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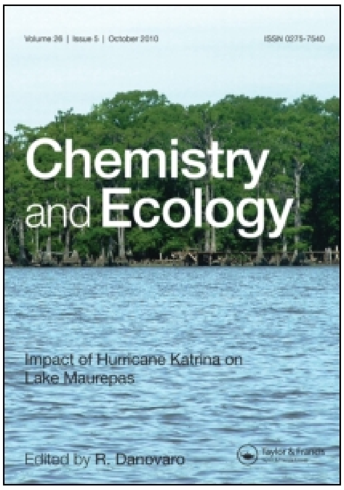

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The Influence of Trace Elements on Environment; Distribution of Thallium in Fluids of Volcanic Areas

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The Influence of Trace Elements on Environment; Distribution of Thallium in Fluids of Volcanic Areas

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During weathering of igneous rocks thallium can be readily mobilized as Tl^+ in aqueous phase and picked up by plants. In this way it can reach the alimentary cycle of both livestock and humans. Since the toxicity of thallium is well-established, an analytical procedure for its determination is optimized in order to contribute to the knowledge of Tl^+ distribution in specific environments. The analytical method is applied to fluid phase samples from Vulcano island (Italy) and from other volcanic areas.

KEY WORDS Environment; Thallium; Fumarolic Gases; Phreatic Waters; Anodic Stripping Voltammetry:

INTRODUCTION

Thallium salts can be very toxic and numerous cases of poisoning have resulted from their incorrect use as a rodenticide or in depilatory creams (Schoer, 1984). The crustal abundance of thallium is 0.45 mg kg^{-1} (Taylor, 1964), while for igneous rocks a value of 0.98 mg kg^{-1} is reported (Heinricks *et al.*, 1980). Thallium is seldom enriched in specific minerals, occurring as a trace element; the volatility of its salts has caused local pollution in proximity to industrial activities like coal combustion (Davison *et al.*, 1974), steel and manganese production (Smith and Carson, 1977) and cement plants (Welzel and Winkler, 1981). In 1979 an atmospheric dust fallout from pyrite roasting plant, in a special cement factory in North West Germany, produced a serious situation (Schoer, 1984). Thallium occurs in small concentrations in natural waters if not enriched by particular geological conditions. Batley and Florence (1975) reported values of 3.7 ± 1 ng Tl l^{-1} in fresh waters at Woronora Weir (Australia) and Bonelli *et al.* (1980), analyzing three river waters from USA, found for one, a concentration of 45 ng Tl l^{-1} while the others did not contain detectable thallium.

In sea water, the thallium content is relatively constant and is a little more than 10 ng Tl l^{-1}. Matthews and Riley (1970) reported values of 9 and 16 ng Tl kg^{-1} for samples from the Bay of Biscay and the Irish Sea. For samples collected off Australia in the south Pacific, Batley and Florence (1975) found a median value of 13 ± 1.4 ng Tl kg^{-1}. More recent measurements of the concentrations of thallium in sea water collected from numerous ocean locations ranged from 12 to 16 ng Tl kg^{-1} (Flegal and Patterson, 1985).

Some igneous minerals and rocks, rich in potassium, contain relatively high concentrations of thallium (Shaw, 1952) and this element, by weathering of rocks, is released into the environment via superficial and shallow waters.

The presence of thallium in minerals of volcanic origin was first observed by Cossa (1868) and Carobbi (1924). Few data giving the concentration of thallium in natural waters of volcanic areas have been published although its presence in waters of Java and Carlsbad was reported in the last century (Mellor, 1956). Water from hot springs in a thermal area near Taupo (NZ) contains up to 7 μg Tl l^{-1} (Weissberg, 1969) and Kothny (1969), using the crystal violet spectrophotometric method, found 14 μg Tl l^{-1} in water from Mercuryville, California.

The diffusion of thallium in areas where a natural enrichment may occur is normally not considered in spite of its toxicity. The aim of this study was to determine thallium concentrations in waters

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of volcanic areas and in condensates of fumaroles. The procedure was optimized for the differential pulse anodic stripping voltammetry method (DPASV).

