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Contamination of Farm Animals and Fishes from Slovenia with Heavy Metals and Sulfonamides

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In order to ensure the safety of consumer in Slovenia we monitor beside other contaminants also the residues of heavy metals and veterinary drugs in domestic animals following our Veterinary residue monitoring program. Imported food of animal origin are also controlled by our inspection services on the board. In this paper is presented the situation in the period from 1994 to 1998 regarding residues of heavy metals (Pb, Cd, As, Hg) and sulfonamides in farm animals and fishes on the market which means samples taken from domestic and imported animals.

MATERIALS AND METHODS

In 5 years period, from 1994 to 1998, we analysed 2727 samples on residues of lead (Pb), 3344 samples on residues of cadmium (Cd), 1462 samples on residues of arsenic (As), 331 samples on residues of total mercury (Hg) and 2363 samples on residues of sulfonamides. Among them there were meat, liver and kidney of cattle, pigs and poultry (farm animals) and meat of freshwater fishes and marine fishes, mussels, crawfishes and cephalopods. Samples of domestic animals were taken regarding the plan of Veterinary residue monitoring program in slaughterhouses and fish farms. Samples of imported food were taken by the inspection service on the board. All the analysed samples represent the situation on Slovenian market.

Pb and Cd were determined with standard method using flame atomic absorption spectrophotometry (AOAC 1990, Snodin 1973). Arsenic

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was determined with spectrophotometric method using Ag-diethylditiocarbaminate in pyridine (AOAC 1990). Total Hg was determined by AAS-cold vapour technique (AOAC 1990). Screening of sulfonamides was performed with ethyl-acetate extraction followed by SPE cleaning. Final detection was done using HPTLC with fluorometric scanning densitometry after dipping the plates in fluorescamine (Thomas et a1.1981, Van Poucke et al. 1991). Limits of detection were 0.05 mg/kg for Pb and As, 0.003 mg/kg for Cd, 0.005 mg/kg for total Hg and 0.01 mg/kg for sulfonamides.

RESULTS AND DISCUSSION

Results of heavy metal contents and distribution in analysed samples are shown in tables from 1 to 5. Results of residues of sulfonamides and the types of found sulfonamides are shown in table 6.

Regarding Pb residues we analysed 1241 samples of meat, 1159 samples of kidney, 74 samples of liver of farm animals and 253 samples of fish (61 freshwater, 174 marine). In majority of the samples the concentration of Pb was < 0.05 mg/kg. Seven samples (0.26 %) exceeded our tolerances for Pb (1 sample of beef muscle 0.92 mg Pb/kg, 1 sample of pig muscle 0.71 mg Pb/kg, 4 samples of beef kidney with the maximum at 1.35 mg Pb/kg and 1 sample of bovine liver 1.38 mg Pb/kg).

From 1774 samples of meat analysed regarding residues of Cd the majority didn't exceeded the limit of detection 0.003 mg/kg. Among 1258 samples of kidney, 69 samples of liver and 243 samples of fishes 72 samples exceeded tolerance for Cd; 61 samples of kidney, 2 samples of liver and 9 samples of marine fishes with maximum concentrations 2.583 mg Cd /kg.

Most of 1392 samples of meat, liver and kidney of farm animals analysed on As didn't exceeded the limit of detection 0.05 mg/kg. Although the content of As in fish samples was usually higher, there were no unsuitable samples of freshwater fishes (among 10 samples

Table 1. Heavy metals in tissues of farm animals and fishes from Slovenia in period from 1994 to 1998 [mg/kg wet weight].

