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## SELENITE RETENTION DIFFERENCES IN SOILS OF HIGH AND LOW GASTRIC CANCER RISK AREAS IN SRI LANKA<sup>†</sup>

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The extraordinary geographic variability in the incidence of gastric cancer in Sri Lanka, strongly implicated geochemical factors in the etiology of the disease. It was noted that the trace element, Se, appears to be a natural cancer protecting agent. Since there were no distinctly significant difference between the total Se level in the soils of high risk gastric cancer area (Nawalapitiya) and low risk gastric cancer area (Angunawela), a study was undertaken to assess its bioavailability. Selenite was absorbed by the soils to Nawalapitiya to a greater extent than by the soils of Angunawela. The adsorption capacities of both soils were maximum at a pH range of 2.0-3.0. The adsorption/desorption processes of selenite in the soils can be best explained by considering the corresponding reaction mechanisms in goethite and gibbsite.

KEY WORDS: Selenite, adsorption, gastric cancer, Sri Lanka.

#### INTRODUCTION

The close relation of the trace elements in the environment with human health is now being increasingly well documented and geomedical research in this direction is fast becoming an established field of study. Except for C, N, H and O, all elements requisite for human nutrition and good health have been derived from soils and food chains<sup>1,2</sup> and from water supplies.<sup>2,3</sup> Therefore, adequate supplies in human nutrition for good health and prevention of diseases depend on adequacy from the sources or alternatively nutritional supplementation to obtain the recommended dietary requirements of each element including 13 for so required in trace amounts. The extraordinary epidemiological distribution of cancer in some parts of the world has suggested that inadequacy of one or more trace elements may have a critical metabolic effect.<sup>4</sup> In some areas of the world,<sup>5</sup> gastric cancer is a leading cause of death. Its regional epidemilogic behaviour, marked by large differences in incidence within small confines and sharp changes in incidence within small confines and sharp changes in incidence over time, suggests a predominant role in geochemical factors. The incidence of gastric cancer is not common in Sri Lanka and there is very little data available regarding its epidemiology. However, several confines of high incidence of this type of tumours were identified in Nawalapitiya, in the mountainous parts of the island.<sup>6</sup> As regards the baseline epidemiologic data, a few differences exist between gastric cancer in Sri Lanka and those reported from other parts of the world. Interestingly the male/female gastric cancer ratio of 37:17 compares well with the worldwide figure of 2:1. The present study was undertaken to determine the

<sup>†</sup> Contribution from the Soil-Vegetation-Health Study Group

bioavailability of  $SeO_3^{3-}$  in soils from high risk and low risk gastric cancer provinces in Sri Lanka. It was felt that a study of this nature would provide useful information to the medical scientists and epidemiologists since a very high percentage of the population of the island literally live close to the soil, depending on the natural environment for their food, shelter and most necessities. The geochemical status of soil and groundwater therefore governs the general health of the community to a great extent.

#### MATERIALS AND METHODS

Soil sampling locations were selected from the high risk (Nawalapitiya) area and the low risk (Angunawela) area of gastric cancer, to investigate the bioavailability of selenite. One garden soil sample was collected from each location. The samples were air dried, and only the powdered material passing through #200 sieve was chosen for the study. The time required to reach the apparent adsorption equilibration was determined by mixing 20 ml of 10 mg/L selenite solutions with 0.1 g of soil. The soil suspension was equilibrated at room temperature in a mechanical shaker. The duration of shaking time was 5, 10, 15 min, ... 12, 24, 48 hr respectively. An equilibration time of 24 hrs was found to be satisfactory since the adsorption process was completed during this period.

In order to determine the optimum pH value for selenite adsorption, the acidity of the 10 mg/L selenite solutions added to the soil samples was adjusted to pH 2 . . . 11 with a dilute 0.2 M HAC/0.2 M NaOAC. The selenite adsorption isotherms of two soil types were obtained by using 12 standard selenite solution of concentrations ranging from 10 to 50 mg/L. A 20 ml solution of pH 2.30 was mixed with 0.1 g soil and allowed to stand for 24 hrs. Desorption studies were carried out by using a solution of 0.1 M NaOH. One gram of selenite soil complex was shaken with 0.1 M NaOH and kept for 24 hrs. The determination of the concentration of selenite in the above solutions was carried out spectrophotometrically using 2,3- diaminonaphthalene (DAN) as the colour complex.<sup>6</sup> The DAN indicator was selective for selenite in selenite/selenate mixture. A sensitivity of 10 mg Se  $M^{-3}$  was observed with this method.

