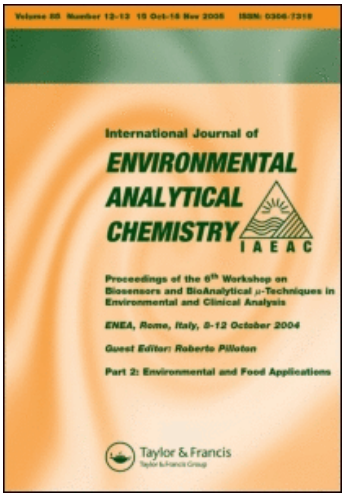

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TRACE METAL AND PESTICIDE LEVELS IN MUSKOXEN FROM VICTORIA ISLAND, NORTHWEST TERRITORIES, CANADA

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Tissue and blood samples were collected from muskoxen harvested in 1989 on Victoria Island, Northwest Territories. Liver and kidney were tested for trace elements and toxic metals, and fat and serum were tested for residues of organochlorine pesticides. Copper, manganese, and zinc levels were in the range considered adequate for sheep and cattle. Selenium levels in the muskoxen (liver mean value, 0.10 $\mu g\ g^{-1}$, kidney mean value, 0.36 $\mu g\ g^{-1}$) would be considered deficient in sheep and cattle. No elevated levels of toxic metals (arsenic, cadmium, lead, mercury) were found. All fat samples tested contained hexachlorobenzene (mean value, 45.4 $ng\ g^{-1}$) and 97% of the fat samples contained trace levels of α-hexachlorocyclohexane (mean value, 5.1 $ng\ g^{-1}$). Twelve percent of the serum samples contained hexachlorobenzene (mean value, 2.8 $ng\ g^{-1}$). Hexachlorobenzene levels in the fat of some unweaned calves exceeded tolerance levels set in Canada for food animals.

KEY WORDS: Trace metals, pesticides, muskoxen, residues.

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INTRODUCTION

Populations of muskoxen in the Canadian Arctic declined significantly in the late 19th and early 20th centuries, due in part to increased hunting pressure from European whalers, traders, and Inuit equipped with firearms,[1] and to the effects of severe winters.[2] Protected from hunting in 1917, muskox numbers recovered sufficiently to allow limited hunting to resume in 1969, based on a quota system.[3] In 1979 approval was given for the commercial sale of muskox meat.[4] A management program was initiated at this time by the government of the Northwest Territories (NWT), and there was an increase in population surveys and studies of muskox ecology.

The increase in muskox numbers has made commercial harvesting possible on some of their ranges,[5] including Victoria Island, NWT. During commercial harvesting there in 1989, muskoxen were sampled during key seasonal periods as part of a three year cooperative study of the nutrition and reproduction of muskoxen by the University of Saskatchewan and the NWT Department of Renewable Resources. Liver, kidney, fat, and serum samples were collected and forwarded to the Health of Animals Laboratory, Saskatoon, for analysis.

No published data could be found on trace element, toxic metal, or pesticide levels in muskoxen. The Western College of Veterinary Medicine, University of Saskatchewan, has maintained a captive herd of muskoxen since 1982, and has conducted limited testing of trace element (J. Blake, J. Rowell, pers. comm.) and organochlorine[6] levels in both wild and captive animals. Liver from 10 animals harvested on Banks Island, NWT, in 1985 was examined for levels of trace elements and organochlorines. The values obtained in our study were compared with these data, and with established values for domestic sheep and cattle.

MATERIALS AND METHODS

Sample collection

Liver, kidney, fat, and serum samples were collected from slaughtered muskoxen on Victoria Island, NWT, in April, May, August, and November of 1989. Sixty-seven animals were taken from randomly-selected herds in the vicinity of Wellington Bay, approximately 60 km west of the community of Cambridge Bay. Four to five animals were removed from each herd, with the majority being 4–5-year-old cows and their calves. Some immature females and males were also taken. Field temperatures in April and November were such that samples were frozen quickly; in May and August precautions were taken to keep samples cool until frozen at Cambridge Bay. Samples were shipped frozen to the laboratory and stored at −20°C until analyzed. The muskox carcasses were released to Central Arctic Meats Ltd (established by a local Hunters and Trappers Association) in Cambridge Bay for commercial sale of the meat within the NWT.[5]

Elemental analysis

Samples of liver and kidney were prepared for analysis using an automated acid digestion procedure.[7] Digested samples were analyzed for arsenic, cadmium, copper, mercury, manganese, lead, selenium, and zinc using atomic absorption spectrometry. Copper, manganese, and zinc were determined by flame analysis, arsenic and selenium by hydride generation, mercury by cold vapor generation, and cadmium and lead by graphite furnace atomization.

