SESSION 5
SELENIUM METABOLISM AND FOOD CHAINS

PHYTOMANAGEMENT OF SOLUBLE SELENIUM AND PRODUCTION OF BIOFUEL AND BIOFORTIFIED NEW PRODUCTS

G. Banuelos

USDA-ARS-WMRU, Parlier, United States

The use of green plants and associated microbes for environmental remediation has been called *phytoremediation.* This green technology is used for the management of selenium (Se) contaminated soils and waters via the processes of phytoextraction, phytovolatilization, and phytostabilization. Using a plant-based system for phytoremediation of Se on a sustained basis will also require the production of viable products from the systems. These include; Se-enriched plant material for humans and animals, biodiesel made from seed oils, and seed meal used as a biological herbicide and as a feed supplement. Long term multi-year field studies were conducted with different Brassica species. These studies showed that Brassica crops were effective for managing Se to a depth of 50 cm. The plants were harvested for seeds, which were mechanically processed on-site for their oil (biofuel). The residual seed meals were used as an organic source of Se for animal feed and also as a biofumigant. All samples were analyzed for Se by ICP-MS and Se speciation was performed by SAX-HPLC-ICPMS. Coupling phytomanagement of soluble Se with the creation of biofortified and other bio-based byproducts may provide California growers with economic benefits, while managing excessive Se. The objective of this presentation is to report on the use of different plants grown for the management of soluble Se in central California soils and on the derivation and novel utilization of potential bio-based products.

PHARMACOKINETICS OF SELENOMETHIONINE AND METHYLSELENOCYSTEINE IN THE HUMAN

J. Marshall [1], C. Ip [2], W. Davis [2], K. Hill [3], M. Perloff [4], R. Burk [3]

[1] Roswell Park Cancer Institute, Cancer Prevention & Population Sciences, Buffalo, United States
[2] Roswell Park Cancer Institute, Buffalo, United States
[3] Vanderbilt University Medical Center, Nashville, United States
[4] National Cancer Institute, Bethesda, United States

The report by Clark et al (1996) indicating that selenium supplementation, with selenium administered as selenized yeast, raised hope that selenium supplementation might prove protective against cancer and other chronic diseases. Clark's trial, which helped motivate the SELECT trial of selenium and vitamin E, was based on the understanding that the critical component of the selenized yeast was selenomethionine. SELECT, with a sample size 30 times that of the Clark trial, showed convincingly that selenomethionine does not protect against cancer or other chronic disease. Ip and others, however, have suggested that selenomethionine is an inefficient source of methylselenol, which is likely to be the protective component of selenium. Methylselenocysteine, readily metabolized to create the methylated selenium molecule methylselenol, was proposed by Ip to be likely to generate chemopreventive activity. The present double-blind study examines the 84-day pharmacokinetics of selenium, 400 mcg/day, in the forms of selenomethionine and methylselenocysteine. Subjects underwent 48-hour plasma and urine pharmacokinetic analysis at the beginning-day one-- and end-day 84--of the trial. An additional fasting selenium measure was taken on day 30. Five subjects were randomized to selenomethionine, five to methyl selenocysteine, and 2 to placebo; all subjects were male. Selenium, selenoprotein P and glutathione peroxidase are measured at each time point. These outcome data will be presented at the meeting

HAIR Se LEVELS IN POPULATION OF EUROPEAN PART OF RUSSIA: CORRELATION WITH DEMOGRAPHIC DATA AND MORBIDITY

A.V. Skalny [1], A.R. Grabeklis [1], M.G. Skalnaya [2], E.S. Berezkina [1]

[1] Russian Society of Trace Elements in Medicine, Moscow, Russian Federation
[2] ANO Centre for Biotic Medicine, Moscow, Russian Federation

During 2004-2010 there were 52161 adults and 9955 children in 50 regions of the European part of Russia, Moscow and Saint-Petersburg clinically investigated. Obtained hair ICP-MS multielement analysis data were compared to medical and demographic data from these territories. We found that the median of hair Se varied in different regions significantly. Minimal hair Se was detected in the most Western Kaliningrad exclave (Me = 0.175 μg/g). Also low data were found in Orenburg, Smolensk, Mari El, Udmurtia, Yaroslavl, Tula, and Lipetsk regions (0.250-0.320 μg/g). These regions are situated in different geographical parts, but all of them are very industrialized and polluted by heavy metals. The highest hair Se was found in North Caucasian regions, especially in Kabardino-Balkaria, Chechnya, Dagestan (0.625; 0.589; 0.525 μg/g). Increased hair Se positively correlated with life expectancy of men and women ($r = 0.37$ and 0.33; $p < 0.005$; $p < 0.001$, respectively). General morbidity of children was higher in regions with elevated rate of Se deficiency. The decrease in hair Se was correlated with elevating asthma, atopic dermatitis, pulmonary diseases, bone and connective diseases morbidity, hypertonic diseases in adults and all population. The obesity, pneumonia morbidity were higher in children with low hair Se. We concluded that decreased Se provision can be due not only to geographic locations, but mainly to industrial pollution of regions. Low hair Se is a good indicator of negative trends in demography and morbidity in population of selected regions.

