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Ionic alkylleads in avian tissues from aquatic and terrestrial environments

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Ionic alkyllead concentrations in soft tissues of pigeons from urban Montreal and environs were appreciably different from the variety and concentrations of alkyllead analytes which characterized mallard ducks culled from a sanctuary in eastern Ontario. The major toxicant in pigeons, triethyllead (Et_3Pb^+) reflected the exclusive use of tetraethyllead as a gasoline additive in both regions. Urban colonies of pigeons were characterized by significantly greater concentrations of Et_3Pb^+ than were specimens from a suburban/rural colony. In contrast, the major toxicant in ducks was trimethyllead although six other alkyllead analytes were also observed. An environmentally mediated methylation of Pb^{2+} which is more active in (but not restricted to) aquatic environments is postulated to account for the ubiquity of trimethyllead in ducks.

Keywords: Alkylleads, determination, avian tissues, methylation, residues, pigeons, ducks, speciation

INTRODUCTION

Tetra-alkylleads (R_4Pb), which frequently form a small component of the total lead emitted from automobiles and related industrial sources, are volatile but environmentally labile. They are degraded abiotically[1–3] and via metabolic processes[4,5] to result sequentially in trialkyllead (R_3Pb^+), dialkyllead (R_2Pb^{2+}) and inorganic lead (Pb^{2+}) salts. The reverse process, an environmental methylation of alkyllead salts, whether biologically[6,7] or chemically[8,9] mediated, is now well established. However, the analogous methylation of lead(II) remains controversial.[10,11] Recently reported evidence,[12] based on alkyllead concentrations in herring gulls, favoured the environmental methylation of lead(II). Separate sources of methyllead and ethyllead salts to this species were demonstrated. The major toxicant in soft tissues of gulls was Me_3Pb^+ despite the fact that only tetraethyllead is used as a gasoline additive in eastern Canada. Host-mediated methylation, as a metabolic response to ingestion of lead(II), Et_2Pb^{2+}, or Et_3Pb^+ salts, seemed unlikely based on feeding trials[13,14] to Japanese quail and to pregnant sows. No methylleads could be detected in quail which had received water amended with 250 mg dm^{-3} $PbCl_2$, with 25 mg dm^{-3} Et_2PbCl_2, or with 2.5 mg dm^{-3} Et_3PbCl for eight weeks. Similarly, no alkylleads were detected in soft tissues from sows (or their progeny) which had received up to 1 g lead (as $PbCO_3$) kg^{-1} body weight throughout gestation.

An environmentally mediated methylation of lead(II) was corroborated by a statistical comparison of the concentrations of individual alkyllead analytes in snails from six sites in lower Chesapeake Bay. This study[15] indicated (1) that environmentally mediated methylation of lead(II) contributed appreciably to Me_3Pb^+ concentrations in this species and (2) that the relative concentrations of individual analytes were consistent with an environmental methylation of ethyllead salts. In the current study, the spectrum and concentrations of alkylleads in soft tissues of an avian species characteristic of a terrestrial urban environment were compared with alkyllead analytes in a second avian species from an aquatic environment, in an effort to delineate the scope of the methylation phenomenon. A unique opportunity existed in that previous studies had indicated that only ethylleads could be detected in urban soils, street dusts and rainwater runoff[16] or in snow samples[17] from metropolitan Montreal.

A small body size, high metabolic turnover and a rather limited mobility have made the feral pigeon (*Columba livia*) a popular indicator species for urban lead pollution.[18–21] This sedentary species forms

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discrete flocks with specific feeding and roosting areas[22] and forages for food at ground level. Thus food items are likely to be contaminated with lead-rich dusts. Inhalation of atmospheric leads may also contribute to the total body burden. Trialkylleads but not dialkyl or tetra-alkylleads were detected in both urban and rural pigeons.[21] Moreover, urban females were burdened with significantly greater concentrations of total lead (in both kidney and bone) than were males.[21]

A second indicator species, mallard duck (*Anas platyrhynchos*) was of interest not only because it is the most widely distributed of the North American duck species but also because it is primarily a herbivorous surface feeder.[23] Mixed macrophytes from the St Lawrence River contained mainly ethylleads with some ethylmethylleads but no methylleads.[24] The diet of the mallard is, therefore, a likely source of ethylleads.