Materials

Analytical grade acids and standards used were as previously described.[7]

Pesticide analysis

Pesticides and polychlorinated biphenyls (PCB) were recovered from rendered fat samples by sweep co-distillation[8] using a Unitrex Universal Trace Extractor (Scientific Glass Engineering, Bucks, England). Briefly, the volatiles were collected on a glass trap containing approximately 1 g activated Florisil between two silanized glass wool plugs. Pesticide and PCB residues were eluted from the Florisil column with 15 ml of 2.5% diethyl ether in hexane into a 15 ml graduated centrifuge tube, evaporated to dryness under a stream of dry nitrogen in a 35–40°C waterbath, dissolved in 1 ml iso-octane, and analyzed by gas chromatography. Any samples that were found to contain PCBs were fractionated on Florisil as described below for serum and reanalyzed by gas chromatography.

Serum samples were analyzed for pesticides and PCBs by the method of Burse *et al.*[9] modified to use Florisil instead of silica gel for column chromatography. Briefly, 2 ml of serum were mixed with 2 ml of methanol and extracted three times with hexane–ethyl ether (1:1), centrifuging each time and collecting the organic layer. The combined organic layers were reduced to 0.5 ml under a stream of dry nitrogen in a 35–40°C water bath and applied to an 8 g Florisil column. Three fractions were collected by eluting in sequence with approximately 50 ml each of hexane, 15% dichloromethane in hexane, and 80% dichloromethane in hexane. Each fraction was taken just to dryness under a stream of dry nitrogen, dissolved in 1 ml of iso-octane, and analyzed by gas chromatography-electron capture detection.

Gas chromatography

A 1 μl aliquot of sample was injected into a 15 m × 0.53 mm DB608 capillary column (Supelco, Oakville, ON) using helium as the carrier gas at a flow of 5 ml min^{-1}. Zone temperatures were as follows: injector, 220°C; detector, 330°C; and oven program, initial 150°C for 1 min, ramp 10°C min^{-1}, final 280°C for 6 min. Argon–methane (95/5) at a flow rate of 25 ml min^{-1} was used as the make-up gas. Quantitation was by external standard, based on an injection of a mixed pesticide standard and/or PCB standard which contained the compounds of interest, with compounds identified by retention time.

Second-column confirmations were done on a 15 m × 0.53 mm DB5 capillary column (Supelco) using the above system with the exception of the oven program: initial 150°C for 1 min, ramp 5°C min^{-1}, final 260°C for 2 min.

Gas chromatography-mass spectrometry

Gas chromatography-mass spectrometry confirmation of pesticides was conducted as previously reported.[10]

Statistical analysis

Data obtained from the animals were compared for significant differences among the age groups and among the periods of slaughter using the null hypothesis (*t*-test) for comparison of means having population standard deviations that are not equal.[11]

RESULTS AND DISCUSSION

The levels of trace and heavy metals found are listed in Table 1. Thirty-seven liver and 54 kidney samples were tested. Means and standard deviations were calculated using those values that were greater than or equal to the detection limit (DL) of the

