Iodine in the Environment of the High Atlas Mountain area of Morocco

DfID KAR Project R7411

Commissioned Report CR/02/196N

BRITISH GEOLOGICAL SURVEY

COMMISSIONED REPORT CR/02/196N

Iodine in the Environment of the High Atlas Mountain area of Morocco

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	Nursing dispenser:	Abdelkarim Elmaghrani
Agadir	Majoral Office of Agadir Commune Drarga Chief:	Badouj Lahgen Ben Mohamed

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Contents

FIGURES

PHOTOGRAPHS

TABLES

Summary

The Ounein Valley in the Atlas Mountains of Morocco has been studied as part of an investigation into the environmental controls in iodine deficiency disorders (IDD). The area was identified from earlier sociological studies that highlighted the area's serious problems with iodine deficiency disorders. In the 1990's it was an area where the under-five mortality rate exceeded 25% and dietary deficiency of iodine reached more than 90% in some villages. Soil, drinking water, and locally grown crop samples have been collected to determine the iodine status of the environment. These results are compared with a control area near Agadir where there is low prevalence of IDD.

In the coastal Agadir area average iodine levels in surface soils are 2.76 µg/g I compared to 1.47 µg/g I in soils from the Ounein Valley some 150 km inland. The water-soluble component of the soil, considered as the mobile bioavailable fraction, is higher in the Agadir area than the Ounein Valley with average values of 0.12 and 0.04 µg/g I respectively. There is three times more "available iodine" in the soils of the Agadir area than in soils of the high IDD prevalence Ounein Valley. Iodine in soils decreases away from the seacoast although both low and high iodine soils are found in the coastal zone. Although the iodine levels in the soils from Ounein Valley are lower in iodine, they are not significantly different from soils from other parts of the world.

The difference in iodine status of the environment is best indicated by iodine in drinking water - 17.8 and 1.6 µg/l for Agadir and Ounein respectively, i.e. a tenfold difference. The correlation between low iodine drinking waters and IDD prevalence is seen in many parts of the world and a < 3 µg/l I threshold is suggested as an indicator for an iodine deficient environment. Interpretation of crop iodine results is limited by the fact that it was not possible to compare like with like. Wheat and barley grains were sampled in the Agadir area whilst vegetables were collected from the Ounein Valley. Beans (mean 9 µg/kg) growing in the same field as carrots (mean 25 µg/kg) were consistently found to contain less iodine than the carrots which still only contained 0.75 - 3.58% of the total soil iodine. The levels of iodine in barley grains ranges from < 10 - 25 µg/kg and the sample of wheat contains 40 µg/kg I (all results for dry matter).

Salt samples bought in the local market were also determined for iodine and contents were considerably less than that advertised. However, even with lower contents, iodised salt contributed substantially more iodine to the diet than uniodised salt. If locals were totally dependent on their local environment for providing iodine, then the diet would be substantially lacking in iodine, a situation that would probably been seen in most non-coastal districts of the world. However, poor development with lack of access to external food sources has greatly increased the risks of IDD to which the local population will be exposed. Improved road access and development in the region in the past five years has clearly reduced the risks. Because most of the Ounein Valley is dependent on irrigation to grow crops, the addition of iodine to irrigation waters could potentially help improve the environmental iodine status. However, the poor sandy soils of the area with little organic matter reduces the soil's ability to fix iodine, whether it be natural iodine deposited from the atmosphere or iodine added to irrigation waters.

1 Introduction

The British Geological Survey (BGS) is looking at environmental controls on the distribution and incidence of iodine deficiency disorders (IDD). This work is carried out under the sponsorship of the UK Department for International Development (DfID) as part of a Knowledge and Research (KaR) Project entitled "Environmental Controls in IDD".

> ***The nomenclature for iodine is sanctioned more by general use than chemical logic. The term "iodine" usually refers to the chemical element in a general sense without specifying its chemical form but it is also used to denote the form I_2. Occasionally salt or another vehicle is described as "iodated" when potassium iodate (KIO_3) is added, or as "iodinated" when iodine (I_2) is added to a vehicle such as water. Recently the World Health Organisation (WHO), the International Council for Control of Iodine Deficiency Disorders (ICCIDD) and UNICEF have recommended that the term "Iodized" (also spelled "iodised") be used when iodine is added in any form.***
>
> ***after Venkatesh Manner and Dunn (1995)***
>
> **BOX 1**

The investigation described here covers the geochemical studies carried out in the Atlas Mountains of Morocco (see Figure 1) in collaboration with geologists from Direction de la Géologie, Rabat. The studies took place in March 2002 the schedule being described in a visit report by Strutt (2002). The investigation was originally planned for the end of September 2001 but disruption to air travel following the 11th September incidents in the USA led to postponement of the work. Dr Stewart carried out tests to investigate the iodine status of the local population in the case study area at the same time as the geochemical sampling and this medical work is reported separately in Stewart (2002).

This account seeks to:

- outline the objectives of the case study
- report the methods used
- present the results of the case study

This report will be used along with other case studies and literature reviews to formulate a strategy for the management of environmental iodine to help reduce the worldwide incidence of IDD. The geochemistry of iodine and the causes and description of IDD will be given in later reports and will not be discussed further here.

> ***"…the under-five mortality rate was 262 per thousand live births in 1991. Because of the dire poverty, high rates of protein-energy malnutrition, poor sanitary conditions and health care, children suffering the most sever micronutrient deficiencies rarely survive to school age in this particular setting."***
>
> ***Oldham et al, (1998)***
>
> **BOX 2**

1.1 OBJECTIVES

A literature search on iodine deficiency disorders in Morocco (project bibliography - Johnson 2003a) revealed a number of references (e.g. Aquaron et al (1993) and Oldham et al (1998)) that describe areas in the High Atlas Mountains where there is a high prevalence of iodine deficiency disorders. The BGS recently completed a programme of regional geochemical mapping in these regions and has an established working relationship with geologists from the Direction de La Géologie in Rabat. The Atlas Mountains was therefore a suitable choice for a case study area to investigate the distribution of iodine in high IDD areas.

The work of Oldham et al. (1998) on "An analysis of iodine deficiency disorder and eradication strategies in the High Atlas Mountains of Morocco" was carried out by sociologists and nutritionists and identified an area called the Ounein Valley for study. This current geochemical investigation can therefore add an additional perspective to the work already done by sociologists and nutritionists.

The plan to work in Morocco was first discussed at a meeting between Dr Johnson and Dr Sabah Benjelloun in Rabat on 2nd March 2000 (Johnson, 2000) and a meeting with Dr Amina Saad (Ministère de la Santé) on 17th May 2001 (Johnson, 2001a). Dr Benjelloun had worked in an area of the Atlas Mountains where there was a high risk of iodine deficiency and was a co-author of the earlier study in the Ounein Valley. The Ounein Valley is a very poor and remote rural area where extraordinary high rates of IDD are recorded (see Box 2).

Objectives for the case study were:

1. To determine the iodine status of the environment in a high prevalence IDD area (Ounein Valley, Atlas Mts)
2. To determine the iodine status of the environment in a control area with no IDD in the Atlas Mts near Agadir)
3. Whilst travelling from the Ounein Valley to Agadir on the west coast collect soil samples so that the relationship between soil iodine content and distance from sea could be determined.

1.2 AREAS OF INVESTIGATION

Two areas were investigated, the first was the area of high prevalence IDD in the Ounein Valley and the second area was an area of low incidence IDD near Agadir (see Figure 1).

The Ounein Valley is a large topographic depression in the Atlas Mountains some 35 km to the southwest of Morocco's and Northern Africa's highest mountain peak, Jbel Toubkal (4165m) and is some 150 km from the Atlantic coast. The valley itself is at topographic heights approaching 1500 m and is accessed by dirt track roads either from the Tazenakht - Agadir main road in the south or from the Tizi-n-Test mountain road at Ijoukak in the north. These dirt tracks become difficult in winter during times of rain and snow and contribute to the areas isolation.

The Ounein Valley is located at the northern boundary of the Anti-Atlas range and is subdivided into three main structural zones (a) the central basin of the Ounein Valley; (b) The Ourg zone; and (c) the Wijdane zone (Shalaby and Stüwe, 2001). The two latter zones are high areas of Pre-Mesozoic basement lithologies bordering the Ounein Valley. The valley itself is characterised by Cretaceous sandstones uncomformably overlying Cambrian schists.