MATERIALS AND METHODS

Reagents and standards

Alkyllead chlorides (R_3PbCl, R_2PbCl_2; R = CH_3, C_2H_5) and alkyllead butyls (R_3BuPb, R_2Bu_2Pb; R = CH_3, C_2H_5; Bu = C_4H_9) standards were prepared as previously described.[25,26] Chromatographic support gases were prepurified grade, all chemicals were ACS reagent grade or better and solvents were distilled-in-glass grade. The ammoniacal buffer consisted of diammonium citrate (22.6 g), potassium cyanide (4.0 g) and sodium sulfite (24.0 g) which was diluted to 250 cm^3 with distilled water. The pH was adjusted to 10.0 with concentrated aqueous ammonia.

Sample collection

Pigeons were collected from three sites in urban Montreal and at one site in the surrounding suburbs during summer 1986. Separate colonies from the Port of Montreal and from two other urban sites – (1) Laurier Metro Station, and (2) St-Laurent and St-Joseph Blvds – provided 14, 10 and 10 specimens respectively. The one suburban site, at Ste Anne de Bellevue, also provided 10 birds. Upon capture, birds were immediately sacrificed and stored on ice to await dissection. Excised tissues were homogenized in a Virtis homogenizer. Brain samples from each site consisted of a pool of 10 (or 14) mixed-sex birds. Heart and liver samples consisted of tissue pools of two birds from each colony whereas kidney samples represented a pool from five (or seven) birds. Whole egg homogenate (minus shells) represented pools of two eggs. The resulting homogenates were stored at −10 °C to await analysis.

All mallard duck tissues were from immature birds. Kidney, liver, brain and breast muscle tissues were taken from tissue pools of five females and five males. Kidney and liver samples from individual birds were examined as well. The samples were collected by the Canadian Wildlife Service from the Upper Canada Migratory Bird Sanctuary located on the St Lawrence River near Morrisburg, Ontario, in September 1983.

Analytical methods

Enzymatic hydrolysis

Samples of avian homogenate (muscle, heart, liver, kidney, egg), 2.5 g, were diluted with 15 cm^3 of 0.5 mol dm^{-3} phosphate buffer (pH 7.50) containing 5 % ethanol and 40 mg lipase (type VII, Sigma Chemical Co., St Louis, MO) and 40 mg protease (type XIV) in 50 cm^3 Nalgene screw-cap centrifuge tubes at 37 °C and incubated for 24 h.

Tetramethylammonium hydroxide (TMAH) digestion

Samples of brain homogenate (2.5 g) were digested with 6 cm^3 tetramethylammonium hydroxide (20 % in H_2O) at 60 °C for 4 h or until the tissue had completely dissolved to a pale brown solution. After the solution had cooled the pH was readjusted to 10.0 with 50 % HCl.

Single extraction (muscle, heart, liver, kidney from pigeons)

Ammoniacal buffer (5 cm^3) was added to the hydrolysate which was then extracted three times with 0.01 % (w/v) dithizone in hexane (10 cm^3). The pooled dithizone extracts were centrifuged at 4400 rpm for 10 min (5 °C, IEC Model PR-1 centrifuge, rotor 845) to hasten phase separation. The organic phase was frozen (−10 °C) overnight (to remove traces of water) and the supernatant was transferred to precalibrated tubes (equipped with screw-cap tops and teflon liners) for derivatization.

Double extraction (egg and brain from pigeons and duck samples)

Ammoniacal buffer (5 cm^3) was added to the hydrolysate or the digestion mixture. The diluted mixture was then extracted three times with 5 cm^3 of hexane (or 5 cm^3 1:1 benzene/hexane for duck tissues) and 0.2 cm^3 of 0.5 % (w/v) dithizone in tetrahydrofuran (THF). The pooled dithizone extracts were centrifuged

at 4400 rpm for 10 min to hasten phase separation. Organic extracts were combined and back-extracted three times with 5 cm^3 0.15 mol dm^{-3} HNO_3. The combined acidic extracts were neutralized with 1 mol dm^{-3} NaOH (4.5 cm^3) and further basified with ammoniacal buffer (5.0 cm^3). Alkyllead analytes were recovered from the basified washes with three extractions (5.0 cm^3) of hexane and dithizone (0.5 %) in 0.2 cm^3 THF. The combined organic extracts were frozen and the supernatant was transferred to precalibrated tubes for derivatization.