EXPERIMENTAL METHODS

Instrumentation

DPASV determinations were carried out with an AMEL mod 473 Polarographic Analyzer in conjunction with a H.P. 7044A X-Y recorder. Working electrodes were the Metrohm E 410 Hanging Mercury Drop Electrode (HMDE) and the Metrohm EA276/2 Glassy Carbon Electrode (radius 1.5 mm). The reference electrode was a saturated calomel electrode (Metrohm EA 404) to which all potentials were referred, and the auxiliary electrode was a paraffin impregnated graphite rod.

The mercury film electrode (MFE), of the preformed type, was prepared daily by electrolyzing 1.10^{-4} M mercury acetate in 3% Suprapur sodium chloride solution with the following program: 5 min at −0.1 V, 5 min at −0.4 V, 10 min at −0.8 V and 5 min at −0.1 V. The determination of the mercury film thickness (Batley and Florence, 1974) was carried out by graphical integration of the dc mercury peak obtained by scanning the potential to −0.1 V. In this case solid potassium iodide was added to the solution (to obtain 0.2 M) in which mercury forms iodomercurate ion (Neeb, 1969).

Reagents

All solutions were prepared with deionized and double distilled quartz water. The supporting electrolyte was an acetate buffer solution ($2.5 \cdot 10^{-2}$ M) obtained from acetic acid and sodium acetate Suprapur Merck (1M + 1M) and EDTA $2.5\,10^{-3}$ M from 0.2 M disodium salt reagent grade. A standard 0.1 M thallium solution was prepared by weighing $TlNO_3$, dried at 110°C. The 10^{-5} to 10^{-6} M solution for addition in the cell was prepared daily. Ultrapure nitrogen was used to remove oxygen from the cell.

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Sampling

Water samples, collected by means of a polyethylene device, were stored in glass bottles with teflon stoppers. Condensates of volcanic gases, obtained through a portable glass condenser using water as cooling fluid (Piccardi, 1982), were stored in polyethylene bottles. All samples, prior to the DPASV procedure, were filtered through a 0.45 μm membrane, and evaporated to dryness in presence of HNO_3.

RESULTS AND DISCUSSION

To characterize the deposition potential (E_d) successive ASV cycles at various deposition potentials were recorded. By plotting peak current against E_d a dc polarogram can be reconstructed because the anodic peak current is proportional to the amount of amalgam deposited and then to the limiting current of the reduction stage. The curve achieved in this way is usually called a pseudopolarogram (Shuman and Cromer, 1979) or neopolarogram (Lovric and Branica, 1980). The two curves of Figure 1 have been constructed with the values obtained using HMDE and MFE respectively. The arrow at the beginning of the curve indicates the value of peak potential. An analogous difference between the two E_p values was observed by

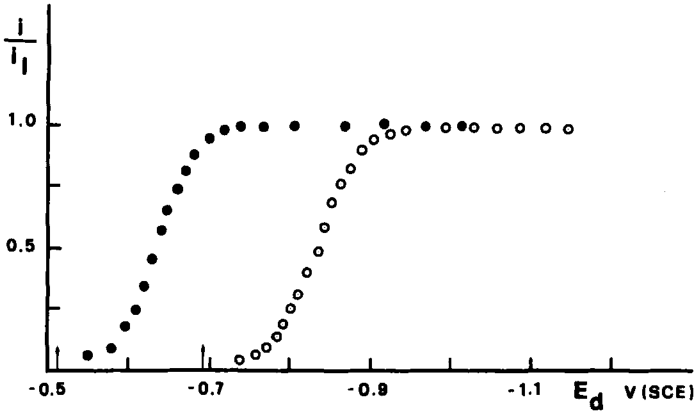

FIGURE 1 Neopolarograms of thallium on HMDE (●) and of MFE (O)

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Batley and Florence (1974) in 0.1 M HCl by linear scan stripping voltammetry. From electrode equations of HMDE and MFE it can be predicted (Vydra *et al.*, 1976) that the greatest shift in peak potential (E_p) will occur with a singly charged ion. As shown in Figure 1 a deposition potential (E_d) of −0.75 V proved suitable with regard to the sensitivity with HMDE while with MFE a $E_d = -0.95$ is required.