	Sample	n	Content min [mg/kg w w]	Content max [mg/kg w w]	Tolerance [mg/kg w w]	Samples which exceed tolerance n	Samples which exceed tolerance %
Pb	Meat bovine	215	<0.05	0.92	0.5	1	0.46
	pig	975	<0.05	0.71		1	0.10
	poultry	51	<0.05	<0.05			
	Kidney bovine	581	<0.05	1.35	1.0	4	0.69
	pig	468	<0.05	0.21			
	poultry	110	<0.05	0.20			
	Liver bovine	9	<0.05	1.38		1	11.1
	pig	15	<0.05	<0.05			
	poultry	50	<0.05	0.34			
	Fishes marine°	192	<0.05	0.44	1.0		
	freshwater	61	<0.05	<0.05			
Cd	Meat bovine	339	<0.003	0.099	0.1		
	pig	1389	<0.003	0.120			
	poultry	46	<0.003	0.007			
	Kidney bovine	595	<0.003	2.344	1.0	20	3.36
	pig	587	<0.003	2.039		40	6.81
	poultry	76	<0.003	1.501		1	1.32
	Liver bovine	18	0.006	0.548	0.5	1	5.55
	pig	12	<0.003	0.209			
	poultry	39	<0.003	1.230		1	2.56
	Fishes marine°	182	<0.003	2.583	0.1 - 1.0*	9	4.94
	freshwater	61	<0.003	<0.003			
As	Meat$^{\Delta}$	925	<0.05	0.09	0.1		
	Kidney$^{\Delta}$	445	<0.05	0.30	0.5		
	Liver$^{\Delta}$	22	<0.05	<0.05			
	Fishes marine°	60	<0.05	24.3	2.0** - 4.0***	9	15.0
	freshwater	10	<0.05	0.36			
Hg	Meat$^{\Delta}$	16	<0.005	0.009	0.03		
	Kidney$^{\Delta}$	243	<0.005	0.106	0.1	1	0.4
	Liver$^{\Delta}$	29	<0.005	0.050			
	Fishes marine°	21	<0.005	0.208	0.5 - 1.0*		
	freshwater	22	<0.005	0.400			

° fishes, mussels, crawfishes, cephalopods (fresh or froze
$^{\Delta}$ bovine, pigs, poultry
* tunny, swordfish, crawfishes, mussels
** blue and white fishes except sea eel and eel
*** other sort of fishes, crawfishes and mussels

Table 2. Distribution of food samples of animal origin into classes with regard to Pb content [mg/kg wet weight].

Sample	n	Concentration class [mg/kg w w]					
		<0.05	<0.05 – 0.10	0.11 - 0.20	0.21 - 0.50	0.51 - 1.00	1.01 - 2.50
Meat bovine	215	207	3	3	1	1	
pig	975	970	2	2		1	
poultry	51	51					
Kidney bovine	581	281	106	120	58	11	5
pig	468	386	50	30	2		
poultry	110	93	9	7	1		
Liver bovine	9	4	1	2	1		1
pig	15	15					
Poultry	50	44	3	2	1		
Fishes marine°	192	174		9	9		
freshwater	61	61					

° see Table 1

Table 3. Distribution of food samples of animal origin into classes with regard to Cd content [mg/kg wet weight].

Sample	n	Concentration class [mg/kg w w]					
		<0.003	<0.003 – 0.010	0.011 - 0.10	0.101 - 0.500	0.501 - 1.000	> 1.000
Meat bovine	339	320	18	1			
pig	1389	1384	1	3	1		
poultry	46	40	4	2			
Kidney bovine	595	41	30	187	247	70	20
pig	587	5	7	150	274	111	40
poultry	76	36	4	17	16	2	1
Liver bovine	18	8	2	5	2		1
pig	12	5	2	3	2		
poultry	39	26	4	5	3		1
Fishes marine°	182	65	28	33	33	13	9
Freshwater	61	59	2				

° see Table 1

the highest concentration was 0.36 mg As/kg). In contrast among 60 samples of marine fishes 9 samples mostly mussels and crawfishes exceeded the tolerance (maxim level found was 24.3 mg As/kg).

Table 4. Distribution of food samples of animal origin into classes with regard to As content [mg/kg wet weight].

