raw milk samples from individually different Anatolian water buffaloes were collected, belonging to different dairy farmers in the Kızılırmak Delta in Samsun, Turkey, in September 2017. Milk samples were stored at -80 °C until analysis.

The cryogenic extraction of the OCPs and PCBs from the samples was performed according to the method stated by Bordet et al. (2002). For the cleanup, two types of ready-to-use cartridges (C_{18} and Florisil, Phenomenex, USA) were used. The method used by Aksoy et al. (2011) was utilized for the analyses of the samples with the GC-ECD. The injection block temperature was 260 °C and the injection mode was set as splitless. The flow rate of the nitrogen used as the carrier gas was set at 1.5 mL/min. The column (TRB-1, Teknokroma, Spain) was 60 m x 0.32 mm i.d. x

0.25 μm (phenyl methyl silicone) and the initial temperature of the column oven was 100 °C. The process conditions of the column were the following: initial oven temperature 100 °C (3 min), 10 °C/min to 200 °C (maintained for 3 min), 3 °C/min to 225 °C (maintained for 3 min), 2 °C/min to 270 °C (maintained for 3 min) and 1 °C/min to 275 °C (maintained for 10 min). The ECD temperature was set at 280 °C. Total analysis time was 67.83 minutes.

Nine OCP (alpha-HCH, beta-HCH, gamma-HCH (lindane), HCB, aldrin, DDT and its metabolites (2,4'-DDE, 4,4'-DDE, 2,4'-DDT, 4,4'-DDT)) and 16 PCB (PCB 28, PCB 52, PCB 70, PCB 74, PCB 81, PCB 99, PCB 101, PCB 118, PCB 128, PCB 138, PCB 153, PCB 156, PCB 170, PCB 180, PCB 187 and PCB 208) standards (Dr. Ehrenstorfer, Germany) were prepared at 7, 10, 30, 70, 100 and 300 ng/g and then injected into the GC-ECD. The OCPs and PCBs were added to milk fat at 25, 50 and 100 ng/g levels to determine the recovery percentages. The limits of detection (LODs) and limits of quantification (LOQs) were calculated automatically by the device's software (Shimadzu, Japan) using the standard chromatograms.

RESULTS AND DISCUSSION

Retention times, LOD and LOQ values, and recovery percentages of the OCPs and PCBs, are given in Table 1, residual levels of the OCPs and PCBs in the milk samples are given in Table 2, the mix standard chromatogram of the compounds shown in Figure 1 and the mix spiked chromatogram of the compounds is shown in Figure 2.

Table 1. Retention times, LOD and LOQ values, and recovery percentages of the OCPs and PCBs

Compound	Retention time (min)	LOD (ng/g)	LOQ (ng/g)	Recovery (%)
alpha-HCH	19.362	0.016	0.053	60
beta-HCH	19.989	0.035	0.117	82
HCB	20.117	0.018	0.060	48
gamma-HCH	20.713	0.018	0.060	74
PCB 28	23.640	0.184	0.613	63
PCB 52	25.446	0.298	0.993	89
Aldrin	26.862	0.021	0.070	55
PCB 74	28.940	0.218	0.727	65
PCB 70	29.137	0.221	0.737	63
2,4'-DDE	30.852	0.038	0.127	54
PCB 101	31.125	0.146	0.487	90
PCB 99	31.502	0.232	0.773	58
PCB 81	32.866	0.341	1.137	76
4,4'-DDE	33.072	0.027	0.090	82
PCB 118	35.650	0.244	0.813	77
2,4'-DDT	36.552	0.053	0.177	80
PCB 153	37.585	0.257	0.857	67
4,4'-DDT	39.138	0.053	0.177	97
PCB 138	39.589	0.214	0.713	71
PCB 187	41.233	0.226	0.753	70
PCB 128	41.617	0.182	0.607	78
PCB 156	43.771	0.177	0.590	71
PCB 180	45.432	0.178	0.593	66
PCB 170	47.668	0.155	0.517	68
PCB 208	51.919	0.185	0.617	44