Table 1 Concentrations of elements ($\mu g\ g^{-1}$ wet wt) in muskoxen

Element	*Tissue*	# > *DL*[a]	*Mean ± SD*	*Range*
Arsenic	Liver[b]	18	0.05 ± 0.09	0.02 – 0.40
	Kidney[c]	22	0.03 ± 0.01	0.02 – 0.05
Cadmium	Liver	34	0.10 ± 0.05	0.01 – 0.22
	Kidney	46	0.42 ± 0.44	0.01 – 1.92
Copper	Liver	37	66.5 ± 23.4	21.4 – 119
	Kidney	54	2.92 ± 0.48	2.05 – 3.87
Lead	Liver	34	0.12 ± 0.10	0.04 – 0.53
	Kidney	37	0.10 ± 0.08	0.04 – 0.38
Manganese	Liver	37	3.21 ± 0.52	2.30 – 4.88
	Kidney	54	1.31 ± 0.34	0.51 – 2.85
Mercury	Liver	32	0.07 ± 0.04	0.01 – 0.14
	Kidney	53	0.23 ± 0.17	0.01 – 0.67
Selenium	Liver	28	0.10 ± 0.07	0.04 – 0.27
	Kidney	52	0.36 ± 0.24	0.06 – 0.98
Zinc	Liver	37	28.1 ± 6.94	18.8 – 57.9
	Kidney	54	27.6 ± 3.71	21.7 – 36.3

[a] Number of samples found to have levels greater than or equal to the detection limit of the test.
[b] $n = 37$ for each element.
[c] $n = 54$ for each element.

analytical method. The DLs (in $\mu g\ g^{-1}$ wet tissue) for the elements tested are: arsenic −0.02, cadmium −0.01, copper −0.60, mercury −0.01, manganese −0.30, lead −0.04, selenium −0.04, and zinc −0.25.

Average manganese and zinc levels in liver from animals slaughtered on Banks Island in 1985 were 3.8 ± 0.5 and $35.3 \pm 8.1\ \mu g\ g^{-1}$, respectively (J. Blake, J. Rowell, pers. comm.). These values are comparable to those found in the animals from Victoria island. The mean level of copper found in livers from Victoria Island animals was more than twice as high as the $28.9 \pm 17.8\ \mu g\ g^{-1}$ value for the Banks Island animals. The mean level of selenium in the livers of the Banks Island animals was two-and-one-half times greater at $0.26 \pm 0.02\ \mu g\ g^{-1}$.

The values obtained were also compared to established values for domesticated sheep and cattle.[12] Copper, manganese, and zinc levels in the muskoxen were in the range considered to be adequate for sheep and cattle. Average selenium levels, however, were in the range considered to be indicative of selenium deficiency for sheep (liver – 0.01–0.1 $\mu g\ g^{-1}$, kidney −0.046–0.6 $\mu g\ g^{-1}$) and cattle (liver – 0.02–0.17 $\mu g\ g^{-1}$, kidney −0.18–0.40 $\mu g\ g^{-1}$). Levels of arsenic, cadmium, mercury, and lead were well below those considered toxic to livestock or a health risk to consumers of meat from muskoxen. Levels of cadmium in kidney increased with increasing age of the animal. The concentration of mercury in kidney averaged $0.02\ \mu g\ g^{-1}$ for animals under one year of age, and $0.29\ \mu g\ g^{-1}$ for animals one year and older.

Comparison of trace element levels in muskoxen to levels in domestic sheep and cattle may not be valid, and is provided here for informational purposes only. The database for muskoxen needs to be expanded, and correlated with field and clinical observations before definitive statements can be made regarding the trace element requirements of muskoxen. Muskoxen have been observed to use mineral licks,[13,14] but analysis of the lick material[15] indicated that obtaining sodium was the most probable reason. Selenium content of the lick material was not reported.

Two chlorinated hydrocarbons were detected in the fat tissue and serum of the muskoxen: hexachlorobenzene (HCB) in fat and serum and alpha-hexachlorocyclohexane (α-HCH) in fat. The levels found are listed in Table 2. No other pesticides or PCBs were detected. Fifty-eight fat samples and 66 serum samples were analyzed. The means were calculated using the values which equalled or exceeded the DL of $1\ ng\ g^{-1}$ for each compound (listed as no. > DL in Table 2).