#### RESULTS

Figure 1 illustrates the effect of equilibration time on the adsorption of selenite into the soils in high risk and low risk areas of gastric cancer. The optimum time required to reach the apparent adsorption plateau was 15 min for both soils. It was noted that the amount of adsorption did not increase significantly for equilibration times longer than 24 hrs. In fact there is apparently a slight decrease in adsorption after 24 hrs. This result may be due to the incorporation of some of the selenite desorbed into the solution with longer periods of equilibration. A 24 hr period was found to be sufficient in order to attain the maximum adsorption of selenite. The adsorption of selenite decreased with increasing pH, with a particularly drastic decrease between pH 9 and pH 11 for the soils in high gastric cancer risk area. In both instances the maximum adsorption capacities were recorded in pH range of 2.00–3.00 (Figure 2). Therefore, this pH range was maintained in subsequent studies. Adsorption iso-



Figure 1 Effect of reaction time on the amount of selenite adsorbed for soils.



Figure 2 The dependence of pH on selenite adsorption for soils.

therms of selenite/soil systems are presented in Figure 3. There was a slight difference in the shape of the adsorption isotherms for the soils between the high gastric cancer risk and low gastric cancer risk areas. However, the soils showed distinctly significant difference in adsorption capacities; the optimum adsorptions of 590  $\mu$ g/g and 420  $\mu$ g/g were recorded for the soils in high gastric cancer risk and low gastric cancer risk areas, respectively. The desorption of selenites from the soils has a direct bearing on the uptake of the anion by the plants, and therefore on animal and human health.



Figure 3 Adsorption isotherms of selenite for soils.



rigure 4 Desorbatinity curves of science for son

The term "desorbability" can be defined as follows:

desorbability = (Original adsorption-adsorption after two washings) × 100 Original adsorption-expected adsorption from the curve at the solution concentration after two washings The desorbability curves for the soils in Nawalapitiya and Angunawela as shown in Figure 4. The desorbability of selenite is significantly low (max. 20%) in the soils of high gastric cancer risk area. However, desorbability in the soils of the low gastric cancer area appears to be independent of initial adsorption and is generally at a high level (max. 60%).

#### DISCUSSION

The results of this investigation demonstrated that the pH, the time and the anion concentration were among the critical factors influencing the selenite retention in soil. For selenite adsorption, there is a rapid initial uptake (app. 15 minutes) followed by a much slower reaction which may last for several days. This behaviour has been attributed to surface bonding (fast step)<sup>7</sup> and solid state diffusion (slow step)<sup>8</sup> respectively. However, these equilibrium times are much shorter than those allowed in the natural systems. Larger reaction times (e.g. by aging the system) favour an increase in the selenite retention. Whether short or long aging times are more representative of natural environments, however, remain an open question.

Possible substrates in soil for the adsorption include clays, organic matter and iron, manganese, aluminium and silicon hydrous oxides. In particular, the important role played by goethite and gibbsite in the adsorption of selenite into soils have been strongly emphasized.<sup>8,9</sup> Yapa<sup>10</sup> has shown, in an unpublished study, that the soils in a high gastric cancer risk area are characterized by appreciable amounts of gibbsite whereas the goethite is abundant in the soils of low gastric cancer risk areas. The mechanisms involved in the adsorption/desorption of selenite into soils can be deduced by considering the selenite–goethite/gibbsite laboratory models. Hansmann and Anderson<sup>11</sup> have divided the free energy involved in the adsorption of selenite into two components namely,

### $\Delta G_{net} = \Delta G_{intrinsic} + \Delta G_{electrostatic}$

and have used electrophoretic mobility of selenite to estimate  $\Delta G_{electrostatic}$  as a function of pH. The  $\Delta G_{intrinsic}$  for selenite was -39.31 kJ/mol. This value is favourable for for adsorption of low pH and unfavourable for high pH. This may be due to the negative charge that develops on the surface of the soil minerals with increasing pH. Therefore, the adsorption and desorption of anions change the net charge on the surface of soil minerals. The lack of reversibility of selenite in soils of high gastric cancer areas is not very clear, however, this can be partially explained by considering the stability of the selenite-goethite complex. The stability of this complex under various chemical conditions has been repeatedly recorded.<sup>11,12</sup> Recent studies<sup>12,13</sup> have shown that the selenite is adsorbed into goethite by replacing two A-type hydroxyl groups (singly coordinated to ferric ions) on the [001] and [010] goethite faces to form bridge complexes of the form FeO (SeO  $\cdot$  OH)  $\cdot$  O  $\cdot$  Fe . The great stability of ring structures is attributed to the increase in entropy resulting from ring formation.<sup>14</sup> However, the formation of this type of complexes are very unlikely with gibbsite. In fact, it is held to the mineral surface by only one bond. It was shown that the gibbsite is very common in the soils of low gastric cancer risk areas of Sri Lanka.<sup>10</sup> Thus the selenite ion would be loosely bonded to these soils and therefore it would be readily available for plants and aquatic systems.

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