Table 2. Residue levels of the OCPs and PCBs in the Anatolian water buffalo milk

Compound	PS	PS>MRL	Mean	Min	Max	MRLs ng/g (EU and Turkey)
alpha-HCH	50	5	6.34	2.07	25.17	10 (*)
beta-HCH	50	43	20.41	4.14	39.03	10 (*)
HCB	0	-	-	-	-	10 (*)
gamma-HCH	50	18	9.77	2.77	33.94	10 (*)
Aldrin	8	-	0.99	0.25	1.89	6 (1)
2,4'-DDE	2	-	2.49	1.89	3.10	-
4,4'-DDE	50	-	4.36	1.71	10.32	-
2,4'-DDT	4	-	1.37	0.09	2.26	-
4,4'-DDT	50	-	13.54	5.08	27.63	-
PCB 28	2	-	15.09	11.72	18.46	-
PCB 52	50	-	122.06	14.86	246.89	-
PCB 70	0	-	-	-	-	-
PCB 74	0	-	-	-	-	-
PCB 81	0	-	-	-	-	-
PCB 99	0	-	-	-	-	-
PCB 101	0	-	-	-	-	-
PCB 118	28	-	8.99	0.47	28.11	-
PCB 128	4	-	9.71	1.18	11.23	-
PCB 138	0	-	-	-	-	-
PCB 153	2	-	109.60	45.18	174.01	-
PCB 156	3	-	5.14	4.60	5.87	-
PCB 170	2	-	5.27	0.55	9.99	-
PCB 180	1	-	11.00	11.00	11.00	-
PCB 187	11	-	8.70	0.58	34.64	-
PCB 208	0	-	-	-	-	-
ΣDDTs	50	-	18.11	8.36	35.68	40
Σin-PCBs	50	48	127.27	14.86	355.09	40
ΣOCPs	50	-	54.77	23.21	105.33	-
ΣPCBs	50	-	135.56	30.72	362.95	-
ΣOCs	50	-	190.33	87.03	431.29	-

PS: Positive samples
(*) Indicates lower limit of analytical determination (EC, 2016, 2017; TFC, 2016)
(1) Aldrin and dieldrin combined expressed as dieldrin (EC, 2016; TFC, 2016)
Σin-PCBs: Sum of PCB-28, PCB-52, PCB-101, PCB-138, PCB-153 and PCB-180 (EC, 2011; TFC, 2011)
ΣDDTs: Sum of p,p'-DDT,o,p'-DDT,p-p'-DDE and p,p'-TDE (DDD) expressed as DDT (EC, 2016; TFC, 2016)

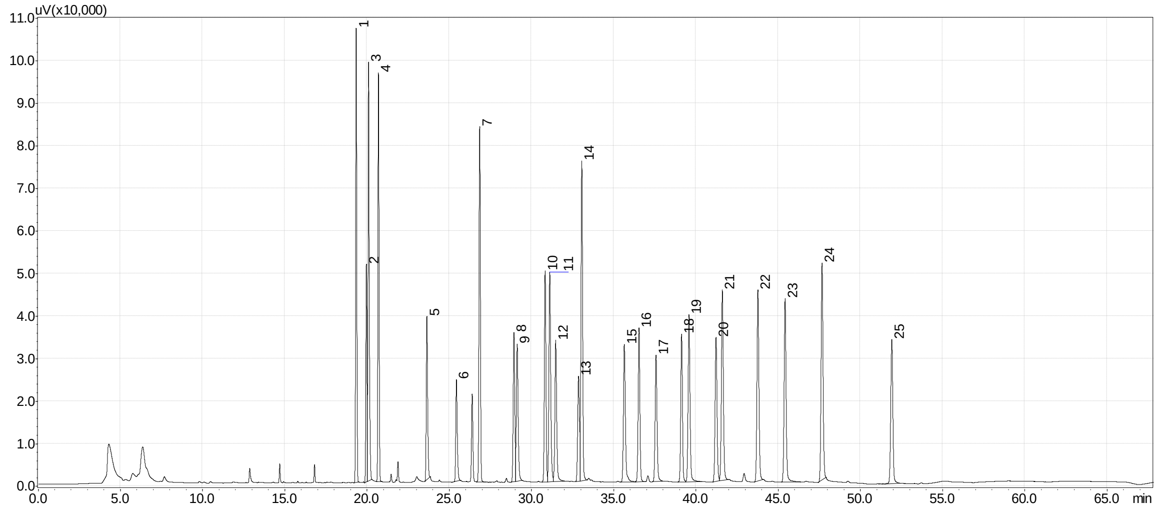

Figure 1. Mix standard chromatogram of the compounds at a concentration of 100 ng/g (alpha-HCH [1], beta-HCH [2], HCB [3], gamma-HCH [4], PCB 28 [5], PCB 52 [6], Aldrin [7], PCB 74 [8], PCB 70 [9], 2,4'-DDE [10], PCB 101 [11], PCB 99 [12], PCB 81 [13], 4,4'-DDE [14], PCB 118 [15], 2,4'-DDT [16], PCB 153 [17], 4,4'-DDT [18], PCB 138 [19], PCB 187 [20], PCB 128 [21], PCB 156 [22], PCB 180 [23], PCB 170 [24], PCB 208 [25])