Table 2 Pesticide levels ($ng\ g^{-1}$) in muskoxen

Pesticide	*Matrix*	# > *DL*[a]	*Mean ± SD*	*Range*
HCB	Fat[b]	58	45.4 ± 33.1	8.0 – 162.4
	Serum[c]	8	2.8 ± 2.0	1.1 – 7.5
α-HCH	Fat	56	5.1 ± 2.9	1.0 – 10.7

[a] Number of samples found to have levels greater than or equal to the detection limit of the test.
[b] $n = 58$ for fat.
[c] $n = 66$ for serum.

All fat samples contained HCB and all but two contained α-HCH. Only the serum samples corresponding to the fat samples containing the highest levels of HCB (85.6–162.4 ng g^{-1}) contained detectable levels of HCB. The overall levels of α-HCH were very low (1/10 those of HCB) and did not show any seasonal pattern. HCB levels on the other hand did exhibit a seasonal trend. The samples were collected during three periods, April–May, August, and November, from animals varying in age from 0.1 to 5.0 years. The mean values of detectable HCB pesticides in fat for each period and for each age group are shown in Table 3. The levels of HCB for all ages were significantly higher ($p < 0.01$) in the April–May samples, and during this period concentrations in samples from the calves (0.1 years) and yearlings were significantly higher ($p < 0.01$) than those found in the older animals. As the season progressed the levels declined for all age groups.

The higher pesticide residue levels found in the mature animals in April–May were attributed to the depletion of fat reserves over the winter, giving rise to a concentration effect. This effect would be greatest in the animals with a smaller body mass, hence the higher levels in the one-year-old animals. Later in the year when more forage is available, the fat reserves are restored, and the levels probably decrease to where a steady state of pesticide concentration is reached.

The higher residue concentrations found in the calves probably resulted from a combination of small body mass and exposure to large quantities of elevated pesticide levels through the fat-rich milk they consumed. As they became older and began to forage, the levels decreased, although even in November the levels were still significantly higher ($p > 0.01$) than in the older animals.

The presence of pesticide residues in the muskox samples is consistent with current findings related to the atmospheric transport of environmental chemicals to Arctic regions.[16–18] Pesticides have been detected in air,[17] snow,[16] soil, plants,[18] fish,[19] seals,[20] and bison in the sub-arctic.[10] HCB and α-HCH are among the organochlorines commonly found in fish and seals and are the major organochlorines found in air, snow, soil, plants, and bison.

The levels found in this study do not appear to be of concern to the health of any of the animals but could affect their suitability for human consumption. The levels of HCB present in 57% of the calves and yearlings during the spring period were above the Canadian tolerance level of 100 ng g^{-1} [21] and could pose a risk. In the

Table 3 Seasonal changes in HCB levels in fat (ng g^{-1}) in muskoxen

Period	*Age of animals (years)*					
	0.1–0.5	*1.0–1.5*	*2.0–2.5*	*3.0–3.5*	*4.0–4.5*	*5.0–5.5*
April-May	133.0 (4)[a]	92.3 (3)	57.3 (5)	44.4 (7)	39.7 (4)	44.3 (11)
August	42.7 (7)	ns[b]	10.4 (2)	8.0 (1)	20.3 (1)	11.2 (2)
November	32.6 (3)	ns	17.3 (1)	ns	19.1 (1)	14.3 (3)

[a] ( ) = Number of values used to calculate mean.
[b] ns = No samples available in this age group.

adult animals the levels were below the tolerance levels of 100 ppb for both HCB and α-HCH which are allowed in domestic animals consumed for meat in Canada, and should not pose any risk to the health of consumers. Our limited study suggests that use of muskoxen as meat animals should be restricted to older animals ($\geq$2.0 years) from spring until late summer. A recent study of the commercial harvesting of muskoxen recommended that hunting be curtailed during the period mid-April to October as meat quality is at its lowest at this time, and because the animals are in the later stages of pregnancy or are lactating.[5] Our findings provide another reason to limit hunting during this time period.

Analysis of liver samples collected from the Banks Island muskoxen in 1985 also indicated the presence of HCB and α-HCH, as well as oxychlordane and PCBs.[6] Average levels of HCB and α-HCH in the liver were 3.2 and 1.5 ng g^{-1}, respectively. These values are lower than the levels in fat reported here, probably reflecting the tendency for organochlorine pesticides to accumulate in fat.

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