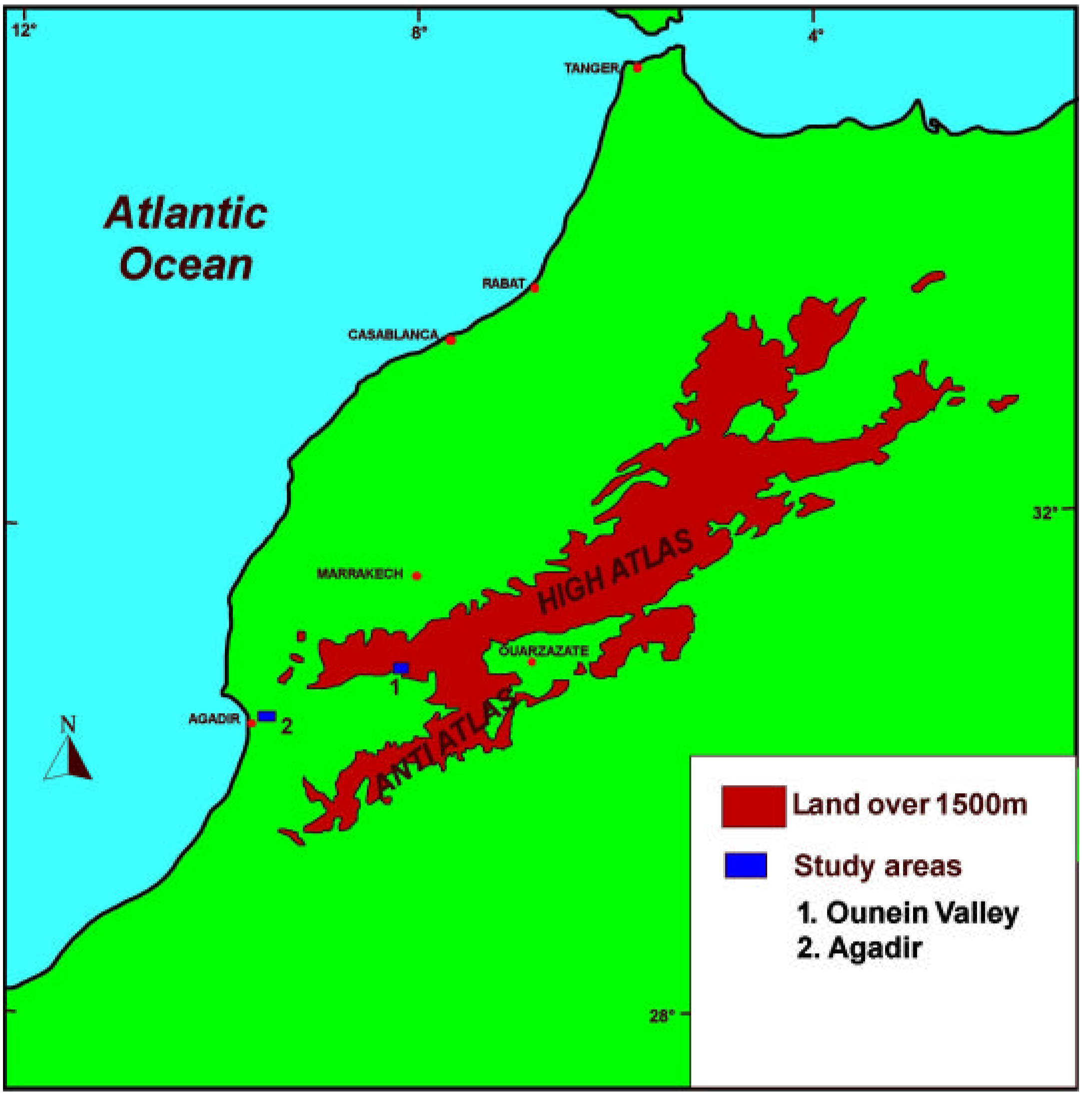

Figure 1: Map of part of Morocco showing location of study areas

> ***"….the valley of Ounein, an isolated region in the High Atlas Mountains in Morocco where geography— distance from sea and soil erosion in a mountainous region — fosters iodine deficiency in the form of goiter and limits access of the population to treatment and to education or information concerning the causes and prevention of IDD. A multidisciplinary rural development project in the region began focusing on iodine deficiency after preliminary studies reported that the dietary deficiency of iodine reaches 91.4% in some villages, touching more than 50% of households..."***
>
> ***Oldham et al, (1998)***
>
> **BOX 3**

The project approached the area from the south, a guide being essential as there are numerous track junctions and few signs. The journey to Adouz (40 km) in a four-wheel drive vehicle took two hours from Oued Lemdad on the Takenakht to Agadir road. Adouz is a central meeting place for the numerous small villages scattered along the Ounein Valley. The area is recognised as one of the poorest in Morocco but will see large scale development in the near future if plans for a major new dam and reservoir come to fruition. The wettest months of the year are November to March with snow falling on the higher ground.

Rainfall is rare in the summer months and the climate can be described as semi-arid. Any arable farming is usually dependant on some form of irrigation system.

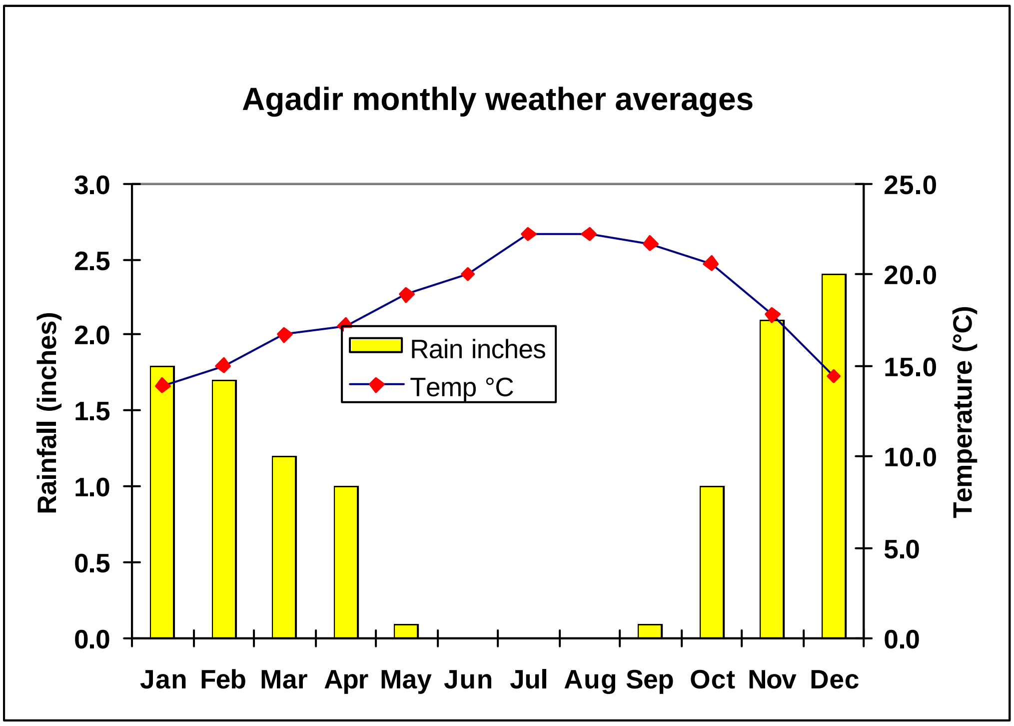

Figure 2: Monthly temperature and rainfall averages for Agadir

(data source http://www.weather.com/weather/climatology)

The Igounane area studied near Agadir lies on the west end of the Atlas Mountain chain near the Atlantic coast and is more accessible by road with heights between 400 - 700 m. Climatic data for nearby Agadir is given in Figure 2 with the wind direction being predominantly south-westerly from the Atlantic Ocean. In Morocco rainfall diminishes progressively from the north to the south and from the west to the east. Agadir is an important seaport and the administrative centre for the region with a population of 0.6 - 0.8 million. It was the epicentre for the infamous earthquake of 1960 that killed 15,000 people.

2 Geochemical Investigations

2.1 SAMPLING METHODS

2.1.1 Sampling Strategy

The main objective was to collect geochemical samples from the two study areas in order to determine the iodine status of the local environment. This was achieved by the collection of surface soil, water and crop samples from both areas. Soils were collected from the fields in which crops were grown. A secondary objective was to collect samples along a line away from the seacoast so that the content of iodine in soils in relation to distance from the sea could be studied. The number of samples collected was primarily controlled by the amount of time available for sampling. The aim was to collect 3 - 5 surface soil and crop samples from around selected villages plus a sample of the village's main water supply.

2.1.2 Soil Sampling and Preparation

Soil samples were collected from cultivated land in and around the targeted villages. Normally the soils from this area are very dry, however, due to recent heavy rain soils were generally moist when collected.

(a) All sampling equipment (stainless steel trowel and plastic sheet) was cleaned before use.

(b) Using the trowel, four holes were made at the corners of a 20 m square and the fifth hole in the centre of the square. The top c.1 cm organic rich layer was discarded and the samples collected from approximately 2 – 15 cm depth. The five sub-samples were placed on a plastic sheet.

(c) Any large rootlets and stones were hand picked from the sample and discarded.

(d) The accumulated sample was homogenised on the plastic sheet.

(e) The sample was placed in a grey securitainer (49 x 75 mm) and black waterproof marker pen was used to write the number carefully on the top, side and bottom of the securitainers (to avoid the number being rubbed off during transport). Sample containers were also coded with the letter S to indicate they contained a soil sample. The grey securitainer samples were transported back to the UK for sample preparation in by BGS.

(f) Sample field cards were completed at each site noting site characteristics (see Appendix A). Longitude and latitude were recorded at each site using a Garmin 12 GPS.

(g) Duplicate soil samples were collected in the same way, from five different holes in the same field as the original sample.

(h) On return to the BGS laboratory samples were again homogenised and coned and quartered. One quarter of the sample was returned to the original contained and stored for future reference.

