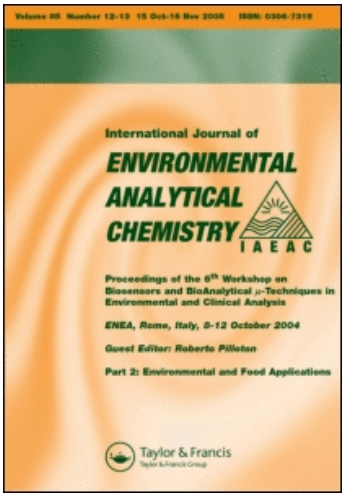

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J. D. Macneil[a]; J. R. Patterson[a]; A. C. Fesser[a]; C. D. Salisbury[a]; S. V. Tessaro[a]; C. Gates[b]
[a] Animal Pathology Laboratory, Agriculture Canada, Saskatoon, Saskatchewan, Canada [b] Department of Renewable Resources, Government of the Northwest Territories, Fort Smith, North west Territories, Canada

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Trace Metal and Persistent Organochlorine Levels in Wood Bison (*Bison bison athabascae*) from the Mackenzie Bison Sanctuary

J. D. MACNEIL, J. R. PATTERSON, A. C. FESSER, C. D. SALISBURY and S. V. TESSARO

Animal Pathology Laboratory, Agriculture Canada, 116 Veterinary Road, Saskatoon, Saskatchewan, Canada S7N 2R3

and

C. GATES

Department of Renewable Resources, Government of the Northwest Territories, Fort Smith, Northwest Territories, Canada X0E 0P0

Tissue samples were collected from ten healthy mature female wood bison (*B. bison athabascae*) for examination. Livers and kidneys were tested for toxic heavy metals and trace metals considered as essential nutrients for successful reproduction, while fat samples were analyzed for persistent chlorinated hydrocarbons. No elevated levels of toxic heavy metals (arsenic, cadmium, lead, mercury) were found and essential trace elements (copper, manganese, selenium, zinc) were within the acceptable ranges established for healthy cattle. All fat samples tested contained trace levels of α-BHC (mean value, 23 ppb) and lindane (mean value, 3 ppb).

KEY WORDS: Trace metals, pesticides, BHC, bison, organochlorine, residues.

INTRODUCTION

Free-ranging bison in the Canadian north-west can currently be found in two protected areas, Wood Buffalo National Park, which straddles the Alberta–Northwest Territories (NWT) border, and the Mackenzie Bison Sanctuary within the NWT. The Wood Buffalo National Park herd consists of hybrid animals produced when the original wood bison (*B. bison athabascae*) which inhabited the park area interbred with plains bison (*B. bison bison*) introduced into the park in the period 1925–28. While the animals currently found in the park are hybrids, a small group of apparently pure wood bison were discovered along the Nyarling River in 1957.[1] Eighteen of these bison were transported to the current Mackenzie Bison Sanctuary in 1963, with a subsequent sustained growth in population to a present level of approximately 1,800.

The hybrid herd in Wood Buffalo National Park has not fared as well during the same period. The count of bison in the Park has varied from a high of 9,828 in 1972 to a low of 4,627 in 1980.[2] Reasons for the difference in success rate of the two herds remain undefined, although theories advanced include disease, predation and nutritional factors. Brucellosis and tuberculosis, diseases known to affect reproductive success, have been recognized in the Park[2] but not in limited testing in the Sanctuary. However, the availability of essential trace nutrients is also a potential area of concern. Shaw and Reynolds[3] determined selenium levels in sedges and reedgrasses in bison habitats and reported a concern about potential deficiencies of this essential nutrient.

Because a characterization of trace chemical levels in free-ranging bison has not previously been reported, we selected the successful Sanctuary herd as a reference group against which other bison could be measured. Essential trace metals, toxic heavy metals and persistent organochlorinated compounds were monitored as part of a larger study being undertaken of these animals.

MATERIALS AND METHODS

Sample collection

Ten mature females, aged approximately 4–10 years, were randomly

selected. The bison were shot by wildlife officers in March, 1986, and carcasses were sampled in the field at temperatures of −30°C. Liver, kidney and fat samples were taken for chemical analysis, shipped frozen on ice by air freight to the laboratory and stored at −20°C until analyzed.

Sample preparation and extraction

Fat samples were analyzed for pesticides and polychlorinated biphenyls, with clean-up of the rendered fat using sweep co-distillation as described by Neidert and Saschenbrecker[4] using a Kontes Sweep Co-distillation Apparatus. Briefly, the volatiles were collected on a chromatographic column consisting of a Pasteur pipet containing 6 cm of activated Florisil®, pesticide residue grade (Supelco Canada Ltd., Oakville, Ontario), 60/100 mesh, 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 waterbath at 35–40°C, dissolved in 1 ml iso-octane and analyzed by gas chromatography.