Figure 2 shows the dependence of the observed peak current on

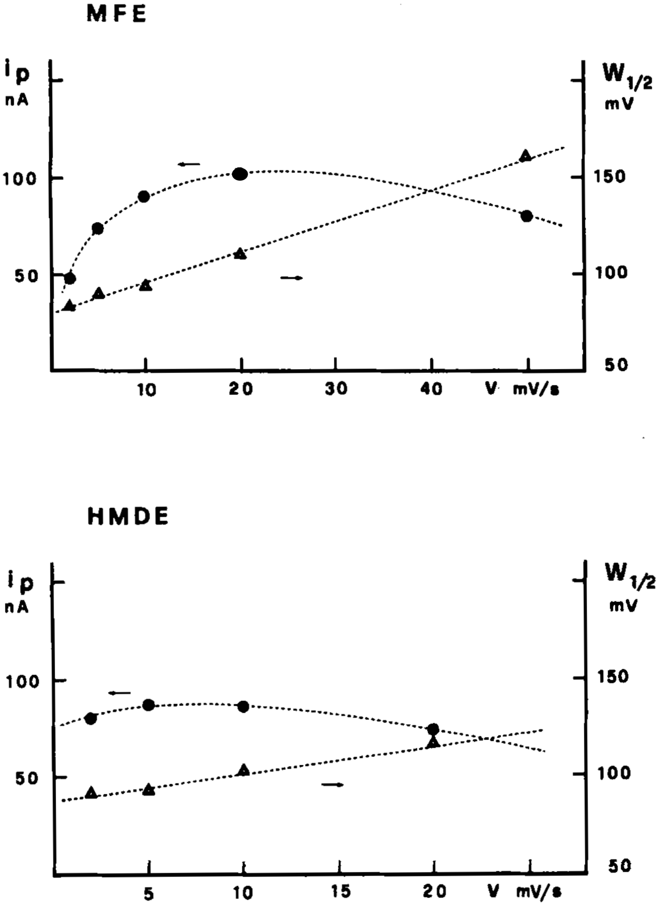

FIGURE 2 Effect of the potential scan rate on peak height (●) and on peak (Δ) width for MFE and HMDE

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the potential scan rate. The values of peak current (i_p) pass through a maximum and values chosen for measurements are 10 and 5 mV s^{-1} for MFE and HMDE respectively. Peak current increases linearly with increasing modulation amplitude (E_{DP}) up to 90 mV for HMDE and 70 mV for MFE (Figure 3). A slight increase in peak width with pulse amplitude is observed but insufficient to modify peak separation. By working with $E_{DP} = 70$ mV we have an increase in sensitivity and a modest increase in peak width.

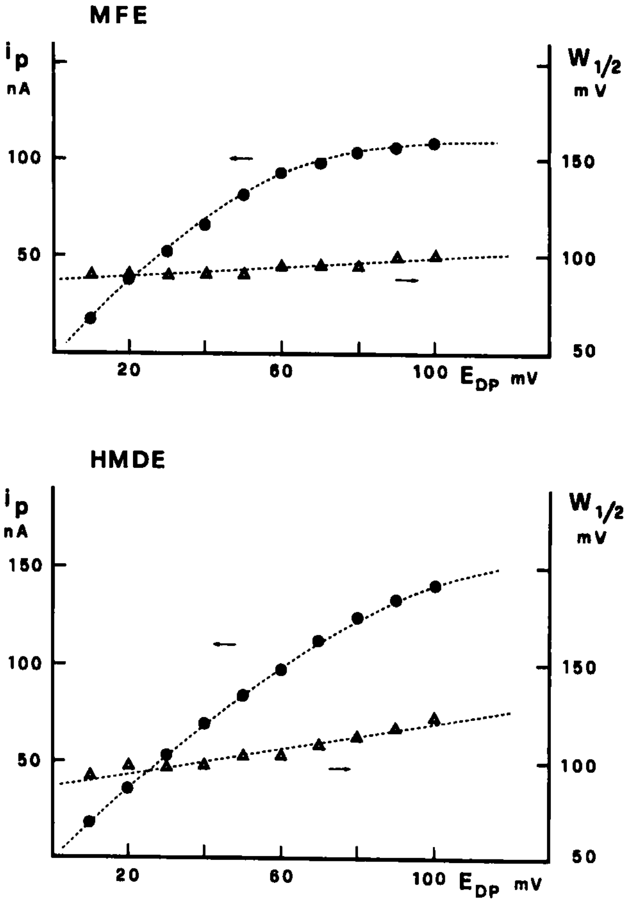

FIGURE 3 Effect of modulation amplitude on peak height (●) and on peak width (△) for MFE and HMDE

