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MAJOR AND MINOR ELEMENTS AND SOME CHLORINATED HYDROCARBONS IN INDONESIAN FOODSTUFFS

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ABSTRACT

A screening study was conducted on the contents of the major elements, calcium, magnesium, potassium and sodium, and the trace elements, arsenic, cadmium, cobalt, copper, iron, lead, manganese, mercury, selenium and zinc in 11 commonly consumed dried or paste seafoods and 2 terrestrial products available on the market in Djakarta. In addition chlorinated hydrocarbon pesticides and polychlorinated biphenyls (PCB) were determined. All samples fell below the FDA guideline of 0.5 mg mercury/kg fresh weight, with a mean level of 0.27 mg/kg based on dry weight. Lead varied from 0.01 to 0.82 with an average of 0.20 mg/kg. Only one product, a dried squid, exceeded 0.1 mg cadmium/kg. All products were low in total DDT, lindane and PCB.

INTRODUCTION

In recent years the concentration of trace elements in different foodstuffs has received increased attention. Much interest has naturally been directed towards marine products considering that marine organisms are living in an environment containing almost all elements and that they generally concentrate some of these elements. The increased pollution to land, air and water from activities of the modern society has resulted in changes in the environmental levels of different substances. Among the pollutants to the sea are different elements from chemical industry, and further organic compounds such as pesticides and insecticides used in agriculture, and chemical offal such as chlorinated hydrocarbons.

The present study was carried out during the years 1975/76 on samples of fish products available on the market in Djakarta, preserved in the local manner, mainly by drying in fresh and salted state. Analysis has been carried out to survey the major elements, calcium, magnesium, potassium, sodium, as well as trace elements, arsenic, cadmium, cobalt, copper, mercury, iron, manganese, lead, selenium and zinc, and in addition some chlorinated hydrocarbons such as DDT and its metabolites and polychlorinated hydrocarbons (PCB).

MATERIALS AND METHODS

DESCRIPTION OF THE PRODUCTS

1. *EMPING MELINJO* — Delicacy from a fruit of the «melinjo» tree. Melinjo fruit was cooked and pounded, sugar added according to taste, and then sun dried.

2. *DENGDENG SAPI* — Small strips of dried ox meat.
Ox meat cut into small pieces, added cooked palm sugar and spices as coriander seeds, salt, ginger root, and then sun dried.

3. *EBI* — Kind of dried shrimps (skinless dried shrimps). Sun dried, cooked shrimps.

4. *LEMPENG IKAN TERI* — Dried small sea fish (Stolephorus, Engraulis). After gutting the fish is salted for one night and then sun dried.

5. *CUMI-CUMI* — Dried squid.
Gutted and with opened cap and left for one night and then sun dried.

6. *KERUPUK IKAN* — Fish crisps.
After cleaning, the fish is ground and salted, water and cassava (tapioka) powder is added. The dough is rolled and steamed until fine, sliced into pieces (about 2 mm), and then sun dried.

7. *KERUPUK UDANG* — Shrimp crisps.
Process as above (Kerupuk Ikan).

8. *DENGDENG BELUT* — Dried eel (Monopterus albus).
Cleaned and sun dried.

9. *IKAN ASIN GABUS* — Dried snake head.
Cleaned, salted (approx. 30—40%), and left for one or two nights, and sun dried.

10. *IKAN ASIN JAMBAL* — Dried type of cat fish.
Process as above (Ikan Asin Gabus).

11. PETIS — Shrimp jelly.
A liquid extract with its oil removed and spiced with palm sugar, laurel leaves (of Eugenia polyantha), ginger root, lemon grass, boiled until half the original volume, and rice powder added to thicken.

12. TERASI — Shrimp paste.
Cooked or uncooked «rebon» (tiny) shrimps. They are cleaned, salted (15%), sun dried for one day, ground until «brabon», dried again, salted (5%), ground again until like clay, and left to ferment until a specific smell has come out.

13. PEDA — Salted chub mackerel.
Cleaned, saltet (15—20%), covered with bamboo mats or planks, and pressed with a stone for three days, dried in the wind, put in a bowl with 10% salt on each layer.

ANALYTICAL PROCEDURES

All samples were ground and freeze-dried. The freeze-dried samples were homogenized and stored in tightly closed jars until analyzed.