(i) Duplicate samples were split to give analytical sub-samples to be used for monitoring analytical precision and accuracy.

(j) The soils were dried in an oven at less than 30º C then disaggregated.

(k) A 10 g split of the sample was set aside for soil pH determination and 5 g for soil colour determination.

(l) The remaining sample was sieved to - 2 mm. From this fraction 2 g was taken for loss-on-ignition determination (LOI).

(m) The -2mm fraction was pulverised in an agate ball mill to -150µm.

(n) 10 g of each pulverised sampled was submitted to the BGS analytical laboratories for iodine determinations.

(o) Excess pulverised material is stored for future reference.

Photograph 1: Collecting a soil sample from a wheat field near Agadir (photograph by A Stewart)

2.1.3 Water Sampling

Drinking and water irrigation samples were collected from a number of sources including wells, irrigation channels, water taps and sources included stored rainwater. The source of the water sample is described in the field information in Appendix A.

(a) At each site, the following suite of water samples were collected:

- One 30 ml filtered water sample collected in trace element free polyethylene Nalgene® bottles for iodine analysis labelled I.
- One 30 ml filtered acidified water sample collected in a polystyrene Steralin® vial for major cation analysis labelled F/A.
- One 30 ml filtered unacidifed water sample collected in a polystyrene Steralin® vial for major anion analysis labelled F/UA.
- One 30 ml unfiltered water sample collected in a polystyrene Steralin® vial for pH and Eh determinations.
- One 250 ml unfiltered water sample collected in a polyethylene bottle for bicarbonate and conductivity determinations.

(b) A waterproof black marker pen was used to write the sample number clearly on the tops and sides of the bottles. Sellotape was used to cover the numbers to stop them rubbing off.

(c) Each filtered water sample was collected using a 25 ml plastic syringe and a disposable Milliepore® 0.45µm filter. A new filter cartridge was used for each site to avoid any possible cross-contamination between sites.

(d) At each site the filtered water samples were collected first avoiding disturbance to water in the container used in each household.

Photograph 2: Collecting a water sample from a well in the Ounein Valley (photograph by A Stewart)

(e) Water was drawn into the syringe which was rinsed out twice. The syringe was filled with water again and connected to the filter cartridge which was also rinsed out twice. The syringe was refilled and the sample bottle was rinsed out twice with filtered water prior to being filled. The 30 ml Nalgene® bottles were filled to the shoulder.

(f) For unfiltered water samples, both the 30 ml Steralin® vial and the 250 ml polyethylene bottle for pH, Eh and conductivity determinations were rinsed out twice in the water. Where possible, the vial and the bottle were both submerged underwater whilst the caps were secured making sure that no air was trapped in the sample container. This minimises the degassing of HCO_3 in the samples.

(g) Care was taken to keep all bottles and filters clean.

(h) Duplicate samples were collected in the same way from the same water source as the original samples.

(i) 30 ml samples collected for major cation analysis were acidified within 4 hours of the end of fieldwork each day by the addition of 0.3 ml (8 drops) ARISTAR grade nitric acid. Addition of 1% vol/vol acid reduces the pH of the samples to approximately 1.0, thus preventing adsorption of dissolved metals to the interior walls of the storage bottle and minimising post-sampling microbial activity.

(j) One NaOH pellet was added to each of the samples collected for iodine analysis to maintain alkaline pH ensuring any iodine present remained in solution

(k) Care was taken to avoid introducing contamination through the plastic dropping pipettes, each of which were stored in a plastic self-seal bag and did not come into contact with bench surfaces.

(l) Eh and pH measurements, bicarbonate and conductivity determinations were also carried out at the end of each day's sampling. Procedures are detailed in Appendix B. Following the measurements, these samples were discarded and the sampling containers reused.

(m) Three field-blank iodine, filtered acidified, and filtered unacidified samples were made up near the start and end of fieldwork. Bottles were rinsed twice with filtered deionised water, filled to the shoulder with the water and acidified/ treated in the same way as the samples. The field-blanks were numbered in the same way as the samples according to the random list.

(n) At all stages great care was taken to ensure that sample bottle tops were securely tightened. All water samples were returned to the BGS laboratories in the UK for analysis.

2.1.4 Vegetable and grain sampling and preparation

The type of crop collected depended on what was growing in the villages at the time of sampling. Crops were collected from the same fields as the soil samples. Potato, bean, carrot, barley and wheat samples were collected (see Appendix A).

(a) Samples were washed with deionised water

(b) Samples were air dried

(c) A coffee blender was used to powder each crop sample.

Photograph 3: Wheat fields in the area around Agadir (left) and the more arid region of the Ounein Valley (right) where only the irrigated valleys support small scale cultivation of vegetables

2.2 ANALYTICAL METHODS

The analytical methods described below were carried out in the BGS laboratories unless specified otherwise.

2.2.1 Field Methods

Water pH, temperature, Eh, total alkalinity and conductivity were determined on the samples during the evening after their collection. These methods are detailed in Appendix B.

2.2.2 Soil Analyses

COLOUR

Soil colour was determined using Munsell® Soil Colour Charts on the dry pulverised powders. A Munsell colour code was determined for each sample and soils were grouped into general colour ranges based on the Munsell soil colour name diagram.

PH

Soil pH was determined on 10g of the unprepared soil sample to which 10ml of 0.01M $CaCl_2$ solution had been added. The pH of the soil paste was measured with a standard Orion® pH meter. This method of soil pH determination generally gives lower results (0.5 pH units) than water based methods (Rowell, 1994).

LOSS-ON-IGNITION (LOI)

Accurately weighed sample powders dried at 35°C ± 5°C were placed in a furnace at 105°C and heated to 450°C for a minimum of 4 hours. The percentage weight loss after ignition at 450°C can be used as an indication of the amount of organic matter present.

TOTAL IODINE AND WATER SOLUBLE IODINE

The iodine was determined by ICP-MS (Reference BGS Analysis reports 10285/1 (crops); 10300/1 (salts); 10284/1 (total iodine in soils); 10284/2(water soluble iodine in soils); and 10280/1 (waters)). The iodine methodology is described in detail in Appendix C. For total iodine the determination by ICP-MS follows an extraction using TMAH on 0.1g of sample. The water soluble iodine was determined on a selected number of samples by shaking 2.5 g of the soil for 15 minutes with deionised water.

To investigate iodine solubility from soils, 25 ml of deionised water was added to 2.5 g of soil and shaken for 15 minutes. The samples were immediately centrifuged at 2,500 rpm for 10 minutes.

An aliquot of the soluble fraction (20 ml) was transferred to a 30 ml nalgene bottle, to which 0.8 ml of 25% TMAH was added to give a final solution in 1% TMAH for storage.

2.2.3 Water and crop analyses

IODINE

The iodine in water and crop samples was determined by ICP-MS (see Appendix C).

2.3 DATA QUALITY CONTROL

In any scientific study it is important to document the reliability of the sampling and analytical methods to prove that the study is robust. During the present study, data quality was assured by the collection of field duplicate samples and the inclusion of blank water samples, analytical replicates and international reference materials in the analytical runs. For example, 20% of the soil samples analysed were control samples used to measure the precision and accuracy of the results. Control data is presented in the following results section.

3 Results

All results received from the laboratory are listed as the raw data in Appendix D. Summaries of these results are presented in the following sections with some statistical analysis.

3.1 CONTROL SAMPLES

Where available, international standard reference materials were included with all batch determinations and these are reported in the laboratory reports in Appendix D. Given the uncertainties associated with iodine standards, the reported recoveries of between >70 - 108% are considered to be acceptable.

For the soil samples a high proportion of duplicate and replicate samples were submitted for analysis. Duplicates are two soil samples collected from one site and a replicate is a laboratory split of the original sample. The results given in Table 1 show excellent agreement for the LOI and iodine but the pH analyses indicate a problem in the laboratory. This is well illustrated by analysis of the data using the nested ANOVA analysis method in EXCEL as described by Johnson (2002). The results of this analysis are shown in Table 2. These show that for the iodine and LOI the variation occurs between sampling sites and not within them or because of the analytical method. However, with pH several of the replicate pairs produce distinctly different answers giving a large variability generated by the analytical method. This arises from the method used to produce the replicates, i.e. the inhomogeneous soil is sub-divided in the laboratory. As pH is determined on the original unprepared soil samples it is not possible to produce two identical sub-samples so such variability is to be expected. Results for normal samples are likely to be valid, although because of the variability caused by inhomogeneity of the soils pH results should be used with caution.