Derivatization

n-Butylmagnesium chloride (0.5 cm^3, 2.27 mol dm^{-3} in tetrahydrofuran; Alfa Products, Ventron Corp., Danvers, MA) was added to the concentrated organolead dithizonates. The tubes were capped, vigorously mixed for 10 s, magnetically stirred for 10 min at ambient temperature and cooled in an ice bath. Excess Grignard reagent was destroyed by the dropwise addition of 1 mol dm^{-3} HNO_3. The reaction mixture was diluted to 10 cm^3 with water, shaken for 30 s and centrifuged for 5 min at 1550 rpm. The hexane layer was removed and the aqueous layer was re-extracted with 5 cm^3 fresh hexane. The organic extracts were combined, dried over sodium sulfate, reduced to 1 cm^3 under a gentle stream of nitrogen, placed in a sample vial and capped for immediate analysis.

Sample analysis

A gas chromatograph (GC)–quartz tube–atomic absorption spectrometer (QT–AA) as previously described[26] was used for the quantitation of samples. Each butylated extract was quantified three times by comparison with external standards containing Me_3BuPb, Me_2Bu_2Pb, Et_3BuPb and Et_2Bu_2Pb. Methylethyllead compounds were identified by prediction of retention times using Kovat's retention index and from retention times of alkylbutyllead standards.[25,26] Actual retention times of methylethylleads were confirmed from transalkylation mixtures and quantitation of these compounds was achieved by comparison with a similar analyte for which standards were available. Thus, quantitation of $MeEt_2Pb^+$ and $MeEtPb^{2+}$ was based on the instrumental response to and recoveries for Me_3Pb^+ and Et_2Pb^{2+} respectively.

Recovery experiments

Three samples of each tissue homogenate (from turkey) or chicken egg homogenate were spiked with 50 to 60 ng g^{-1} (as lead) with a mixture of Me_3PbCl, Et_3PbCl_2, Et_3PbCl and Et_2PbCl_2. The percentage recovery of each analyte was determined by dividing the mean peak area of the recovered butylate by the mean peak area of a butylated spike solution diluted to the expected (assuming 100 % recovery) concentration. Recoveries, the average of three replicate determinations, are recorded in Table 1.

Table 1 Mean[a] percentage recoveries[b] (± 1 standard deviation) of ionic alkylleads from avian soft tissues or egg

Source	Me_3Pb^+	Me_2Pb^{2+}	Et_3Pb^+	Et_2PbCl^{2+}
Brain	83 ± 9	25 ± 4	84 ± 9	60 ± 9
Muscle	100 ± 9	23 ± 5	95 ± 7	75 ± 11
Heart	90 ± 5	28 ± 4	71 ± 2	68 ± 8
Liver	91 ± 8	24 ± 4	74 ± 7	63 ± 5
Kidney	82 ± 8	35 ± 4	73 ± 7	70 ± 4
Egg	103 ± 13	28 ± 7	81 ± 5	79 ± 17

[a]Based on three replicate determinations. Each butylated extract was quantitated three times. Thus $n = 9$. [b]Spiked with 50–60 ng g^{-1} (as Pb) of each alkyllead chloride.

RESULTS AND DISCUSSION

Although less than quantitative, recoveries of trialkyllead and diethyllead were acceptable and comparable with previously reported values.[12,15] Variations among replicates were also low, reflecting the good reproducibility of the procedures. In contrast, recoveries of Me_2Pb^{2+} from various tissues or from egg were low and were not improved by prolonged hydrolysis, the use of other complexing agents or the addition of various thiols, dithiols or thiophenol which might have served to displace the analyte from binding sites. The recoveries of analytes from brain homogenate were somewhat better using the TMAH digestion procedure than with the enzymatic hydrolysis.