Extreme caution was necessary to avoid contamination of glassware and reagents. The analysis of all elements except mercury were carried out on a Perkin-Elmer 403 atomic absorption spectrophotometer. Potassium and sodium were measured in the emission mode, and the other elements were measured by atomic absorption technique. The atomic absorption spectrophotometer was equipped with a three-slot burner, and a deuterium background corrector for the elimination of the combined effects of flame absorption, molecular absorption and scattering. An argon protected hydrogen flame was used for arsenic and selenium and acetylene-air for the remaining elements. Mercury was determined by a flameless technique on a Perkin-Elmer 370 instrument. EDL-lamps (Electrodeless discharge lamps) were used for arsenic, mercury and selenium and hollow cathod lamps for the other elements.

Calcium, magnesium, potassium, sodium, copper, iron, manganese and *zinc* were analyzed in the same extract. Portions of 0.25 g freeze-dried samples were used for the determination of these elements. The samples were

weighted into 10 ml Sovirel tubes and three replicates were used. The samples were pre-ashed over night with 4 ml of $HNO_3/HClO_4$ (1:1). The bottles were placed in a pressure boiler and heated for two hours. The mixtures were cooled and 4 ml distilled water were added and warmed on a waterbath to expel the nitrous gases. After cooling, the solutions were transferred to 25 ml volumetric flasks and made up to volume with distilled water (JULSHAMN and BRAEKKAN 1974). Calcium and magnesium were diluted to an appropriate concentration with a 1 % lanthanum oxide solution before measuring. Potassium was diluted with a sodium solution of an appropriate concentration and sodium similarly with a potassium solution in order to avoid depression effects in the flame. The trace elements were determined in accordance with a method described by JULSHAMN and BRAEKKAN (1975), with the modification that the extraction procedure was not used.

Arsenic was determined in duplicate by an analytical procedure based on dry ashing reported by UTHE et al. (1974) and EGAAS and JULSHAMN (1977). $NaBH_4$-pellets were used as the reduction agent and the hydrides were collected in a purgable balloon before venting them to the flame (MANNING, 1971). The absorption was measured at 193.7 nm.

Cadmium, cobalt and *lead.* Portions of 10 g freeze-dried samples were pre-ashed in infra-red heat and ashed at 480°C. The final white residue was dissolved in 0.1 N hydrochloric acid, chelated with methyl isobutyl ketone (MIBK) and the elements measured. The method has been described for cobalt only (JULSHAMN and BRAEKKAN, 1974). An extensive comparison between dry and wet digestion of different marine samples will be published.

Mercury and *selenium* were determined in the same extract. The digestion procedure started with 0.5 g of homogenized sample, accurately weighed into a modified Bethge flask. Twenty ml of a 1 : 1 mixture of nitric acid and sulfuric acid containing 0.1 % V_2O_5 was added, and the mixture boiled gently under reflux for 20—30 min. After cooling, 1—2 drops of H_2O_2 was added, and the solution was diluted to 100 ml with dist. water. A 50 ml aliquot was taken out for the determination of selenium, and the remaining solution used for the determination of mercury. For the latter purpose, $KMnO_4$ was added to oxidize the mercury ions. The Hg (II)-salts were reduced to metallic Hg by the addition of $SnCl_2$, and the mercury vapour blown through a gas cuvette fitted to a Perkin-Elmer atomic absorption spectrophotometer, and measured at 253.7 nm. Selenium was measured at 196.0 nm after hydride formation as described for the arsenic analysis. Three determinations were carried out for each solution, and the average was calculated (EGAAS and JULSHAMN, 1977).

Total DDT and *polychlorinated biphenyls* were determined by a gas chroma-

tographic method after purifying the hydrocarbons on a Celite-sulphuric acid column followed by separation on a silicagel column. DDT and PCB were both chromatographed on a Perkin-Elmer 900 equipped with an ECD-detector and a glas column (160 × 0.4 cm) containing 2.5% OV-17 on Chromosorb G. As PCB standard was used Arocloro 1254 and the pesticide standard was supplied by Chemical Manufactures Laboratory, USA.

RESULTS AND COMMENTS

In Table I are reported the major elements calcium, magnesium, potassium and sodium and in addition percentage dry matter based on freeze-drying. In Table 2 are given the corresponding values of the trace elements arsenic, cadmium, cobalt, copper, iron, lead, mercury, selenium and zinc, and in Table 3 those for chlorinated hydrocarbons, such as DDT and its metabolites and lindane and polychlorinated biphenyls (PCB) and percentage total fat. The first two samples in each table were from terrestrial products and the others were of marine origin.

Calcium and *magnesium*. The values for calcium and magnesium were of the same order as literature values for marine organisms. The high values for magnesium in product number 4, (dried fish), may be noted. The concentrations of calcium and magnesium in the muscle tissue of sea fish are generally in the order of 300 and 800 mg/kg respectively (JULSHAMN and UTNE, 1977). Sample number 6 was low in calcium and sample number 10 was low in magnesium.