TABLE I
Peak currents (i_p) observed for different values of radius (r) of the drop ($5\,10^{-8}$ M Tl)

r/cm	i_p/nA
0.330	48.5
0.415	65.0
0.475	75.5
0.523	83.7
0.564	92.0
0.600	97.5

Plating time for deposition of metals on to mercury is another important parameter related to sensitivity. As expected, the peak currents were found to be proportional up to an electrodeposition time (t_d) of 15 min for both electrodes. In this interval of t_d the correlation coefficient with i_p is 0.9999. For HMDE the peak current is proportional to the radius (r) of the mercury drop (Table I). The linear relationship was confirmed for values of r, obtained from the weight of mercury between 0.33 and 0.60 mm. A drop radius of 0.56 mm was used throughout this work. The effect of the mercury film thickness l (Batley and Florence, 1975) was studied by varying the mercury acetate concentration in solution used for the electrolysis. The increase of film thickness to the range 0.02–0.5 μm produces a slight decrease in peak current and a shift of peak potentials from −0.72 to −0.63 V. In agreement with the equation for linear scan stripping voltammetry (Vydra *et al.*, 1976), the shift is proportional to log l and this may be utilized to obtain an increase in sensitivity. With an appropriate value of l it is possible to obtain the same E_p value of the minimum current of base electrolyte making the reading of i_p easier.

Interferences

Environmental samples are undoubtedly constituted of a mixture of metals, including those that interfere with the determination of thallium. In particular, oxidation potentials of Cd and Pb amalgams are the same as Tl(Hg) using respectively MFE and HMDE. The problem of overlapping peaks can be overcome by addition of

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EDTA that masks both interfering elements at pH > 3.5 (Neeb, 1959). Copper, invariably present at much higher concentrations than thallium in natural waters, is codeposited with thallium at the electrode.

The determination of thallium ($0.5\,\mu g\,l^{-1}$) by MFE may be carried out with no interference if the Cu^{2+} concentration is less than $0.5\,mg\,Cu\,l^{-1}$. The copper concentration in the amalgam, determined from the area of the oxidation peak obtained with the linear sweep ASV in the same buffer-EDTA solution ($n = 2$), is 0.17% w/w, 60 times higher than its solubility (Vydra *et al.*, 1976). Also Bonelli *et al.* (1980) observed that codeposited copper from a solution of $5\,mg\,Cu\,l^{-1}$ could apparently be tolerated on a 10 times volume of mercury film. From the visible alteration of the metallic surface, Bonelli *et al.* (1980) suggest that determinations in the presence of a copper concentration $> 0.5\,mg\,l^{-1}$ may be suspect. On HMDE the minor separation of copper and thallium peak potentials (0.21 V) produces a deformation of the thallium peak when the ratio of weights (Cu/Tl) in solution is 300. Better resolution may be obtained at a lower pH of the supporting electrolyte because E_p of thallium remains constant while that of copper decreases 56 mV for each unit of pH (Pecsok, 1953). At pH < 4 the low conditional stability minimizes the masking effect of EDTA. The direct determination of metals in various real samples may be complicated by the presence of organic compounds which inhibit the metal deposition and/or stripping processes.

As the behaviour of thallium is scarcely affected by surface active agents the presence of these natural compounds in the sample does not produce any interference. Neeb and Kiehnast (1970) added 3.4 dichloro benzil triphenyl phosphonium chloride as an inhibitor in the determination of thallium in the presence of a large amount of bismuth and Triton X 100 for the determination of thallium in the presence of copper, bismuth and antimony. Lukaszewski *et al.* (1980) found that the electrochemical activity of cadmium, which usually interferes in the determination of thallium is inhibited by addition of 0.01% of polyethylene glycol of M.W. 4000.

