

Effects of General Soil Fertilization with Sodium Selenate in Finland on the Selenium Content of Meat and Fish

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All agricultural multinutrient fertilizers in Finland have been supplemented with sodium selenate since fall 1984 in order to raise the selenium (Se) content of Finnish foods. Se contents of key foods have been monitored on a regular basis since the program began to chart the effect of the intervention. In the present study, samples of beef and bovine liver, pork and porcine liver, broiler, venison, reindeer meat, and eight species of fish were analyzed for Se by electrothermal atomic absorption spectrophotometry. The Se fertilization has clearly increased the Se content of meat and edible offals but not of fish or wild animals. The mean Se values (mg/kg of dry matter) in 1988 were as follows: beef, 0.60; bovine liver, 1.30; pork fillet, 0.92; porcine liver, 2.30; broiler, 0.78. The present average Se intake in Finland is 3-4 times as high as that in the mid-1970s (0.11 vs 0.03 mg/day). Meat, edible offals, and fish contributed about 52% of the Se intake in 1988, as compared with about 63% in 1975.

Finnish authorities made a decision to increase the Se content of domestic agricultural products by adding sodium selenate to all agricultural multinutrient fertilizers beginning in fall 1984 (Ministry of Agriculture and Forestry, 1984; Koivistoinen and Huttunen, 1985; Varo et al., 1988). Se-supplemented fertilizers were in general use beginning in the growing season 1985.

Two levels of supplementation are being used: 16 mg of Se/kg in multinutrient granular fertilizers intended for grain production and horticulture and 6 mg of Se/kg in fertilizers intended mainly for fodder and hay production. The primary target of the action was to increase the Se content of cereal grains. It was foreseen, however, that all other agricultural products would be affected as well.

A state-nominated committee of experts evaluates and reports annually on the effects of Se fertilization (Ministry of Agriculture and Forestry, 1984). It monitors the Se levels of commercial fertilizers, soils, animal feeds, grain crops, basic foods, human sera, and some environmental samples.

During the 1970s the human Se intake in Finland was found to be very low (0.02-0.03 mg/day), due to the low Se content of domestic agricultural products (Varo and Koivistoinen, 1980; Varo and Koivistoinen, 1981; Mutanen, 1984). The contribution of meat and meat products to the daily Se intake was then about 0.01 mg/day, which was approximately 30% of the total. Meat, meat products, and fish together contributed up to two-thirds of the total Se intake (Varo and Koivistoinen, 1980). At the beginning of the 1980s the significance of cereal foods as a source of Se increased due to abundant grain imports. The proportion of meat and meat products as a source of Se decreased to 20% even though the absolute intake from these increased to 0.015 mg/day (Varo, 1984).

Monitoring of the Se content of some key Finnish foods (13 items) was initiated in 1983, the sampling being carried out systematically every second month. This article reports the effects of Se fertilization on the Se con-

tents of four of these items: beef, pork, bovine liver, and porcine liver. In addition, the Se content of some other meat products, and, for comparison, that of fish caught in Finnish waters are also reported.

MATERIALS AND METHODS

Sampling. Samples of beef, pork, and liver (16 random samples per item per sampling period) were collected regularly every second month beginning in 1982. The sampling procedure is outlined in Table I. All meat samples were purchased from retail food stores in the Helsinki area, except porcine liver samples, which were taken from a communal slaughterhouse. This sampling procedure was considered adequate since the whole agricultural area of Finland supplies food for the city of Helsinki. In addition to the samples included in the systematic monitoring program, samples of other items were collected occasionally. The fish and reindeer samples were obtained from wholesale houses in Helsinki and Rovaniemi, and the other meat items were obtained from retail food stores.

The 16 purchased samples (about 0.5 kg each) were combined for analysis into four pooled samples per item per sampling period. Fish were cleaned and boned. The samples were cut to ca. 1-cm cubes, packed on plastic-lined aluminum trays, frozen, and freeze-dried. The dried samples were homogenized, packed into polyethylene bags, and stored at -20 °C until analyzed.

Analytical Method. Se was analyzed by a previously described electrothermal atomic absorption method for food samples (Kumpulainen et al., 1983). The dried samples were digested in a mixture of concentrated HNO₃, HClO₄, and H₂SO₄. Se was reduced to Se(IV), chelated with ammonium pyrrolidinedithiocarbamate, and extracted into methyl isobutyl ketone for the determination. The accuracy of the method was tested by determining three certified reference materials. Three unofficial control materials were analyzed continuously as blinds to test the precision of the analytical method (Table II).

The data were tested statistically by applying Kruskal-Wallis and Mann-Whitney tests. The standard deviations were tested using the *F* test.