Table 1. *The concentration of some major elements of some Indonesian foodstuffs.*

	Dry weight	Ca mg/kg	Mg mg/kg	K mg/kg	Na mg/kg
1 Emping Melinjo	97.21	840	4 790	8 800	4 700
2 Dengdeng Sapi	99.00	720	910	4 900	27 300
3 Ebi	96.97	5 080	4 230	7 020	17 600
4 Lempeng Ikan Teri	92.22	13 750	33 700	9 840	10 100
5 Cumi-Cumi	96.42	640	1 060	5 900	8 500
6 Kerupuk Ikan	93.04	370	2 940	330	11 190
7 Kerupuk Udang	95.28	640	9 820	330	11 190
8 Dengdeng Belut	94.47	20 050	1 550	8 950	20 100
9 Ikan Asin Gabus	63.81	5 740	1 530	8 000	28 200
10 Ikan Asin Jambal	50.60	900	660	10 700	33 300
11 Petis	84.74	5 070	890	5 300	10 400
12 Terasi	65.86	3 410	5 670	13 300	7 470
13 Peda	51.95	3 470	960	5 300	35 500

Potassium and *sodium*. With a few exceptions sodium predominated over potassium, but not very markedly. Probably the natural ratio between these two elements was changed during the processing of the products.

Arsenic. Arsenic was found in higher concentration than cadmium, lead and mercury in most of the products. The terrestrial samples were lower than those of marine origin. High levels of arsenic in some fish products have been known for a considerable time. Both CHAPMAN (1926) and COULSON et al. (1935) demonstrated that arsenic occurs in shrimp in a form which is excreted upon intake and harmless to animals or man. The overall arsenic mean was 3.0 mg/kg in the present study. The lowest value was found in No. 1, a fruit product, but arsenic was also low in products number 7 and 9. The sample of catfish (No. 10), showed the highest value, 21.3 mg As/kg.

Cadmium. The cadmium content in all products analyzed in this survey was less than 0.1 mg/kg, except for number 5, a squid product which contained 0.50 mg/kg. Normally, the contents of cadmium in marine organisms in the North Sea are less than 0.1 mg/kg dry weight (JULSHAMN and UTNE, 1977).

Cobalt. The concentration of cobalt was less than 0.05 mg/kg, except in one product of shrimp (No. 11), which contained 0.14 mg/kg. The values for cobalt were generally of the order found in marine organisms from the North Sea (JULSHAMN and UTNE, 1977).

Copper. Copper was not found in high levels in any of the products analyzed. The fish products varied from 0.64 mg/kg in fresh water fish to 6.2 in marine fish, and the shrimp products varied from 20.8 to 45.8. Canada has a tolerance level for copper in food of 100 mg/kg (Food and Drug Regulations, 1972). All values reported here are well below this level.

Iron. Iron was present in higher concentrations and varied more than the other trace elements analyzed in this work. The concentrations ranged from 22.2 to 479 mg/kg. The high levels may reflect pollution during the industrial processing, as also observed in fishmeal.

Lead. The overall mean for the lead content in the fish products was 0.22 mg/kg, that is in the order found for fish in uncontaminated waters. The highest value, 0.82 mg/kg, was found in a fresh water fish sample. Canada has given an upper limit recommendation of 10 mg/kg wet weight and U.K. a recommendation of 5 mg/kg wet weight in canned fish products.

Mercury. As could be expected the contents of mercury in the fruit and meat samples showed lower levels than those in the marine products. The highest values were found in the dried snake head and dried catfish samples, 0.58 and 0.57 mg/kg respectively. These values, calculated on freezed-dried samples, are well below the permissible level in several countries of 0.50 mg Hg/kg food.