SiteNo	Control	pH	%LOI	I (µg/g)
69	DUPA	7.52	6.93	1.86
12	REPA	7.63	7.02	1.87
90	DUPB	7.50	7.18	1.83
86	REPB	7.51	7.39	1.83
39	DUPA	7.70	3.50	1.16
11	REPA	7.68	3.30	1.18
19	DUPB	6.50	3.79	1.35
87	REPB	7.58	3.59	1.29
21	DUPA	7.08	3.45	2.40
2	REPA	7.64	3.30	2.48
95	DUPB	7.43	3.43	2.36
92	REPB	7.50	3.33	2.33
74	DUPA	7.42	4.21	4.08
14	REPA	7.68	4.00	4.39
97	DUPB	7.50	4.18	3.98
81	REPB	7.54	4.06	4.25

Table 1: List of control sample results

Element	Between Site %	Between Sample %	Within Sample %	Total %
pH	-22.57	6.84	115.73	100
%LOI	98.74	0.54	0.72	100
Iodine	99.00	0.67	0.33	100

Table 2: Nested ANOVA results for control samples

3.2 SOILS

3.2.1 Total Iodine

Total iodine in the soils ranges from 0.32 - 7.14 µg/g with an arithmetic mean of 2.05 µg/g (Table **3**). The Agadir area has soils with generally higher iodine levels than the soils of the Ounein Valley (Figure 3). The range of soil iodine results is also greatest in the Agadir region. The highest result is sample MRS71, a soil from Ait Ahmed some 10 km from the Atlantic coast. The distribution of results is shown as a classified symbol map (Figure 4) and as a plot of iodine in soil against distance from sea coast. (Figure 5). These show that iodine generally decreases away from the coast but there is great variability. The sample collected just up from the beach in Agadir (i.e. within 200 m of the sea) is not particularly enriched in iodine with only 0.59 µg/g I whilst the most distal samples from the coast at Takoucht (Ounein Valley, samples MRS32 and MRS46) contain more than 2 ug/g I. If the data is smoothed by classifying it into kilometre intervals from the coast, then a general trend of iodine depletion is seen from Agadir to inland (Figure 6) though much of the drop-off is in the first 20 km.

	pH	*LOI*	*Iodine*
		%	(µg/g)
Mean	7.57	4.09	2.05
Median	7.56	3.75	1.80
Std Dev.	0.192	1.624	1.377
Range	1.10	7.14	6.82
Minimum	6.99	0.66	0.32
Maximum	8.09	7.80	7.14
Count	64	64	64

Table 3: Summary statistics for pH, LOI, and total iodine determined on all soil samples

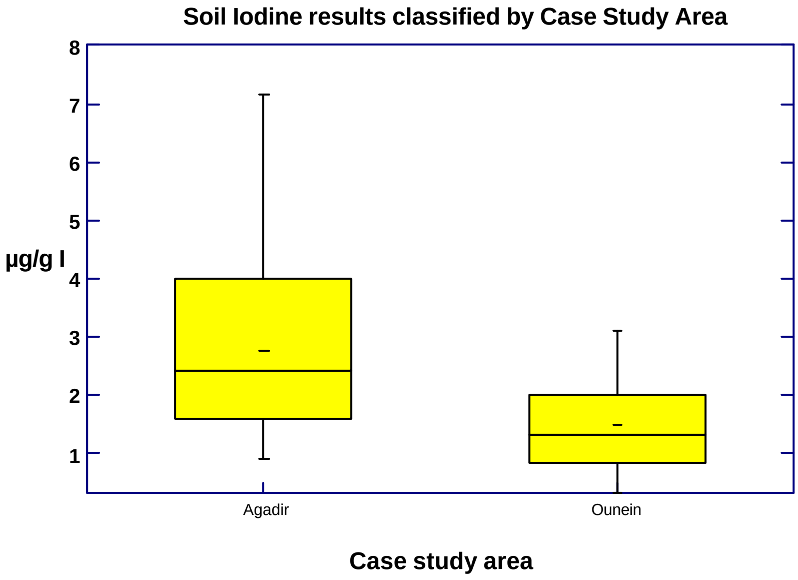

Figure 3: Box and whisker plot for total iodine in soils classified by case study area

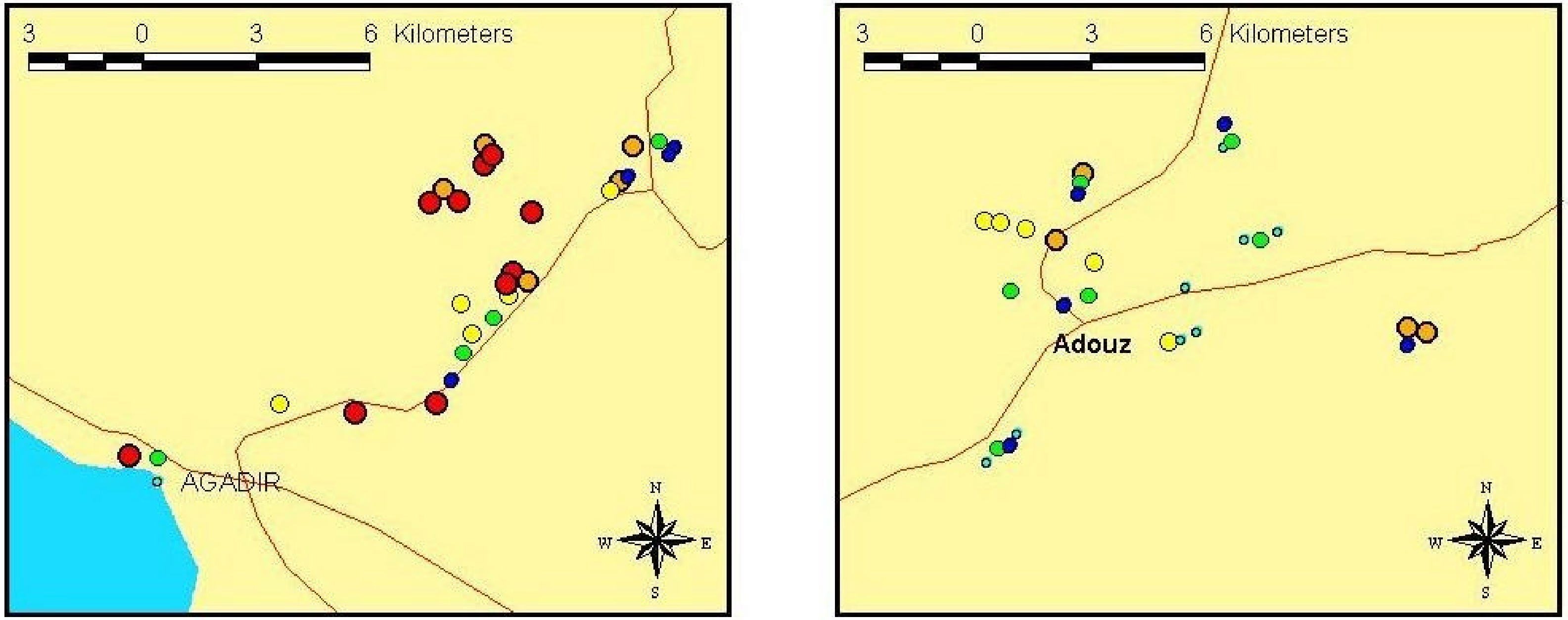

Figure 4: Map showing the disribution of total Iodine in soils from the Agadir area (left) and Ounein Valley (right)

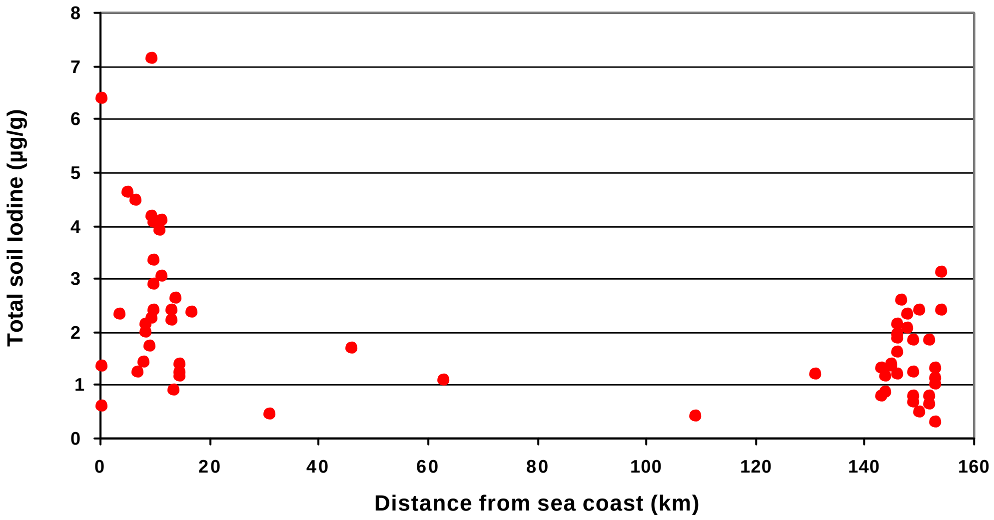

Figure 5: A plot of total soil iodine against distance from the sea coast (at Agadir)

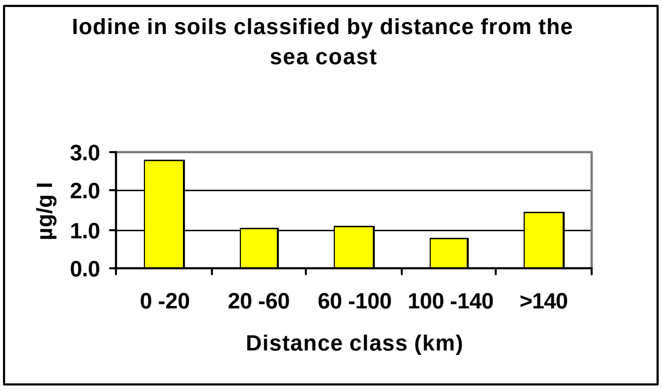

Figure 6: Total soil iodine classified by distance from the sea coast (at Agadir)

If the data is classified into the two areas studied, i.e. the low/no incidence IDD area around Agadir and the high incidence IDD area of the Ounein Valley, then it can be seen that the latter area has lower levels of total iodine in the soils (Figure 3). The average value for the Agadir area (24 soils) is 2.76 µg/g I whereas that for the 28 soils from Ounein Valley is 1.47 µg/g I. These are generally the same as in Sri Lankan soils reported by Fordyce et al. (1998) but higher than values reported by Fordyce et al (2003) for China (see Table 4).