RESULTS AND DISCUSSION

The annual means of Se in pork, beef, and porcine and bovine livers are given in Table III. The Se content of meat and bovine liver increased between the years 1975/

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Table I. Sampling System^a

sample	origin	no. of subsamples collected per sampling period	no. of pooled samples analyzed per sampling period
beef, pork, bovine liver	retail food stores	16	4
porcine liver	slaughterhouse	8	4
fish, reindeer meat	wholesale house	10	1
others	retail food stores	16	4

^a Samples of beef, pork, and livers were collected regularly every second month starting in 1983; other samples were collected occasionally. Sample size, 0.5–1.0 kg each. Original samples pooled in pairs (porcine liver), fours (beef, pork, bovine liver, others), and tens (fish and reindeer meat) for analysis.

Table II. Accuracy and Precision of the Analytical Method

sample	n	mg of Se/kg of dry matter		certified value
		present study		
Certified Standards				
NBS 1577a bovine liver	9	0.66 ± 0.03		0.71 ± 0.07
NBS 1569 brewers yeast	7	0.95 ± 0.04		0.92 ± 0.09 ^a
IAEA H-9 human diet	1	0.10		0.11 ± 0.01
Noncertified Controls				
rye flour	71	0.028 ± 0.002		
bovine liver	47	0.567 ± 0.024		
milk powder	47	0.076 ± 0.003		

^a Not certified by the National Bureau of Standards; Gladney, 1980.

Table III. Se Content of Meat and Liver Samples (mg/kg of Dry Matter)^a

	beef steak	bovine liver	pork fillet	porcine liver
1975/77 ^b				
n ^c	32	8	4	4
mean ± SD	0.04 ± 0.02	0.24 ± 0.11	0.20 ± 0.07	1.38 ± 0.25
range	0.02–0.10	0.10–0.30	0.10–0.30	1.00–1.50
1983				
n	24	24	24	24
mean ± SD	0.18 ± 0.06	0.50 ± 0.21	0.33 ± 0.06	1.40 ± 0.54
range	0.10–0.31	0.14–0.85	0.19–0.43	0.49–2.50
1984				
n	24	24	24	24
mean ± SD	0.17 ± 0.06	0.65 ± 0.29	0.35 ± 0.07	1.60 ± 0.29
range	0.06–0.32	0.24–1.20	0.22–0.53	0.96–2.20
1985				
n	24	24	24	24
mean ± SD	0.20 ± 0.12	0.77 ± 0.26	0.36 ± 0.09	1.70 ± 0.27
range	0.05–0.53	0.12–1.20	0.21–0.57	1.00–2.00
1986				
n	24	24	24	16
mean ± SD	0.46 ± 0.08	1.00 ± 0.22	0.70 ± 0.11	1.80 ± 0.29
range	0.35–0.61	0.65–1.50	0.37–0.89	1.30–2.40
1987				
n	24	24	24	12
mean ± SD	0.57 ± 0.11	1.30 ± 0.24	0.94 ± 0.16	1.90 ± 0.28
range	0.35–0.79	0.90–1.80	0.65–1.30	1.40 ± 2.40
1988				
n	24	24	24	12
mean ± SD	0.60 ± 0.08	1.30 ± 0.24	0.92 ± 0.13	2.30 ± 0.15
range	0.44–0.74	0.76–1.60	0.66–1.10	2.10–2.70

^a Se fertilization started in 1985. ^b Nuortamo et al., 1980. ^c n = number of samples.

77 and 1983, probably due to the intensified use of selenite-supplemented commercial feedstuffs, but it was still low when the fertilization program began in 1984. The effect of Se fertilization has been very clear (Figures 1 and 2). The samples taken after the year 1985 generally differ significantly ($P < 0.001$) from the samples collected before the Se fertilization began. In 1988, beef contained about 15 times and pork 4 times as much Se as in 1975/77. Only a moderate increase was observed in the Se level

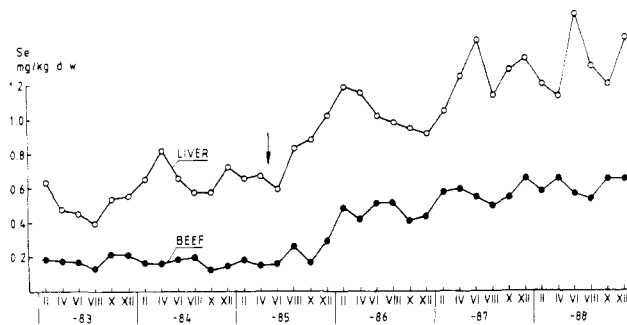


Figure 1. Trend in Se content of beef and bovine liver. Se fertilization started in May 1985.