Manganese. The samples of fruit and eel had the highest manganese

Table 2. *The concentration of some trace elements of some Indonesian foodstuffs.*

	Dry weight%	As mg/kg	Cd mg/kg	Co mg/kg	Cu mg/kg	Fe mg/kg	Pb mg/kg	Hg mg/kg	Mn mg/kg	Se mg/kg	Zn mg/kg
1 Emping Melinjo	97.21	0.04	0.04	0.02	9.4	112	0.01	< 0.02	34.2	0.10	84
2 Dengdeng Sapi	99.00	0.26	< 0.02	0.01	6.0	79.9	0.07	0.04	4.1	0.02	58
3 Ebi	96.97	1.42	0.02	0.05	30.1	92.2	0.29	0.13	3.3	0.74	79
4 Lempeng Ikan Teri	92.22	1.03	< 0.02	0.04	2.8	44.2	0.11	0.04	7.2	2.50	98
5 Cumi-Cumi	96.42	5.41	0.51	0.01	20.8	53.0	0.51	0.20	2.1	2.18	108
6 Kerupuk Ikan	93.04	1.62	< 0.02	0.01	6.2	300	0.22	0.06	2.9	0.40	24
7 Kerupuk Udang	95.28	0.10	< 0.02	0.01	4.5	36.0	0.07	0.11	2.9	0.16	29
8 Dengdeng Belut	94.47	0.61	0.02	0.01	5.6	300	0.12	0.21	61.8	1.94	127
9 Ikan Asin Gabus	63.81	0.10	< 0.01	< 0.01	0.64	37.6	0.82	0.58	10.9	1.18	32
10 Ikan Asin Jambal	50.60	21.3	< 0.01	< 0.01	0.67	22.2	0.02	0.57	0.63	0.94	15
11 Petis	84.74	1.83	0.06	0.14	45.8	251	0.17	0.04	2.7	2.00	29
12 Terasi	65.86	3.04	< 0.01	< 0.01	30.0	479	< 0.02	0.06	16.2	0.20	43
13 Peda	51.95	2.94	< 0.01	< 0.01	0.97	50.3	0.04	0.05	5.1	1.76	24

Table 3. *The concentration of chlorinated hydrocarbons of some Indonesian foodstuffs.*

	Fat content (%)	pp DDT mg/kg	op DDT mg/kg	pp DDE mg/kg	pp TDE mg/kg	Total DDT mg/kg	PCB mg/kg	Lindane mg/kg
1 Emping Melinjo	3.05	0.034	0.004	0.003	< 0.001	0.041	0.003	0.004
2 Dengdeng Sapi	6.95	< 0.002	< 0.001	0.002	< 0.001	0.002	< 0.001	< 0.001
3 Ebi	17.14	0.004	0.001	0.006	0.001	0.012	0.002	0.003
4 Lempeng Ikan Teri	6.34	0.013	0.001	0.010	0.002	0.026	0.007	0.005
5 Cumi-Cumi	6.55	< 0.002	< 0.001	0.002	< 0.001	0.002	< 0.001	0.001
6 Kerupuk Ikan	0.49	< 0.002	< 0.001	0.001	< 0.001	0.001	< 0.001	0.024
7 Kerupuk Udang	2.48	0.002	0.001	0.005	0.001	0.009	0.002	0.002
8 Dengdeng Belut	9.44	0.002	< 0.001	0.014	0.001	0.017	0.001	0.004
9 Ikan Asin Gabus	6.44	< 0.002	< 0.001	0.003	< 0.001	0.003	< 0.001	0.002
10 Ikan Asin Jambal	6.30	< 0.002	< 0.001	0.008	< 0.001	0.008	< 0.001	0.001
11 Petis	4.25	0.005	0.001	0.012	0.033	0.051	0.010	0.001
12 Terasi	11.23	< 0.002	< 0.001	0.004	0.001	0.005	< 0.001	0.001
13 Peda	10.88	< 0.002	< 0.001	0.003	< 0.001	0.003	< 0.001	0.001

contents, 34.2 mg/kg and 61.8 mg/kg respectively. The fish and shrimps products showed levels of about 2—16 mg/kg.

Selenium. Very few data are available for selenium in different products of terrestrial or marine origin. The marine products showed the highest values with contents varying from 0.16 to 2.50 mg/kg. This range has also been reported for fishmeal by LUNDE (1973).

Zinc. The levels for zinc in the fish products were 15—127 mg/kg, with the highest value in the eel product, which normally is high in trace elements. The fruit and meat products showed values of 84 and 58 mg/kg respectively.

Organochlorine Pesticides and *PCB.* The analyses of the contents of organochlorine pesticides, DDT and its metabolites, and PCB gave extremely low values. Residues of DDT were found in all samples and the highest content of the metabolite p'p-DDE. The fruit sample gave a value of 0.041 mg/kg of total DDT. The levels of total DDT in marine products were 0.002–0.051 mg/kg. The PCB residue ranged from 0.001 to 0.01 and lindane ranged from 0.001 to 0.024 mg/kg. All values for total DDT were well below the tolerance level recommended by FAO/WHO (1972), 7 ppm based on fat weight, and for the content of lindane 2 mg/kg in fat of meat.

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