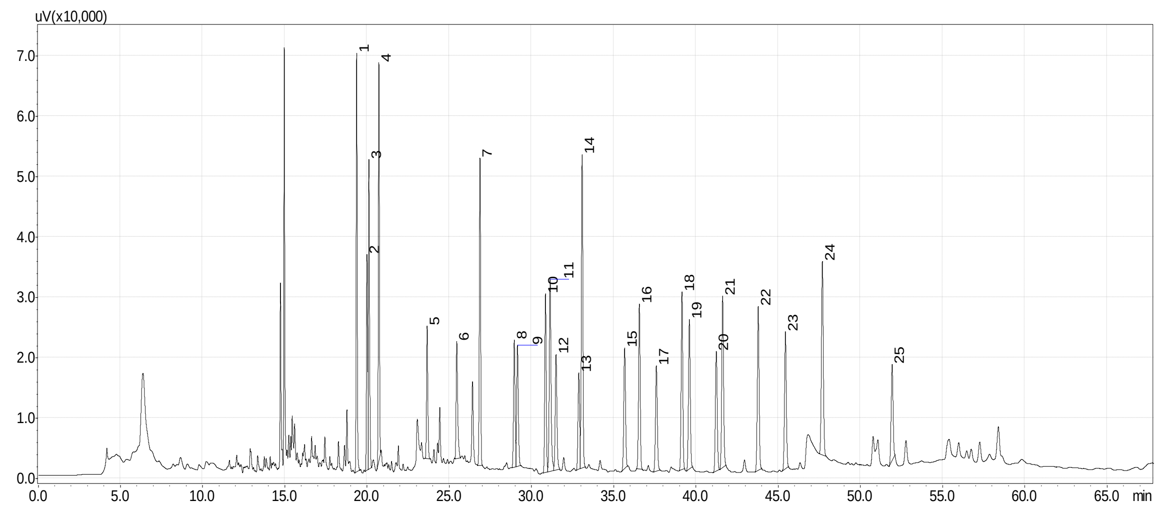

Figure 2. Mix spiked chromatogram of the compounds in buffalo milk fat at a concentration of 100 ng/g (alpha-HCH [1], beta-HCH [2], HCB [3], gamma-HCH [4], PCB 28 [5], PCB 52 [6], Aldrin [7], PCB 74 [8], PCB 70 [9], 2,4'-DDE [10], PCB 101 [11], PCB 99 [12], PCB 81 [13], 4,4'-DDE [14], PCB 118 [15], 2,4'-DDT [16], PCB 153 [17], 4,4'-DDT [18], PCB 138 [19], PCB 187 [20], PCB 128 [21], PCB 156 [22], PCB 180 [23], PCB 170 [24], PCB 208 [25])

In the present study, levels of certain OCPs and PCBs were examined in the water buffalo milk by using a validated analytical method. This work provides the first data on the contamination status of the milk of Anatolian water buffaloes by OCPs and PCBs, breeded in the Kızılırmak Delta in Samsun, Turkey. The results indicate that the Kızılırmak Delta is still being contaminated with some OCP and PCB compounds. The residual levels of ΣPCBs predominated, followed by Σin-PCBs, ΣDDTs, beta-HCH, gamma-HCH, alpha-

HCH and Aldrin. PCB 52 was the dominant congener among the indicator PCBs, showing the highest incidence (100%) and concentration in the milk samples. PCB 70, PCB 74, PCB 81, PCB 99, PCB 101, PCB 138 and PCB 208 were not detected in any milk samples. With respect to organochlorine pesticides, 4,4'-DDE, 4,4'-DDT, alpha-HCH, beta-HCH and gamma-HCH were detected in all milk samples. HCB was not detected in any milk samples. The OCPs were detected in descending order of concentration as follows, beta-HCH > 4,4'-DDT > gamma-HCH > alpha-HCH > 4,4'-DDE > 2,4'-DDE > 2,4'-DDT > Aldrin. The frequencies of occurrence of the contaminated samples above MRLs were 96%, 86%, 36% and 10% for Σin-PCBs, beta-HCH, gamma-HCH and alpha-HCH, respectively. In contrast, there was no sample above MRLs contaminated with ΣDDTs and aldrin.

Although buffalo milk is the second most consumed milk worldwide (Pasquini et al., 2018), there have been limited reports on PCBs (Cirillo et al., 2008; Esposito et al., 2010; Santelli et al., 2006) and OCPs (Abbassy, 2017; Aslam et al., 2013; Barman and Mishra, 2015; Bulut et al., 2011; John et al., 2001; Makadiya and Pandey, 2017; Sajid et al., 2016; Shaker and Elsharkawy, 2015). However, comparing the results was not feasible as the researchers did not state the OC levels in water buffalo milk on fat weight basis except a small number of studies (Abbassy, 2017; Aslam et al., 2013; Bulut et al., 2011; Cirillo et al., 2008; Esposito et al., 2010).