Gas chromatography

A 2 μl aliquot of sample was injected onto a 2 m × 4 mm I.D. glass column packed with 1.5% SP-2250/1.95% SP-2401 on 100/120 Supelcoport (Supelco, Inc.). All analyses were conducted on a Hewlett-Packard 5880 gas chromatograph equipped with a Ni-63 electron capture detector and a model 7671A autosampler. Zone temperatures were as follows: injector, 230°C; oven, 220°C; detector, 330°C. Argon-methane (95:5) was the carrier gas at a flow rate of 25 ml/min. Quantitation was by external standard, based on an injection of a mixed pesticide standard which contained the compounds of interest, with compounds identified by retention time.

Confirmations by gas chromatography were done using a 2 m × 4 mm I.D. glass column packed with 5% Dexsil 300 on Gas Chrom Q, 80/100 mesh (Chromatographic Specialities, Ltd.), also with the HP5880 as described above. Zone temperatures were: injector, 290°C; oven, 260°C; detector, 330°C. A carrier flow rate of 30 ml/min argon-methane (95:5) was used.

Gas chromatography–Mass spectrometry

GC–MS confirmations were conducted on a Finnigan 4000 system equipped with a PIPINICI detector, using both electron impact (EI) and chemical ionization (CI) modes. Samples were introduced to the mass spectrometer via a 30 m × 0.252 mm DB-5 capillary column (J & W Scientific, Inc.), 0.25 micron film thickness using Grob splitless injection technique. A temperature program of 50°C for 1 min, then 20°C/min to 290°, followed by 10 min at 290°C was used. For EI work, an ionizing potential of 70 eV was chosen, while CI analyses were conducted using methane as reactant gas. Analyses were carried out in the MID mode, based on characteristic peaks observed in the spectra of standards injected under the same conditions of analysis.

Confirmation of the presence of BHC (benzene hexachloride) isomers was provided by GC–MS. Using the EI mode, characteristic ion fragments for BHC of 290, 254, 219, 181 and 109 were monitored. Using CI negative ion, the characteristic fragments selected were 259, 257 and 255. A window of ±0.5 amu was used in each mode.

Trace metal analyses

Liver and kidney samples were analyzed for arsenic, cadmium, copper, lead, manganese, mercury, selenium and zinc by atomic absorption spectrometry using a Varian 975 AA equipped with the VGA 76 hydride generation accessory, graphite furnace and standard flame. Analytical modes used were as follows: copper, manganese, zinc—flame; cadmium, lead—graphite furnace; mercury—cold vapour; arsenic, selenium—hydride generation. An automated sample digestion procedure previously described by Salisbury and Chan[5] was used to prepare all samples for analysis. Operating settings and detection limits for the atomic absorption work were as recommended in the operating manual from the manufacturer.

Materials

Solvents Pesticide analysis grade ethyl ether, hexane and iso-octane; deionized water.

Acids Analytical grade: nitric acid, 69–71%; perchloric acid, 70–72%; sulphuric acid, 95–98%.

Pesticide standards Purified standards as required by EPA and OSHA for qualitative and quantitative analysis (Chem. Service Inc.).

Atomic absorption standards Fisher Certified AA Standards for arsenic, cadmium, copper, manganese, mercury, lead, selenium and zinc (100 μg/ml); NBS Bovine Liver No. 1577a.

Florisil PR grade, Floridin Corporation, pre-wash with 10 ml diethyl ether per 1 g Florisil, air dry in fumehood to remove solvent, activate in convection oven (4–5 hr at 135°C), store in dessicator until used.

RESULTS AND DISCUSSION

Chromatographic analyses of the perirenal fat samples from the bison revealed very low levels of chlorinated compounds. All samples contained low levels of α-BHC and γ-BHC (lindane), as reported in Table I. No correction for recovery was used, as recoveries for BHC's on spiked fat samples exceeded 80%. Any other chlorinated pesticides and PCB's present in the samples were at levels below

Table I Pesticide levels (ppm) in mature female bison

Sample no.	α-BHC	Lindane
1	0.018	0.002
2	0.017	0.002
3	0.040	0.002
4	0.030	0.001
5	0.030	0.002
6	0.023	<0.001
7	0.022	0.007
8	0.019	0.007
9	0.014	0.006
10	0.019	0.005
Mean	0.023	0.003
s.d.	0.008	0.003

reliable detection limits and were not confirmed (i.e., less than 1–5 ppb). The lack of other significant peaks in the chromatograms may readily be seen by comparing chromatograms of the calibration standard (a) and a typical bison sample (b) in Figure 1.