Differential pulse mode may also give rise to organic absorption-desorption peaks which may obscure the stripping peak of thallium. This positive interference has been commonly observed in the natural samples examined. The presence of these peaks is evidenced also in differential pulse voltammetry without a preliminary deposition step. These tensammetric peaks can lead to high results being reported for metals. The correction of peak current by subtracting the peak current obtained without a pre-electrolysis step is not possible because it does not take into account absorptive accumulation at low concentrations of surface active compounds (Kalvoda, 1982).

A partial decomposition of organic materials, but sufficient to obtain voltammograms free from tensammetric peaks, was carried out with a wet ashing of the sample just to dryness, at 100°C, in the presence of nitric acid. To the beaker containing the residue, a known volume of base electrolyte was added and the solution stirred for 30 min. During this period, silica, possibly present in the sample, and not insolubilized during evaporation at low temperature, is once more dispersed. It is important to avoid the presence of solid silica because of the possible adsorption of components of the solution.

The choice of particular instrumental parameters may increase the peak current, as previously seen, but normal conditions are sufficient to determine low concentrations of thallium. So by using the operating condition of Table II it is possible to obtain a detection limit, using the arbitrary definition as $2x$ standard deviation of the blank, of 4 ng Tl l^{-1} for HMDE and 2 ng Tl l^{-1} for MFE. If a lower detection limit is desired, deposition time may be increased within reasonable limits. Using the same instrumental parameters the standard deviation for 10 determinations of a

TABLE II
Operating conditions for hanging mercury drop electrode and mercury film electrode

HMDE	$E_d = -0.9$ V, $E_{DP} = +70$ mV, $v = 5$ mV/s, $r = 0.56$ mm, $t_d = 300$ s, $t_r = 30$ s
MFE	$E_d = -1.0$ V, $E_{DP} = +70$ mV, $v = 10$ mV/s, $l = 0.09$ μm, $t_d = 300$ s, $t_r = 30$ s

E_d – deposition potential, E_{DP} – modulation amplitude, v – potential scan rate, t_d – deposition time, t_r – rest time, l – mercury film thickness, r – mercury drop radius.

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natural water having a mean concentration of $3.17\,\mu g\,Tl\,l^{-1}$ was 2.3%.

APPLICATION TO NATURAL SAMPLES

The recommended method was applied to the determination of thallium in a number of samples collected during 1985 in volcanic areas.

In the island of Vulcano (Aeolian islands, Italy) the area surrounding the harbour (Figure 4) is characterized by a high density of population in summer. Waters from wells within this area, even if not used for drinking supply, are largely exploited for irrigation. Thallium contained in these waters, in addition to that coming from soil weathering, can be accumulated by horticultural plants (Hoffmann *et al.*, 1982) and then introduced into the alimentary cycle. The thallium content of plants seems to be a function of thallium concentration in soils with a very high concentration factor in some cases (Zyka, 1972).

The analytical results obtained by the addition method are reported in Figure 4. As it can be seen, thallium concentrations in the studied samples are 100 times higher than the mean content of natural waters. The geochemical behaviour of thallium, commonly present in igneous rocks as a substituent of potassium (Shaw, 1952), can account sufficiently for this. In fact, the weathering of rocks produces an enrichment of thallium in solution. A sample of volcanic ash, collected at "Sciara del Fuoco." (Stromboli) during the eruption of December 1985, released $0.5\,\mu g\,Tl\,g^{-1}$ solid after a simple washing with fresh water.

A similar origin can be hypothesized for the thallium content of phreatic waters from Vulcano Porto, where the highest concentrations are observed in the central zone where the composition is due to the alteration of the rocks by superficial waters as reported by Martini (1980). For the volatility of its compounds high thallium contents are observed in the condensates of Vulcano fumaroles at the crater (Table III).