(A) Feral pigeons

Three urban colonies and one suburban/rural colony of pigeons were chosen for study. One of the urban colonies was based within the Port of Montreal. The colony, within this restricted-access facility, was thought to forage within the port facilities and to consume a diet rich in grains. The suburban colony came from our own campus and the surrounding agricultural lands. The mean and range of ionic alkyllead concentrations in various tissue pools are recorded in Table 2. Three separate determinations were performed on each sample pool. As might be expected, the variation in burdens among separate pools of the same tissue from the same colony was somewhat greater than the variation observed among replicate analyses of the same sample pool.

Table 2 Mean and range of trialkyllead concentrations (ng g^{-1} wet weight) in tissue pools of pigeons from urban or rural colonies

	Et_3Pb^+				Me_3Pb^+			
	Colony[a]				Colony[a]			
	1	2	3	4	1	2	3	4
Muscle	N.D.[b]	0.6 ± 0.4^{1}	0.5 ± 0.4^{1}	N.D.	N.D.	N.D.	N.D.	N.D.
Range		0.0–1.5	0.0–1.5					
n	10	10	14	10	10	10	14	10
Liver	$7.1 \pm 2.4^{1,c}$	6.1 ± 2.7^{1}	$3.0 \pm 2.0^{1,2}$	1.6 ± 0.7^{2}	N.D.	N.D.	N.D.	N.D.
Range	4.6–10.7	3.0–9.5	0.0–5.4	0.0–3.9	N.D.	N.D.	N.D.	N.D.
n	5	4	7	5	5	4	7	5
Kidney	25.2 ± 4.7^{1}	11.7 ± 2.0^{2}	6.8 ± 1.1^{3}	2.1 ± 0.5^{4}	2.9 ± 1.2^{4}	3.6 ± 0.8^{4}	N.D.	N.D.
Range	20.5–29.9	9.7–13.7	5.7–7.9	1.3–4.4	1.7–4.1	2.8–4.4	N.D.	N.D.
n	2	2	2	2	2	2	2	2

[a]1, St-Laurent and St-Joseph; 2, Laurier Metro station; 3, Port of Montreal; 4, Ste Anne de Bellevue. [b]N.D., none detected. [c]Means within the same row bearing the same superscript number are not significantly different at the 95 % confidence level.

Table 3 Ionic alkyllead (as alkylbutyllead) levels in separate tissues from mallard ducks

		Mean concentration ± S.D.[a] (ng g^{-1} wet wt)						
Source		Me_3Pb^+	Me_2EtPb^+	$MeEt_2Pb^+$	Me_2Pb^{2+}	Et_3Pb^+	Et_2Pb^{2+}	$MeEtPb^{2+}$
Liver								
Female	1	0.4 ± 0.2	N.D.[b]	N.D.	N.D.	N.D.	5.5 ± 0.8	N.D.
	2	0.6 ± 0.1	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	3	1.3 ± 0.1	N.D.	N.D.	N.D.	0.5 ± 0.2	0.3 ± 0.1	N.D.
	4	0.7 ± 0.2	N.D.	N.D.	N.D.	N.D.	0.3 ± 0.3	N.D.
	5	0.4 ± 0.1	N.D.	N.D.	1.7 ± 0.4	0.3 ± 0.1	0.8 ± 0.3	N.D.
	(P)[c]	0.6 ± 0.1	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Male	1	0.9 ± 0.2	0.2 ± 0.1	N.D.	0.8 ± 0.5	0.5 ± 0.1	0.7 ± 0.3	N.D.
	2	4.3 ± 0.2	1.2 ± 0.2	1.3 ± 0.2	2.2 ± 0.5	2.0 ± 0.5	1.5 ± 0.4	0.6 ± 0.1
	3	0.8 ± 0.1	N.D.	0.6 ± 0.1	N.D.	0.8 ± 0.4	0.7 ± 0.1	N.D.
	4	0.5 ± 0.2	N.D.	N.D.	N.D.	0.6 ± 0.3	0.8 ± 0.3	N.D.
	5	0.6 ± 0.1	0.2 ± 0.1	N.D.	N.D.	0.7 ± 0.1	1.3 ± 0.2	N.D.
	(P)	1.4 ± 0.1	0.5 ± 0.2	0.7 ± 0.1	N.D.	1.3 ± 0.2	1.0 ± 0.2	N.D.
Kidney								
Female	(P) A	1.4 ± 0.1	0.4 ± 0.2	0.3 ± 0.1	N.D.	0.6 ± 0.1	0.4 ± 0.4	N.D.
	B	1.4 ± 0.1	0.3 ± 0.1	0.4 ± 0.1	N.D.	0.7 ± 0.1	1.0 ± 0.2	N.D.
Male	(P) A	4.0 ± 0.3	1.7 ± 0.1	1.7 ± 0.1	1.9 ± 0.7	3.5 ± 0.5	3.0 ± 0.3	0.7 ± 0.1
	B	4.3 ± 0.2	1.8 ± 0.2	1.8 ± 0.2	2.0 ± 0.4	3.3 ± 0.1	1.3 ± 0.5	N.D.
Brain								
Female	(P)	0.6 ± 0.1	N.D.	N.D.	N.D.	0.3 ± 0.2	0.7 ± 0.1	N.D.
Male	(P)	1.1 ± 0.1	0.5 ± 0.1	0.8 ± 0.2	1.4 ± 0.2	1.2 ± 0.3	0.5 ± 0.5	N.D.
Breast muscle								
Female	(P)	0.4 ± 0.2	N.D.	0.4 ± 0.2	N.D.	N.D.	0.5 ± 0.4	N.D.
Male	(P)	1.6 ± 0.1	0.6 ± 0.1	0.9 ± 0.1	1.7 ± 0.2	1.4 ± 0.3	0.8 ± 0.4	N.D.