Both mass spectral techniques confirmed the presence of the α-BHC and lindane in these samples, as well as indicating possible traces of β-BHC. Typical reconstructed ion chromatograms for samples analyzed using the two mass spectral modes are shown in Figure 2.

The predominance of α-BHC over other residues in these samples requires some explanation, as this isomer is not an insecticide. It was the predominant isomer in commercial BHC mixed isomer formulations used as insecticides, but these were last registered for use in Canada in 1972. An extensive sampling of prairie waters by Environment Canada[6] revealed that 84% of samples analyzed contained quantifiable residues of α-BHC, while about 58% of the stations monitored had lindane residues. Local usage of pesticides would not seem to account for the presence of detectable residues in the more remote northern areas. Previous investigators[6] have postulated that long-range atmospheric transport mechanisms may account for the finding of lindane residues in more remote areas. There have, furthermore, been suggestions that α-BHC may be formed as a metabolite of lindane, based on a study of organochlorine residues in wild moose in Idaho.[7] The source of the α-BHC remains an open question, but it may be explained in terms of long-range transport phenomena associated with the use of formulations containing either predominantly α-BHC or other BHC isomers which have been environmentally transformed into α-BHC elsewhere in the northern hemisphere. Certainly, the widespread occurrence of α-BHC in tissue samples, such as poultry in Ontario, Canada[8] and predatory birds in Spain[9] suggests that the pathways leading to these residues warrant further study. The levels found in this study, however, would not appear to offer any threat to the health or reproductive ability of the Mackenzie bison.

As no baseline data for typical metal levels in free-ranging bison have previously been reported, we have referred to previously published data on cattle[10] to indicate acceptable levels for this study. Results of our analyses are given in Table II. Means and standard deviations have not been calculated for arsenic and lead, as these

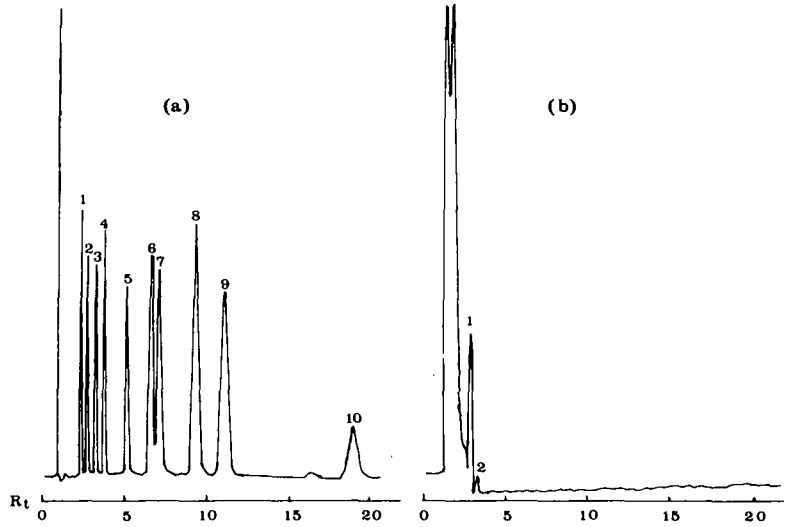

Figure 1 Chromatograms of pesticide calibration standard (a) and extract from bison fat (b). Peak identification is as follows, with retention time in minutes in brackets: 1, α-BHC (2.28); 2, lindane (2.71); 3, heptachlor (3.23); 4, aldrin (3.79); 5, heptachlor epoxide (5.25); 6, DDE (6.80); 7, dieldrin (7.37); 8, DDD (9.66); 9, DDT (11.46); 10, methoxychlor (19.70).

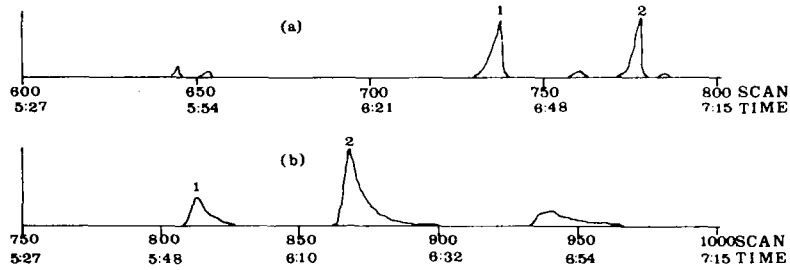

Figure 2 Reconstructed ion chromatograms for bison sample analyses by GC–MS showing presence of α-BHC (peak 1) and lindane (peak 2) using electron impact (EI) mode (a) and negative ion chemical ionization (NICI) mode with methane as reactant gas (b).