	CHINA[1]			**SRI LANKA[2]**			**MOROCCO**	
Location	Commune 148	Kuqa	Wushi	Anurad-hapura*	Kandy	Kalutara	Agadir*	Ounein Valley
Number of soils	25	25	25	25	30	20	24	28
minimum	0.3	0.3	0.3	0.13	0.13	1.0	0.88	0.32
maximum	3.90	2.93	1.73	10.0	4.6	9.6	7.14	3.12
average	1.11	1.16	0.89	3.19	2.20	4.38	2.76	1.47
geometric mean	0.91	1.06	0.80	2.26	1.77	3.91	2.43	1.29

Table 4: Total iodine in soils from this study and other BGS investigations. All locations (except those marked with *) have historical or present IDD incidence. All results in µg/g. [1]Fordyce et al (2003) and [2]Fordyce et al (1998).

3.2.2 Cold water-soluble iodine

Twenty four soil samples were selected for determination of cold water-soluble iodine ($I_{(sol)}$) selected on the basis of a full range of total iodine ($I_{(tot)}$) and LOI results. These results are given in Table 5 along with the results for total iodine and other soil parameters. The percentage of the total iodine in the soil that is cold water soluble is between 2 - 10% although the "beach sand" (MRS89) collected 200 m from the sea has a high percentage of readily soluble iodine i.e. 35.4% of the $I_{(tot)}$. Sample MRS73, also from close to the sea had the second highest percentage of $I_{(sol)}$ at 9.9%. Although samples very close to the sea obviously are influenced by sea spray, the Agadir samples from further inland (1 - 12 km) are not much different in their percentage of $I_{(sol)}$ to the Ounein Valley samples. However, the amount of $I_{(sol)}$ in coastal areas is much greater than that seen in land (see Figure 7) and falls within a greater range. The geomeans for $I_{(sol)}$ in the Agadir and Ounein Valley are 0.12 and 0.04 µg/g respectively (excluding the result for MRS89). There is three times more mobile iodine ($I_{(sol)}$) available in the Agadir region than in the Ounein Valley. Based on the geomeans for total iodine, the Agadir region has 1.9 times more total iodine than the Ounein Valley.

Sample Number	**Dist. from sea (km)**	**pH**	**% LOI**	**Total I (I_{tot}) (mg/kg)**	**Water sol. I (I_{sol}) (mg/kg)**	**I_{sol} / I_{tot} x 100 %**
MRS04	8.5	7.61	7.80	2.39	0.071	2.96
MRS07	150	7.70	1.59	0.47	0.028	6.05
MRS17	146	7.58	7.03	2.15	0.068	3.14
MRS24	109	7.57	1.51	0.40	0.035	8.79
MRS26	153	7.48	1.55	0.32	0.020	6.17
MRS28	143	7.77	4.88	1.30	0.049	3.76
MRS32	154	7.79	7.28	2.40	0.079	3.27
MRS38	149	8.09	4.81	0.81	0.042	5.15
MRS39	144	7.70	3.50	1.16	0.033	2.87
MRS43	0.5	7.64	6.63	6.38	0.253	3.96
MRS44	5	7.48	4.13	4.63	0.119	2.58
MRS46	154	7.29	6.91	3.12	0.066	2.13
MRS51	10	7.56	5.56	4.06	0.145	3.57
MRS52	9	7.58	4.15	1.74	0.103	5.93
MRS56	153	7.81	7.05	1.33	0.047	3.51
MRS58	14.5	7.59	2.96	1.17	0.088	7.57
MRS60	8.5	7.51	3.74	2.00	0.091	4.54
MRS62	144	7.45	3.51	0.87	0.030	3.49
MRS71	9.5	7.53	4.73	7.14	0.221	3.09
MRS73	0.5	7.91	3.36	1.36	0.135	9.90
MRS74	11.5	7.42	4.21	4.08	0.170	4.16
MRS89	0.2	7.87	0.66	0.59	0.209	35.41
MRS96	7	7.28	2.05	1.23	0.059	4.78
MRS99	149	7.21	3.09	1.23	0.064	5.23

Table 5: A table showing the water soluble iodine results for 24 selected soils

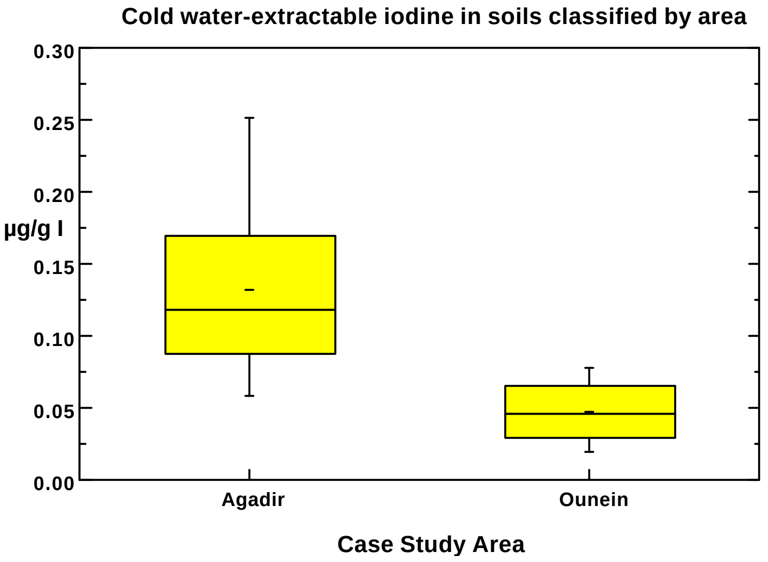

Figure 7: Box and whisker plot of soil cold water-extractable iodine classified by case study area

3.2.3 Loss-on-ignition

Loss-on-ignition (LOI) is an excellent indicator of the total organic carbon (TOC%) of a soil. Johnson et al (1996) determined the relationship - LOI% = 2.8(TOC%) +1.37 - for soils from Zangjiakou, China. Soil organic matter contains on average 58% carbon (Rowell, 1994) so the organic matter content can be calculated from LOI as:

$$\text{LOI\%} = 2.8(\text{Organic matter}/(100/58)) + 1.37$$

LOI results range from 0.66 - 7.80 with a mean value of 4.09% (Table **3**) The majority of soils were from cultivated areas and would generally contain more organic matter than uncultivated soils which, in this semi-arid area, would generally considered to be depleted in organic matter.

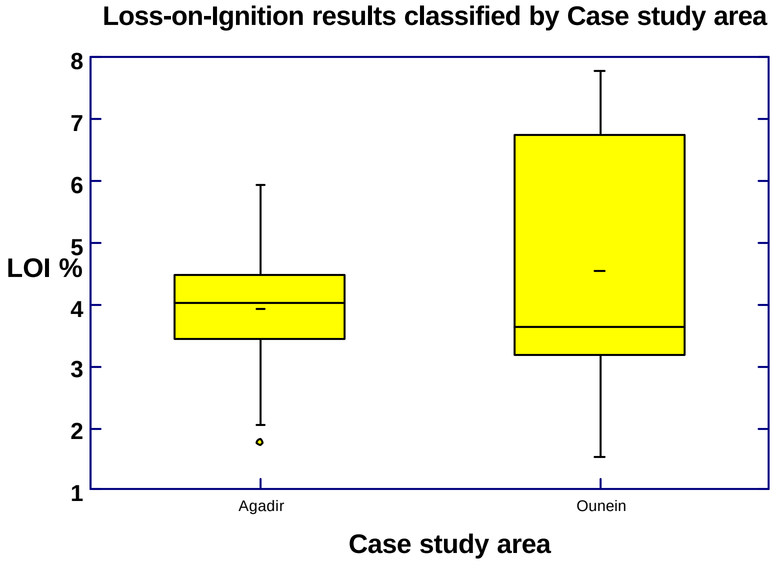

Figure 8: Box and whisker plot of soil loss-on-ignition classified by case study area

Figure 8 shows that the soils from the more mountainous Ounein Valley area have a higher organic content and a greater range of values. The mean values for LOI for Agadir and Ounein are 3.94 and 4.55% respectively.

3.2.4 Soil pH

The soil pH results range from 6.99 - 8.09 with a mean value of 7.54. The soils are therefore generally alkaline in nature. The control samples suggest caution should be used when interpreting the pH results (section 3.1) with the analytical methodology probably giving pH results to ± 0.5.