[a]Calculated from three replicate injections. [b]N.D., none detected. [c](P), pooled sample from five individuals.

In contrast to previous avian samples, neither dialkylleads (Me_2Pb^+, Et_2Pb^{2+}) nor mixed alkylleads (Me_2EtPb^+, $MeEt_2Pb^+$, $MeEtPb^{2+}$) were detected in any of the pigeon tissues. In addition, no alkylleads were detected in brain, in heart or in egg homogenates. The egg samples from the three urban sites were analyzed prior to the scheduled collection of egg samples from the suburban site. Because no alkylleads were detected in any of the urban eggs, further sampling was not considered to be justified. The analyses of alkylleads in eggs from the suburban site were not performed. Triethyllead was detected in all liver and kidney samples and in some of the breast muscles from two of the urban sites. Trimethyllead was present in kidney from two urban colonies but was not detected in any of the other samples and tetra-alkylleads (R_4Pb) were not detected in any of the samples.

An analysis of variance (ANOVA) of the mean alkyllead concentration in tissue from different colonies (Table 2) indicated that the pigeons from the two urban colonies were burdened with significantly ($P < 0.05$) more triethyllead than the pigeons from the suburban/rural colony. In addition, mean concentrations of Me_3Pb^+ in kidney from these colonies were significantly ($P < 0.01$) less than Et_3Pb^+ concentrations in the same tissue. The presence of Me_3Pb^+ in kidney from the two urban sites was somewhat surprising in that Me_4Pb is not formulated into gasolines in eastern Canada and our previous studies with Japanese quail had indicated that the metabolic methylation of Pb^{2+}, Et_3Pb^+ or Et_2Pb^{2+} were not important processes (at least in this species).

(B) Mallard ducks

Kidney, liver, brain, and breast muscle samples were taken from tissue pools of five females or five males. Kidney and liver samples from individual birds were examined as well. The results, representing the average of three replicate injections into the GCQT-AA, are recorded in Table 3. Analyte values determined from replicates of the male and female kidney pool samples indicated that a reasonable precision of results was obtained for the extraction methods and analytical instrumentation during this phase of the study as well.