ANALYSIS AND RECOVERY OF SELENIUM SPECIES AND THE INFLUENCE OF PROCESSING OF WHEAT GRAIN FOODS

W. Tjong, D.M. Small, P.D. Morrison

RMIT University, School of Applied Sciences, Melbourne, Australia

It is known that different species of selenium follow distinct metabolic pathways in the human body and organic forms are more bioavailable than inorganic Se. The essential and toxic nature of Se may therefore depend not only upon concentration but also the chemical forms in which this element is present in the sample. Amongst the cereal crops, wheat is a relatively efficient accumulator of Se and therefore it provides an important Se source for human consumers. Accordingly, the aim of this study has been to investigate the concentrations of total selenium and the chemical species present in Australian wheat flours and cereal foods. For analysis of total Se, microwave digestion with nitric acid and hydrogen peroxide was applied and ICP-MS was used to determine the amount of Se in the sample extracts. The procedure was validated, including the use of a certified reference material from NIST. In the speciation study, extraction involving enzymatic hydrolysis with proteolytic enzymes as well as lipases, followed by HPLC-ICP-MS analysis was applied. The data show that selenomethionine is the predominant species in wheat flours, accounting more than 80% of total selenium, with smaller amounts of selenocystine and selenite. When biofortified materials were compared with normal products, similar species distribution was found. In the context of the high starch contents of the matrices, the inclusion of amylase preparations in the extraction was observed to have little effect on recovery values. The analysis procedures were applied to samples taken at various stage during processing. Although some effects on species distribution were observed, generally these were minor and the conditions which appear to be most important will be described.

IDENTIFICATION OF SELENIUM METABOLITE IN CULTURED CELLS AND ELUCIDATION OF ITS BIOLOGICAL ROLE

Y. Ogra, M. Kimura, S. Hasegawa, M. Tokumoto, Y. Anan

Showa Pharmaceutical University, Laboratory of Chemical Toxicology and Environmental Health, Tokyo, Japan

Se is excreted into urine as selenosugar and trimethylselenonium. However, the intracellular metabolic pathway of Se is not fully understood. In this study, we exposed sodium selenite to human hepatocellular carcinoma cells (HepG2) at a concentration of 10 µmol L^{-1}. An unknown Se metabolite was detected in the supernatant of HepG2 by an HPLC-inductively coupled plasma mass spectrometry (ICP-MS). Namely, the retention time of the Se metabolite did not matched with those of any standard Se compounds which we had. The unknown Se peak was also detected in the homogenate of several mammalian cell lines such as HepG2, pheochromocytoma cells of the rat adrenal medulla (PC12) and mouse fibroblast-like cells added with selenite plus glutathione (GSSeH) *in vitro*. To obtain molecular information of the Se metabolite, it was applied to HPLC-electrospray tandem mass spectrometry (ESI-MS-MS). The results obtained by the molecular mass spectrometers, *i.e.*, the molecular mass of the Se metabolite (Mw = 106) and the fragment ions suggest that the unknown Se metabolite was selenocyanate ($SeCN^-$).

The spike of authentic $SeCN^-$ increased the peak height of the unknown Se metabolite, and then, simultaneous exposure of GSSeH and cyanide (CN^-) increased the peak corresponding to the unknown Se metabolite. The cytotoxicity of selenocyanate was less than those of selenite and cyanide, suggesting that the cells ameliorated the toxicity of selenite by forming selenocyanate with endogenous cyanide although the biological source of endogenous cyanide was unclear. In whole animal experiments, selenocyanate recovered the concentrations of serum selenoproteins such as extracellular glutathione peroxidase and selenoprotein P. These results suggest that selenocyanate is a novel Se metabolite formed in the cultured cells. Seleno-cyanate seems to act as an Se pool because it is less toxic than selenite but is assimilated as effectively as selenite.