Samples from Phlegrean Fields also display rather high concentrations with a maximum at "Stufe di Nerone." This can probably be accounted for by the extensive reaction between hot

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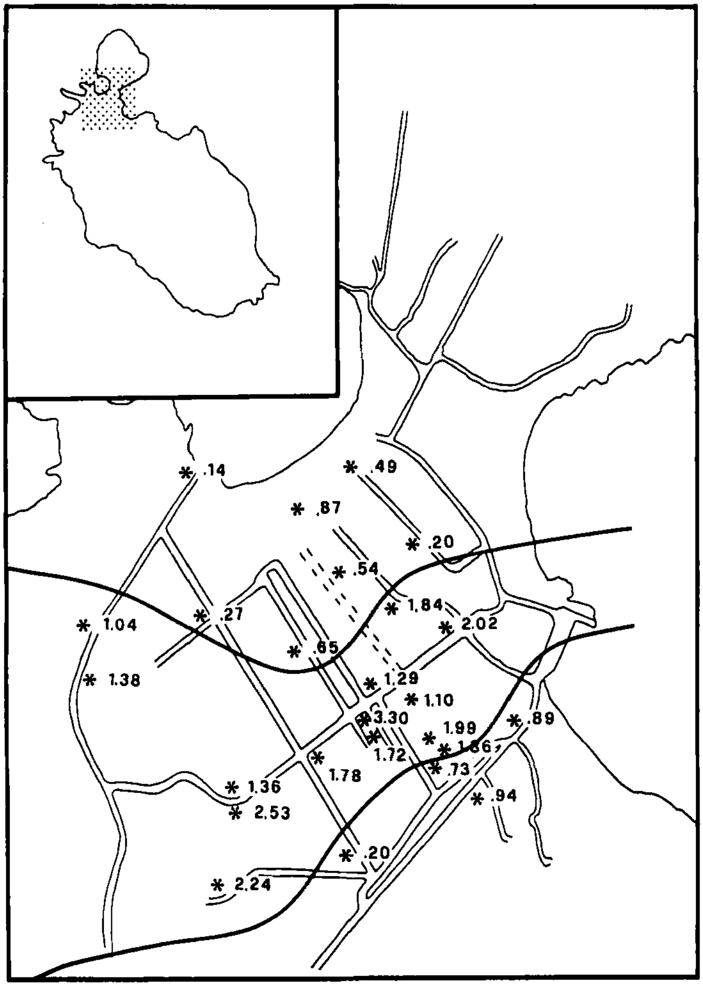

FIGURE 4 Map of Vulcano Porto (Aeolian Islands, Italy) showing sites of sampling and the relative thallium concentrations (μg Tl l^{-1})

TABLE III
Measurement of thallium concentration in waters and volcanic gas condensates. Temperatures measured in ambient water or at the mouth of the fumarole

	concentr. $\mu g\, l^{-1}$	t °C	collect. date (day/month) 1985
Waters			
Phlegrean Fields (Naples, Italy)			
Lake Lucrino	0.55	19	23/4
Spring "Stufe di Nerone"	13.80	73	24/4
Well "Terme Puteolane"	2.16	51	24/4
Hot pool Pisciarelli	5.80	86	23/4
Pool Solfatara	5.70	25	04/12/84
Well Capuano	0.30	38	23/4
Others			
Hot Creek (Calif.)	1.50	75	09/7
Casa Diablo (Calif.)	2.0	93	10/7
Noboribetsu (Jap.)	0.30	92	27/6
Volcanic gas condensates			
Vulcano (Italy) F5	5.70	306	26/4
Vulcano (Italy) F14	0.80	199	26/4
Usu (Japan)	0.43	704	28/6
Nevado del Ruiz (Colombia)	17.3	85	19/10*

* eruption day: 13/11/85

waters circulating at depth and the surrounding rocks. The lower values observed for Japanese areas can be explained by the lower potassium concentration in the rocks of that country.

CONCLUSIONS

Thallium is significantly enhanced in concentration in waters draining areas of recent and active volcanism, as has been shown for mercury (Cellini-Legittimo *et al.*, 1986). Chronic thallium poisoning is not easily diagnosed and risk of exposure has not been carefully assessed. Identification of thallium-rich areas and of levels of thallium in drinking water or diet are useful in considering risk of exposure.

Although thallium is a minor element it can be considered as a significant ecological factor especially in volcanic areas.

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