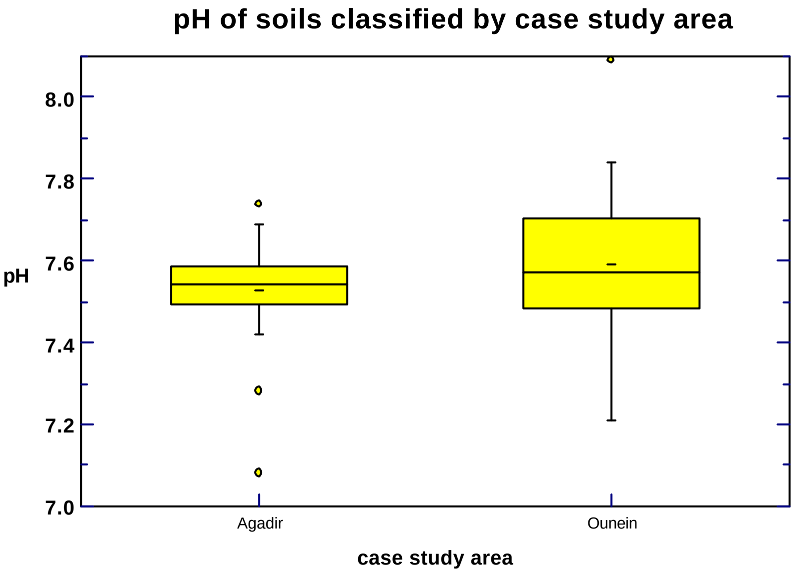

Figure 9: Box and whisker plot of soil pH classified by case study area

Figure 9 shows that there is little difference between the pH results from the Agadir and Ounein Valley areas with mean results of 7.53 and 7.59 respectively, although the Ounein Valley has a greater range.

3.2.5 Correlation of soil results

A Pearson correlation coefficient matrix for the soil results is given in Table 6. This shows that there is significant high correlation between the total iodine content of the soil and the LOI results and an inverse relationship between the iodine content of the soils and the distance from the sea. That is, iodine content decreases with increasing distance from the sea. These correlations would confirm generally accepted ideas that there is a strong relationship between the iodine content of soils and the organic matter content and that iodine in soils is highest nearest the coast. The analysis is based on 64 samples and the I v LOI and I v Dist. correlations are significant at >99% confidence interval.

	pH	*LOI*	*Iodine*	*Distance*
pH	1			
LOI	-0.0128	1		
Iodine	-0.1485	0.4068	1	
Distance	-0.0190	0.2151	-0.4650	1

Table 6: Pearson correlation matrix for soil results

3.3 WATERS

3.3.1 Iodine

The iodine content of the nineteen water samples ranges from 0.5 - 35.2 µg/l with a mean value of 8.4 µg/l. There is a marked contrast between the waters of the Agadir region and the Ounein Valley as shown by the box and whisker plot (Figure 11) and on the classified symbol map (Figure 10). The eight samples from Agadir are an order of magnitude greater than the waters from the Ounein Valley with mean values of 17.8 and 1.6 µg/l respectively (see Table 7).

All water results are listed in Appendix D.

	Iodine (µg/l)			**pH**			**Eh (mV)**			**Conductivity (µS)**			**Alkalinity (mg/l $CaCO_3$)**		
	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3
No.	19	8	11	19	8	11	19	8	11	19	8	11	19	8	11
mean	8.42	17.8	1.6	7.82	7.62	7.96	102	89.9	112	594	669	540	312	362	276
max.	35.2	35.2	2.8	8.64	8.04	8.64	136	103	136	1355	1355	769	1169	1169	413
min.	0.52	3.1	0.52	7.13	7.13	7.28	66.2	66.2	102	158	158	272	106	106	110
std. dev.	10.09	9.42	0.75	0.40	0.268	0.434	16.20	12.42	12.16	353	529	143	233	351	89.9

Table 7: Summary statistics for water iodine results

(1= all data; 2 = Agadir; 3 = Ounein Valley)

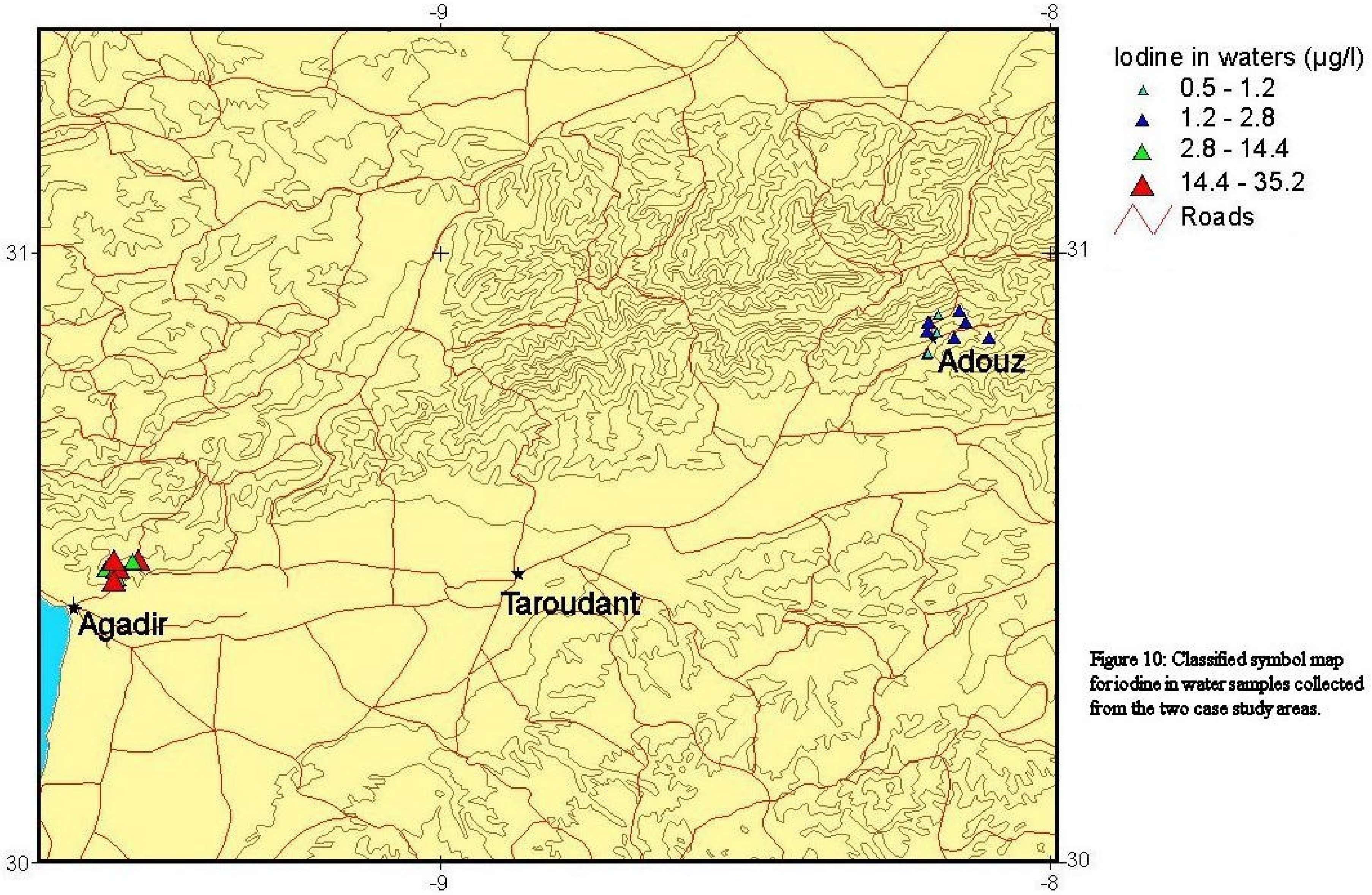

Figure 10: Classified symbol map for iodine in water samples collected from the two case study areas.