Ionic alkylleads were detected in all duck tissues examined. A typical chromatogram is recorded in Fig. 1. The relative burdens of alkylleads in the various tissues (kidney > liver = brain = breast muscle) were independent of analyte or sex. Generally males contained higher burdens than females although only Et_3Pb^+ levels were significantly different ($P = 0.05$, paired comparison t-test). Further sampling would be necessary to establish whether a true sexual difference in analyte levels existed. Trimethyllead was ubiquitous whereas Et_3Pb^+ was not detected in some female liver samples or in the female breast muscle sample. The ubiquity of Me_3Pb^+ was somewhat surprising in that Canadian gasolines contain only Et_4Pb whereas American leaded gasolines contain either Et_4Pb or

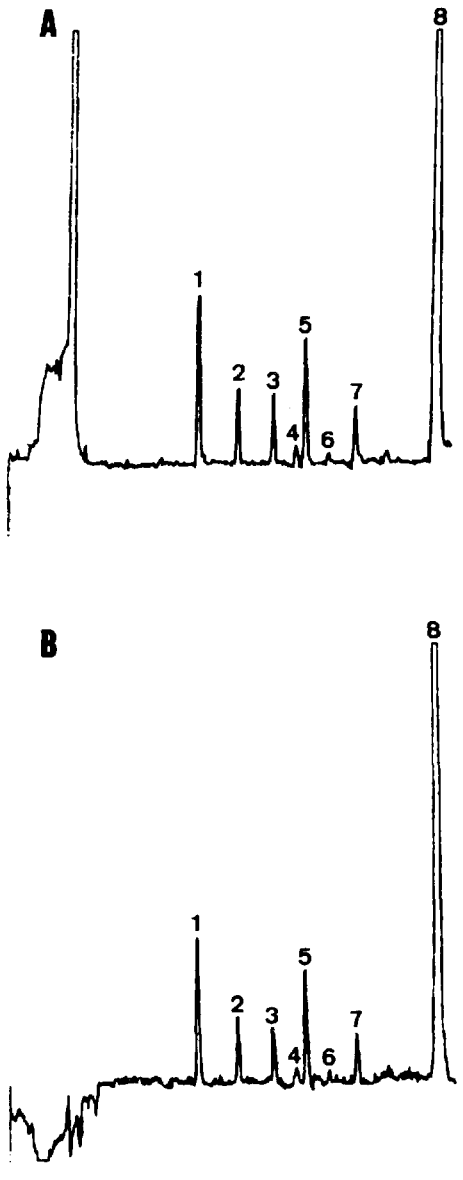

Figure 1 GCAA chromatograms of male mallard kidney pool sample at (A) 217 nm and (B) 283.3 nm, containing: 1, Me_3BuPb; 2, $EtMe_2BuPb$; 3, $Et_2MeBuPb$; 4, Me_2Bu_2Pb; 5, Et_3BuPb; 6, $EtMeBu_2Pb$; 7, Et_2Bu_2Pb; 8, Bu_4Pb. The sample was concentrated approximately two-fold prior to analysis at 283.3 nm.

tetra-alkyllead mixtures with Me_4Pb comprising a minor fraction of the total lead mixture. In contrast to herring gulls from the Great Lakes,[12] mallard ducks contained appreciable quantities of mixed trialkyllead salts (Et_2MePb^+ and $EtMe_2Pb^+$).

To the extent that concentrations of analytes in different species can be meaningfully compared, there were appreciable differences in alkyllead concentrations in soft tissues of birds from terrestrial environments and birds representative of an aquatic environment. It is suggested that the higher concentrations of methylleads relative to ethylleads observed in mallard ducks and in herring gull tissues reflect increased exposure to ionic methylleads. An environmentally mediated methylation which is more active in aquatic environments is suggested to account for these phenomena. Our most recent work using Me_3PbCl has indicated that this toxicant is rather unstable in sediment or in soils (from relatively pristine sites). Preliminary experiments have indicated that it is degraded to lead(II) by both chemically and microbially mediated processes with a half-life between four and seven days. It is possible that long-range transport of methyllead compounds (either adsorbed to particulate matter or in the gaseous state[27] may provide a source of these toxicants to aquatic environments in regions where Et_4Pb is the only gasoline additive. It seems unlikely, however, that ionic methylleads would be persistent in this environment given the rapid sediment-induced decomposition of Me_3Pb^+ to inorganic lead(II). An environmentally mediated methylation is postulated to counteract this degradative route, (see for example Ref. 28).

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