Cirillo et al. (2008) investigated the presence and the levels of six non dioxin-like (NDL) PCBs (PCB 28, 52, 101, 138, 153 and 180) and one dioxin-like (DL)-PCB 118 in water buffalo milk and mozzarella cheese produced in Campania region, Italy. The mean concentration of ΣNDL-PCBs (indicator PCBs) was found as 13.53 ng/g fat weight with a minimum level of 3.40 ng/g fat and a maximum level of 43.00 ng/g fat. These amounts in the milk were 9 fold lower than in the present study as well as the distribution pattern of individual PCBs were different. The Toxic Equivalency Factor (TEF) methodology is used to evaluate human health risks posed by DL compounds. The TEF value (Toxicity Equivalency Factor) of 0.00003 was attributed to PCB 118 by World Health Organisation (WHO) (Van den Berg et al., 2006). TEQ (Toxic Equivalency) value was found 0.270 pg TEQ/g fat which calculated considering the mean concentration of PCB 118 in the samples. This value was 8 to 9 times higher than that found by Cirillo et al. (2008).

It was reported that the North and Middle Basin areas of Kızılırmak River receive remarkably higher pollutant loads, due to domestic and industrial wastes which are discharged into the river without any treatment (Bakan et al., 2010). Gedik and İmamoğlu (2012) examined the occurrence and distribution of PCBs in surface sediments of the Kızılırmak River near a scrap yard in Kırıkkale province. ΣPCB amounts were detected up to 19.5 ng/g in sediments downstream of the yard and concentrations of individual PCB congeners were lower than 1 ng/g. One of the reason of PCBs pollution in the Kızılırmak Delta may be due to the drift followed by the distribution of these compounds to the catchment with the stream of the Kızılırmak River. In the present study, higher amounts of ΣPCBs (30.72 to 362.95 ng/g fat) were detected in the milk than in the sediments, probably due to the bioconcentration process of OC compounds in the animals (Shaker and Elsharkawy, 2015).

In Turkey, Bulut et al. (2011) investigated the contamination status of 50 milk samples of water buffaloes by OCPs from Afyonkarahisar region. They found beta-HCH levels above the MRL established in EC regulation and reported that the incidence were 64%, 16%, 8%, 6% and 2% for beta-HCH, 4,4'-DDT, Aldrin, gamma-HCH and delta-HCH, respectively. For alpha-HCH, beta-HCH, gamma-HCH, 4,4'-DDT and 4,4'-DDE the incidence were 100% in the milk samples and beta-HCH level exceeded the LODs stated in EC and TFC in the present study (EC, 2017; TFC, 2016). The water buffaloes in the Kızılırmak Delta stay in wetlands, lakes, marshes and swamps for resting and getting cool on the hot hours of the day (Selcuk, 2012). Therefore, they could have been exposed to the organochlorine compounds much higher by dermal and/or oral routes. In another study, 100 raw cow milk samples collected from Samsun province were analysed for nine OC and five synthetic pyrethroid pesticides. They did not detect any pesticide residues in the cow milk samples (Güvenç and Aksoy, 2009).

The present results showed lower levels of OCPs in water buffalo milk than in the study conducted in Delhi City, India (Aslam et al., 2013). They reported that mean values were 48 ng/g fat, 137.60 ng/g fat, 164.05 ng/g fat and 156.77 ng/g fat for alpha-HCH, beta-HCH, gamma-HCH and ΣDDTs, respectively. In another study conducted in Rosetta region Northern of Delta, Egypt, OC pesticide residue levels in buffalo milk were 2.0 ng/g fat, 1.58 ng/g fat, 1.70 ng/g fat, 2.09 ng/g fat and 1.29 ng/g fat for alpha-HCH, beta-HCH, gamma-HCH, 4,4'-DDE and 4,4'-DDT, respectively (Abbassy, 2017). These quantities in the water buffalo milk were lower than in the present study. It has been thought that various distribution patterns and concentrations of OC compounds in the milk of water buffaloes from different parts of the world may be related to pollution status of the environments, seasonal variations and some ethological characteristics of the water buffalo species.

CONCLUSION

It can be concluded from the present study that the OCPs, HCHs, 4,4'-DDE, 4,4'-DDT and PCBs 52 and 118 were detected at high occurring frequencies in the milk samples of Anatolian water buffaloes breeded in the Kızılırmak Delta in Samsun, Turkey. The mean values, except for aldrin and ∑DDTs, were above the maximum residue limit (MRLs) stated in the EC and TFC. Due to its fat rich content and high nutritional value, buffalo milk and milk products such as butter, yogurt, cream and cheese are consumed worldwide as well as in Samsun region. Hence, biomonitoring of hazardous chemical compounds in the water buffalo milk or milk products has a great importance for consumers health. In addition, further research is needed involving the pesticides which currently in usage in agricultural purposes beside banned OCPs and PCBs, to protect both human and animal health.

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