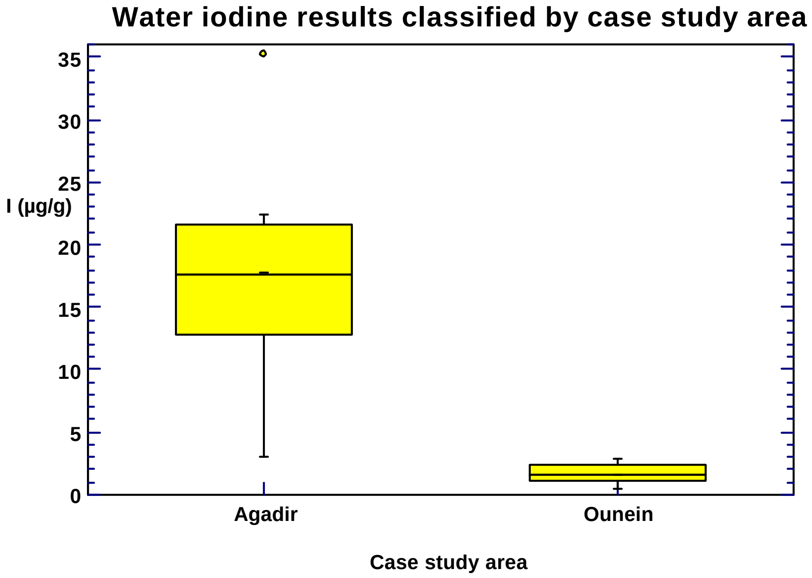

Figure 11 : Box and whisker plot for water iodine results classified by case study area

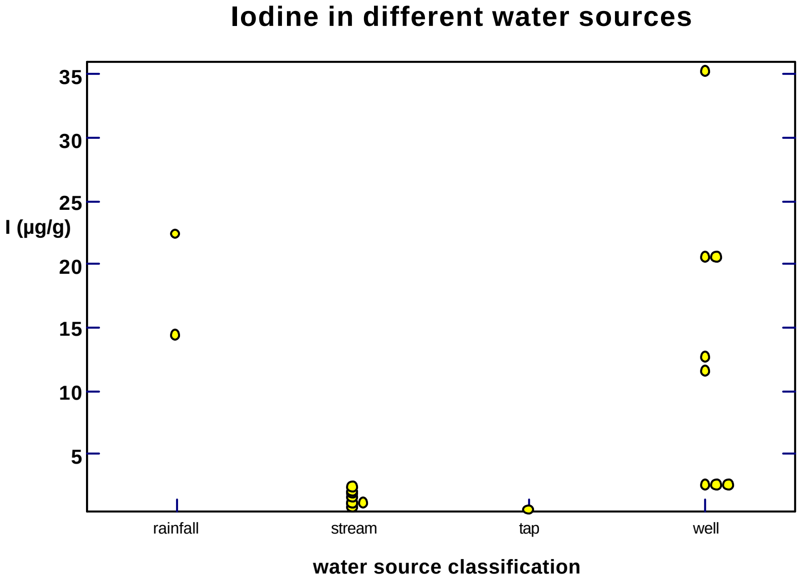

Figure 12: A plot of iodine results for the different water sources

Figure 12 shows the range of results classified by different water sources. All the streams sampled were from the Ounein Valley and generally had their origins as springs or seepages. These streams all have low iodine content with results being less than 2.5 µg/l I. The rainfall samples, or more correctly water collected from rainfall storage tanks, have some of the highest values which is not surprising in view of their proximity to the sea coast. Well waters show a full spread of results, whilst the tap water from Adouz in the Ounein Valley is the lowest result of only 0.52 µg/l. This tap water is pumped from a local well into a storage tank. Note that Aquaron et al (1993) also report low iodine in drinking waters from the endemic areas of Tenghout and Taourirt (0.92 and 1.19 µg/l I, respectively).

3.3.2 Eh, pH, Conductivity and Alkalinity

A summary of results for these parameters is given in Table 7. The data is also summarised graphically, classified by case study area, in *Figure 13.*

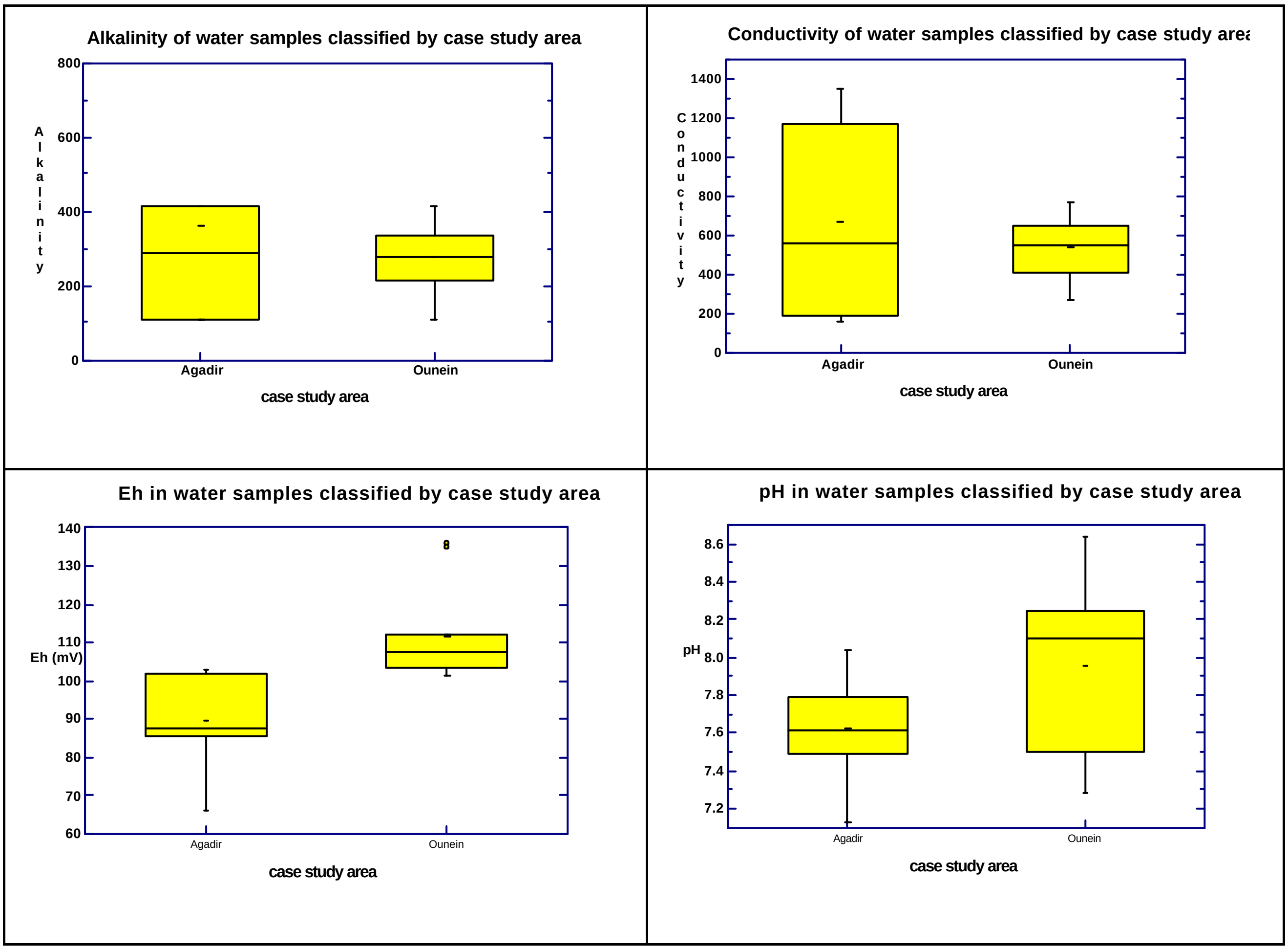

Figure 13: Box and whisker plots for water alkalinity, conductivity, Eh and pH classified by case study area.

(alkalinity units - mg/l $CaCO_3$, conductivity in µS)

There is no significant difference in the alkalinity or conductivity of water samples from Agadir and the Ounein Valley. The Eh of the predominantly stream waters from the Ounein Valley is higher than the samples from Agadir. The water samples from the Ounein Valley (mean pH 7.96) are also more alkaline than the waters from the Agadir region (mean pH of 7.62) and display a greater range of results.

	Eh	pH	Alk.	Cond.	Iodine
Eh	1				
pH	-0.0598	1			
Alkalinity	-0.1675	-0.32039	1		
Cond	-0.2106	-0.25812	0.0761	1	
Iodine	-0.5513	-0.35884	-0.224	0.1258	1

Table 8: Pearson correlation matrix for parameters determined on water samples

The increased Eh in the Ounein samples corresponds to the decreased iodine for the same region giving a good negative correlation between Eh and iodine in the water samples (see Table 8). This correlation is significant at the > 99% confidence interval and shows that iodine decreases with increasing Eh. However, the difference between Eh in the two case study areas is probably due to water source and is insignificant on the Eh scale. The correlation is likely to be more circumstantial than causative.

The relationship between distance from the sea and the water measurements is not considered as water samples were not collected along the soil profile line inland.

3.4 CROPS

Crop samples were collected from many of the soil sample sites and results are listed in Appendix D. In four instances bean and carrot samples were collected from the same site. The results are shown graphically in Figure 14 (classified by crop type) and Figure 15 (classified by case study area).