Table II Trace metal levels (ppm) in mature female bison

		Mean	Range	s.d.
Arsenic	L[a]	—[c]	0 – 0.02	—
	K[b]	—	0 – 0.02	—
Cadmium	L	0.30	0.14– 0.48	0.11
	K	3.87	1.61– 7.11	1.77
Copper	L	35.3	12.7 –52.1	11.3
	K	6.7	5.5 – 8.0	0.8
Lead	L	—	0 – 0.06	—
	K	—	0 – 0.04	—
Manganese	L	3.55	2.75– 4.30	0.49
	K	1.14	0.84– 1.40	0.19
Mercury	L	0.01	0 – 0.02	0.004
	K	0.03	0 – 0.05	0.01
Selenium	L	0.22	0.11– 0.88	0.24
	K	0.91	0.55– 1.40	0.27
Zinc	L	33.7	26.9 –49.4	6.1
	K	20.4	15.8 –26.9	3.1

[a]Liver.
[b]Kidney.
[c]Means and s.d.'s not calculated when metals were detected in less than 3 of the 10 samples.

were only detectable in 1–3 each of the 10 livers and 10 kidneys analyzed.

Our data revealed that arsenic, cadmium, lead and mercury levels are well below those which would cause concern. In cattle, acute toxic levels for arsenic are 2–15 ppm in liver and 3.5–38 ppm in kidney. We found 100-fold lower levels. For lead, toxic levels are in excess of 5 ppm in liver and 10 ppm in kidney. Again, we observed levels 100-fold below this. Toxic levels for mercury are in excess of 2 ppm in liver and 50 ppm in kidney, but our mean levels for these tissues were 0.02 ppm and 0.05 ppm, respectively. For cadmium, levels of 50 ppm in liver and in excess of 100 ppm in kidney are considered toxic. Levels reported in this study were well below those of concern. Heavy metal levels for these four potentially toxic elements would therefore not appear to pose a threat to this herd,

nor, based on these data, would there appear to be reason to expect significant levels of these metals to appear in bison on typical open habitat.

Mean values for copper, manganese, selenium and zinc were within the range considered acceptable in cattle.[10] Low levels of copper, manganese, selenium and zinc are associated with reproductive problems in cattle. The reproductive rate of the bison in the Mackenzie Sanctuary does not indicate any such problems, so it may therefore be reasonable to apply data obtained for cattle in terms of required levels of essential trace nutrients to bison. Moreover, levels of these essential metals found in this successful population may be used as a basis for comparison with other free-ranging bison. The concern expressed in a previous study about low selenium levels found in bison forage[3] is not reflected in the selenium levels in tissue collected from animals selected in this study.

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References

1. G. W. Calef. In: *Northern Ecology and Resource Management* (R. Olson, R. Hastings and F. Geddes, eds.) (Univ. Alberta Press, Edmonton, Alberta, 1984), pp. 183–200.
2. Wood Buffalo National Park Management Plan, Parks Canada (1985).
3. G. G. Shaw and H. W. Reynolds, *Arctic* **38,** 61 (1985).
4. E. Neidert and P. W. Saschenbrecker, *J. Assoc. Offic. Anal. Chem.* **67,** 773 (1984).
5. C. D. Salisbury and W. Chan, *J. Assoc. Offic. Anal. Chem.* **68,** 218 (1985).
6. W. D. Gummer. In: *Pesticide Monitoring in the Prairies of Western Canada* (Water Quality Interpretive Report no. 4, Inland Waters Directorate, Environment Canada, 1979).
7. W. W. Benson, M. Watson and J. Wyllie, *Pestic. Monit. J.* **7,** 97 (1973).
8. R. Frank, J. Rasper, H. E. Braun and G. Ashton, *J. Assoc. Offic. Anal. Chem.* **68,** 124 (1985).
9. M. J. González, L. M. Hernández, M. C. Rico and G. Baliya, *J. Envir. Sci. Health* **B19,** 759 (1984).
10. R. Puls. In: *Veterinary Trace Mineral Deficiency and Toxicity Information* (Agriculture Canada/B.C. Ministry of Agriculture and Food, Publication 5139, Information Services, Agriculture Canada, Ottawa, Ont., Canada K1A 0C7, 1981).