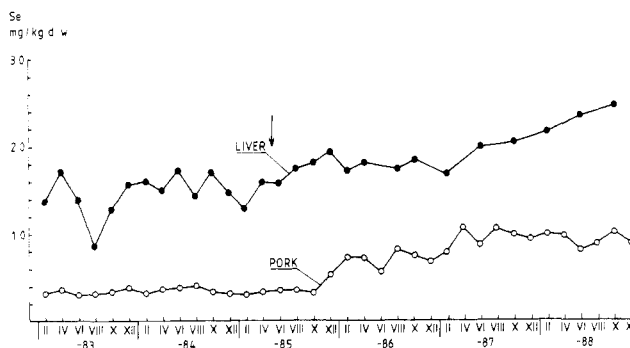


Figure 2. Trend in Se content of pork and porcine liver. Se fertilization started in May 1985.

of porcine liver during this period (Figure 2): its Se content was high already in the 1970s probably as a result of the general use of Se-supplemented commercial feedstuffs and Se medication in pig farming (Nuortamo et al., 1980).

The Se contents of meat and liver seem to be slightly increasing still. The Se levels of both meat and liver samples collected in 1988 differ highly significantly ($P < 0.001$) from those collected in 1986. The Se contents of feedstuffs (grain and hay) have been at a more or less constant level since 1985 (Ministry of Agriculture and Forestry, 1989).

The variation in beef Se has decreased since commencement of the fertilization practice in 1984. The standard deviation of the samples has decreased highly significantly during the fertilization period ($P < 0.001$) (Table III). Likewise the Se content of bovine liver has become more uniform. However, the Se fertilization has not increased the homogeneity of Se in pork or porcine liver.

There tends to be a slight decrease in the Se levels of beef and bovine liver in summer and an increase in winter (Figure 1), but the seasonal fluctuation is not statistically significant ($P > 0.05$).

The Se contents of some other meat items were monitored occasionally (Table IV). The effect of Se fertilization was distinct in the samples from domestic ani-

Table IV. Se Content of Various Meat and Fish Samples outside the Regular Monitor Program (mg/kg of Dry Matter)

sample	1975/77 ^a			1986/88		
	n ^b	mean ± SD	range	n ^b	mean ± SD	range
Meats and Meat Products						
broiler	4	0.37 ± 0.10	0.30–0.52	4	0.78 ± 0.06	0.71–0.88
reindeer meat	2	0.68	0.54–0.81	1	0.54	
venison	2	0.15	0.09–0.20	5	0.17 ± 0.05	0.13–0.27
sausage, frankfurter	4	0.06 ± 0.02	0.04–0.09	4	0.29 ± 0.01	0.28–0.29
Offals						
kidney, bovine	4	2.30 ± 0.29	2.00–2.50	8	5.70 ± 0.68	4.70–6.50
heart, bovine	7	0.16 ± 0.09	0.06–0.30	8	0.92 ± 0.38	0.62–1.30
liver, moose	1	0.33		1	0.45	
kidney, moose				1	2.00	
heart muscle, moose				1	0.43	
Fish						
baltic herring (<i>Clupea harengus membras</i>)	6	0.78 ± 0.24	0.50–1.00	3	0.87 ± 0.13	0.74–0.99
rainbow trout (<i>Salmo gairdnerie</i>)	5	0.76 ± 0.18	0.50–1.00	2	0.53	0.50–0.55
salmon (<i>Salmo salar</i>)	2	0.65	0.60–0.70	1	0.51	
pike (<i>Esox lucius</i>)	5	1.12 ± 0.38	0.60–1.50	1	0.91	
burbot (<i>Lota lota</i>)	4	1.03 ± 0.37	0.60–1.50	1	0.78	
perch (<i>Perca fluviatilis</i>)	5	1.40 ± 0.20	1.00–1.50	1	1.09	
pike perch (<i>Lucioperca lucioperca</i>)	2	1.50	1.50–1.50	1	0.44	
breem (<i>Abramis</i> sp.)	6	1.33 ± 0.26	1.00–1.50	2	1.32	1.08–1.56

^a Nuurtamo et al., 1980. ^b n = number of samples.

mals. However, no effect was evident in the samples of reindeer, a semidomesticated animal, or of moose (*Alces alces*), a wild animal. The Se content of reindeer meat was fairly high already in the 1970s probably because of the high Se content of their main fodder, lichens (Nuurtamo et al., 1980; Garmo et al., 1986).