Sample	n	Concentration class [mg/kg w w]						
		<0.05	<0.05 – 0.10	0.11 - 0.50	0.51 - 1.00	1.01 - 2.00	2.01 - 4.00	>4.00
Meat bovine	69	69						
pig	789	786	3					
poultry	67	67						
Kidney bovine	28	28						
pig	359	349	7	3				
poultry	58	57		1				
Liver bovine	3	3						
pig	4	4						
poultry	15	15						
Fishes marine°	60	4	3	8	18	18	3	6•
freshwater	10	3		7				

° see Table 1

- squid 7.70 mg As/kg; octopus 24.3 mg As/kg; sardel 4.60 mg As/kg; crawfish 6.01; 6.23 and 13.27 mg As/kg

Table 5. Distribution of food samples of animal origin into classes with regard to total Hg content [mg/kg wet weight].

Sample	n	Concentration class [mg/kg w w]					
		<0.005	<0.005 – 0.020	0.021 - 0.050	0.051 - 0.100	0.101 - 0.500	0.501 - 1.000
Meat bovine	10	6	4				
pig	4	4					
poultry	2	1	1				
Kidney bovine	127	57	58	10		2	
pig	95	90	4			1	
poultry	21	19	1	1			
Liver bovine	8	3	3	2			
pig	5	5					
poultry	16	13	2	1			
Fishes marine°	21	2	2	11	3	3	
freshwater	22	2	4	12	1	3	

° see Table 1

Total Hg was analysed in 331 samples and only in 1 case of pig kidney the tolerance level was lightly exceeded. The highest

concentration of total Hg found in freshwater fishes was 0.400 mg/kg and in marine fishes was 0.208 mg Hg/kg.

The comparison of heavy metal residues in meat of farm animals and fishes indicates that the concentration of Cd was often higher in fishes then in meat of farm animals. It also indicates that the concentrations of total Hg and especially As were higher in fishes. There were only few samples of meat of farm animals which contained more than 0.05 mg As/kg. In fact in the marine fish samples 60 % lies in range 0.5 - 2.0 mg As/kg, 5 % between 2 and 4 mg As/kg and 10 % samples exceed 4 mg As/kg.

Total Hg was practically not present in meat of farm animals. More than 61 % of all analysed samples did not exceed the limit of detection 0.005 mg Hg/kg. The residue level of total Hg in fish was found to be higher. About 50 % of samples of freshwater and marine fishes lied between 0.02 to 0.05 mg Hg/kg.

Among analysed samples on sulfonamides there were 95.73 % of meat and organs of slaughtered animals such as bovine, pigs and poultry and 4.27 % were fishes (freshwater and marine). In most of analysed samples (99.37 %) no residues were found. In 14 samples we detected sulfonamide residues - 7 different sulfonamides were identified. No residues were found in poultry tissues. Half of positive samples belong to pig tissues and the majority of samples exceeding the MRL-value was also found in pig tissues, in all cases sulfamethazine was identified (0.41, 0.17, 0.18 mg/kg). In one sample of freshwater fish sulfamerazine exceeded the MRL-value (0.13 mg/kg).

We can conclude that the heavy metal residues in meat of farm animals and fishes are not concerned, but it is obvious that fishes are more contaminated specially with As and total Hg. Analysis on sulfonamides show, that the control has to be performed to prevent samples with their residues on the market. Residues of sulfonamides can be present in samples where the withdrawal time was not

respected or the sulfonamides were present in the feed without proper declaration.

Table 6. Sulfonamides in farm animals and fishes from Slovenia in period from 1994 to 1998; distribution into classes with regard to sulfonamides content [ng/g wet weight] and type of found sulfonamides.

Sample	n	Non detected	Concentration class [ng/g w w]						
			<10	10 <50	50 <75	75 <100	100 <150	150 <200	>200
Bovine[a]	937	934			1	1			
Pig[a]	946	939	1	1	2			2	1
Poultry[a]	379	379							
Fishes[b]	101	96		4			1		
Total	2363	2348	1	5	3	1	1	2	1
Found sulfonamides									
Sulfamethazine				1	2			2	1
Sulfathiazole				1					
Sulfadiazine					1				
Sulfamerazine				1			1		
Sulfaphenazole			1		1				
Sulfamethoxazole				1					
Sulfamonomethoxine				2					
							⇑		

[a] meat and organs
[b] freshwater and marine
⇑ MRL for sulphonamides: 100 ng/g

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