As expected, the Se content of Baltic Sea fish continues to be about the same as it was in 1975/77. The amount of Se added to fields is <10 g/ha annually, and leaching is known to be minimal (Ylärinta, 1982). The dilution capacity of the sea is very large, of course.

The Se fertilization has rapidly affected the human Se intake in Finland. Intake in 1986–1988 averaged 0.09–0.10 mg/day (energy level 10 MJ; 2400 kcal), which is 3–4 times more than in the mid-1970s and 2–3 times more than in the early 1980s (Varo et al., 1988; Koivistoinen and Varo, 1987). In 1988, the Se intake from meat, meat products, and edible offals was about 0.045 mg/day and that from fish about 0.010 mg/day. Together meat, meat products, edible offals, and fish presently contribute about 52% of the total Se intake (Varo et al., 1988).

The average Se intake in Finland now meets recommendations, both in respect to safe and adequate intake defined by the U.S. National Research Council (0.05–0.20 mg/day; Food and Nutrition Board, 1980) and to recommendations of the Nordic Council of Ministers (0.04–0.08 mg/10 MJ; 1989). Although it would be possible with the present Se levels to compile diets with Se contents exceeding 0.20 mg/day, it can be assumed that such diets are exceptional. Excessive food-based intakes are not possible over a long period of time. It can be also supposed that even vegetarian diets now contain more than 0.05 mg of Se/10 MJ (Eurola et al., 1989).

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Characterization of Anthocyanin-Containing Colorants and Fruit Juices by HPLC/Photodiode Array Detection[†]

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The anthocyanin pigment profiles of commercial black currant, blackberry, black raspberry, elderberry, cherry, plum, grape, bilberry, and red cabbage products were characterized by high-performance liquid chromatography (HPLC)/photodiode array detection. Removal of acylated anthocyanins by alkaline hydrolysis and selective removal of anthocyanins on a reversed-phase cartridge with borate buffer were auxiliary techniques that proved helpful in making peak assignments. Both the retention properties on reversed-phase HPLC and the spectral properties by photodiode array detection were used to characterize the anthocyanins. Other properties including tinctoral strength, total anthocyanin concentration, browning, titratable acidity, and Hunter tristimulus values were also determined for these colorants.

The recent banning of Red No. 2 in the United States along with the questionable status of Red No. 40 has led to the increased use of natural red pigments as coloring agents (Wallin and Smith, 1977). The anthocyanins are one such class of natural red pigments that have found use as a suitable alternative for synthetic colorants in many applications.

The anthocyanins are widely distributed in nature, occurring in most higher plants. They are found in all parts of the plant but are most obvious in fruits and flowers (Brouillard, 1982). Pigment extracts are commercially available, grape skin extract (GSE) being the most common. In the United States only two sources of anthocyanin extracts are allowed to be used in foods. GSE is restricted for use in coloring beverages while grape color extract (GCE), an extract of concord grapes, can be used to color nonbeverage foodstuffs (Office of the Federal Register, 1986). In the European Economic Community (EEC) countries, anthocyanin extracts from food sources are generally allowed (for specific information this class of colorants is listed under EEC E163).

In addition to extracts, the concentrated juice of red fruits such as cranberries, raspberries, elderberries, etc., can also be used in food products that are compatible with the acidity and flavor of the fruit juice concentrate involved (Riboh, 1977). In the United States and for most

EEC countries, fruit juice and concentrates can be used without restriction.

The demand for anthocyanin-containing colorants is increasing. Fruit juice concentrates have become an important ingredient in the manufacture of many foods and beverages. Production of fruit juice concentrates has become highly competitive in both domestic and foreign markets. Analytical methodology able to identify the anthocyanins and to determine their source are needed for quality control and for determination of the authenticity of fruit juice concentrates and color extracts as well as for regulatory activities (Wrolstad et al., 1981).

Chemical analysis of plant constituents (chemotaxonomy) is an excellent objective method for identification and classification of plants. The anthocyanin composition of many fruits is quite distinctive (Wrolstad et al., 1981), and analysis of anthocyanins has been successfully used to detect adulteration of Concord grape juice with *vinifera* or hybrid varieties (Mattick et al., 1967; Fitelson, 1967), adulteration of blackberry and cherry juice with elderberry or grape skin extract (Fitelson, 1968), and adulteration of cranberry juice cocktail with grape skin extract (Hale et al., 1986; Hong and Wrolstad, 1986).

The objectives of this work are 2-fold: First, the general coloring properties of several commercially available anthocyanin colorants and juice concentrates are compared. This information is useful in product development and in quality assurance. The data presented may be helpful in selecting a colorant with the appropriate hue and/or tinctoral strength. The second objective is to use HPLC coupled with photodiode array detection

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