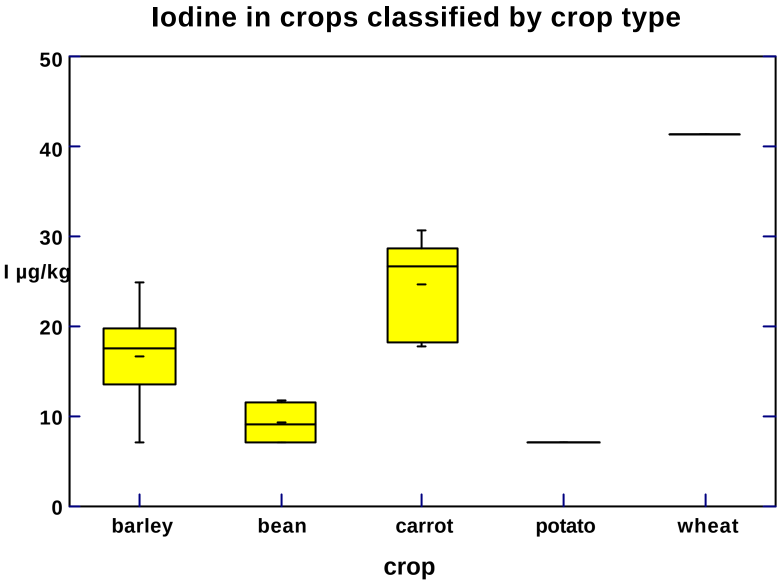

Figure 14: Box and whisker plot for iodine in crop samples classified by crop type

For the grain samples collected (wheat and barley) the results reported here are for the grain seed. The bean samples collected were runner beans and the bean and the pod were collected and determined as a single sample. All results quoted are for dry weight of sample. The barley and wheat samples are from Agadir whilst the beans, carrots and potato are from the Ounein Valley. The highest result is the wheat sample from site MR66 with 40 µg/kg I. The seven carrot samples have a range of 18 - 31 µg/kg I (mean value 25 µg/kg I). This is higher than the mean value for barley of 17 µg/kg I (range < 10[1] - 25 µg/kg I). The four bean samples are relatively low in iodine ranging from < 10 - 12 µg/kg I (mean value 9 µg/kg I). The one potato sample analysed contained < 10 µg/kg I.

The cereal grain results are lower than those reported for corn/barley/wheat by Aquaron et al (1993) (90-227 µg/kg) but similar to that reported by CIEB (1952) (44 µg/kg). The result of 15 µg/kg for wheat from Germany reported by Anke et al (1993) is much lower. The bean and

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[1] The detection limit is quoted as 10 µg/kg. For statistical calculations a value two thirds of this is used.

carrot results reported here are much lower than average values reported by the CIEB (1952) which are 202 and 245 µg/kg resepectively.

Table 9 shows the results from the four sites in the Ounein Valley where beans and carrots were collected from the same field. The carrots are all more enriched in iodine than the beans but all the crops are depleted in iodine relative to soils on which they grow. The carrots contain 0.75 - 3.58 % of the total soil iodine.

Site No.	**Location**	**bean (µg/kg)**	**carrot (µg/kg) (A)**	**soil (µg/kg) (B)**	**A/B x 100 %**
MR4	Taqourdmi	< 10	18	2390	0.75
MR17	Larb'-a-n-Tantarya	11	28	2150	1.30
MR28	Anzi	< 10	18	1300	1.38
MR38	Agardane	12	29	810	3.58

Table 9 : A comparison of total iodine (dry weight of sample) in beans, carrots and soils from the Ounein Valley

It was not possible to collect comparable crops from the two case study areas because of the differing styles of agriculture. The area around Agadir was more intensively farmed with better irrigation than the small holdings of the mountainous area of the Ounein Valley (Photograph 3). Figure 15 shows there is no significant difference between the levels of iodine in the crops from Agadir and Ounein but as this does not compare like with like no conclusions can be made about the relative iodine status of foodstuffs. However, as grains are generally more depleted in iodine than vegetables (see Section 4), the Agadir crops could be said to be relatively enriched in iodine.

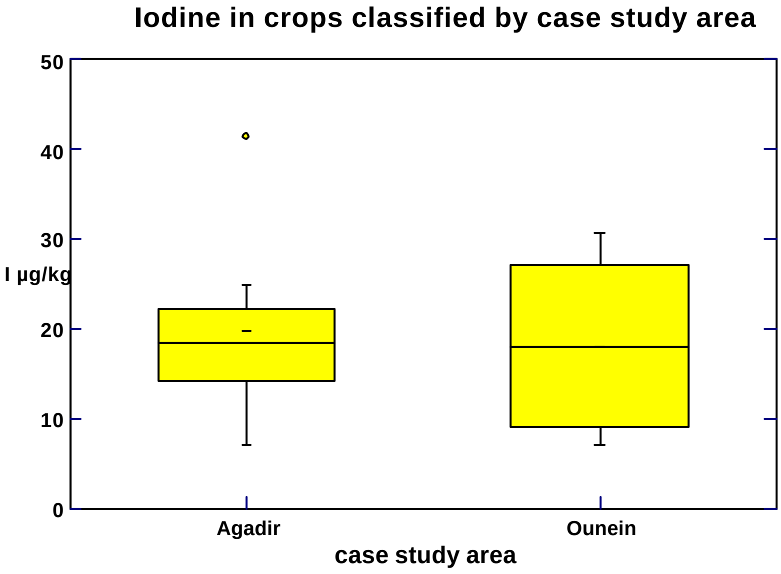


Figure 15: Box and whisker plot of total iodine in crops classified by case study area

3.5 SALT

Three salt samples were purchased from local markets and the results for iodine content are shown in Table 10. The two samples purchased as iodised salt do have higher levels of iodine than the standard table salt. However, the levels of iodine are far less than the manufactures claim indicating a loss of iodine during storage or a manufacturing process that does not produce homogeneous results.

Sample ID	**Description**	**Iodine µg/g**	**Claimed iodine content µg/g**
Salt 1	Purchased at Amalon on 25/3/02; labelled "Milah 'en Alshfa"; 800g;	12.0	80
Salt 2	Purchased at Amalon on 25/3/02; labelled "Sel de Cuisine - luxe"; 800g	0.14	-
Salt 3	Purchased in Taroudant on 16/3/02; labelled "Sel Super Trois / Milah Mzud Balewd"; 500g	3.24	80

Table 10: Total Iodine content of salt samples purchased at local markets

4 Discussion and Conclusions

The catalyst for this study was the report of Oldam et al (1998) which looked at the IDD problem in the Ounein Valley from a sociological perspective. The work of Oldam et al, which was carried out in the spring 1995, indicated an alarmingly high prevalence of IDD and promoted nutritional solutions to reducing IDD (see Box 4).

> ***"An effective strategy to reduce the high incidence of iodine deficiency disorder among children in the valley must attend to four crucial issues: fish consumption, salt iodization, nutrition education and market access."***
>
> ***Oldham et al, (1998)***
>
> **BOX 4**

During our study it is evident that progress has been made with the iodinisation of salt and the provision of fish. Iodised salt and tins of sardines were available from local markets (see Photograph 4). A new hospital has been built in Adouz and this will be staffed by full time medical workers. Improved roads have certainly helped to make the area less isolated than was described by Oldham et al.

The results from the medical investigations show that whilst there are still some historical goitres to be seen **(**Photograph 5) and the mean thyroid sizes 18.4 mls (average age 9.7 yrs; cf. Agadir 10.9 mls, av. age 10.0 yrs) (Stewart, 2003), the risks from IDD in the region are now very much reduced. This is a testimony to the work of the medical community who have successfully helped to bring down the incidence of IDD with a national salt iodinisation programme and better nutrition education for the local population.

Photograph 4: Samples of table salt and sardines purchased at the local market - all good sources of iodine in the diet

However, in this region of Morocco there is resistance to the purchase of iodised salt because it costs more; people generally prefer traditional cheaper sources as was seen in the Chinese case study (Fordyce et al, 2003). Also, the analysis of two iodised salt samples purchased at the market, yielded results of 12.0 and 3.2 µg/g, much lower than the 80 µg/g advertised by the manufacturer. Based on a salt consumption of 5 - 20 g per day (Venkatesh Manner and Dunn, 1995), these salt products could be delivering anything between 16 - 240 µg per day, assuming no further loss of iodine during cooking. The salt analyses indicate that less iodine is being added to an individuals diet than might be expected.

The objectives of this study are to look at the levels of iodine in the environment of Morocco and determine whether it is possible to improve the level of iodine available in the local food chain. The following discussions are based on fundamental questions that relate to the prevalence of IDDs.

Photograph 5: Resident from the Ounein Valley with a large goitre (by Alex Stewart)

4.1 IS THE OUNEIN VALLEY AN IODINE DEFICIENT ENVIRONMENT?

An iodine deficient environment is one that cannot provide the sufficient daily intake of iodine for the local population or the livestock reared in it. The deficiency arises from low concentrations of iodine in the rocks, soil, vegetation, drinking water or atmosphere and the local population need an additional external supply of this essential element. This may be in the form of food imported from outside the area, or direct supplementation of the diet or the environment by the addition of iodine (e.g. iodised salt or iodisation of irrigation water). This general definition of iodine deficiency would actually render most land areas of the world as being iodine deficient. The exception being coastal areas where adequate supplies of environment iodine are available because of the proximity to the marine environment, probably the single most important supply route in the iodine geochemical cycle.

This investigation has collected geochemical samples from the coastal area near Agadir and along a line to the Ounein Valley some 150 km inland. The variability of iodine in soils means that with insufficient samples the trend along the line is not conclusive (see Figure 5). However, it is clear that in the zone 0-20 km from the sea coast there is a much higher average total iodine in the soils than 150 km inland. Furthermore, there is a greater range and variability in the iodine content of the samples from nearer the coast. This would confirm data presented elsewhere, for example Fuge (1996) and Johnson (2003b). The latter is a compilation of more than 2000 soil results from published literature and includes a figure that shows the decrease in soil iodine away from the see coast (see Figure 16).

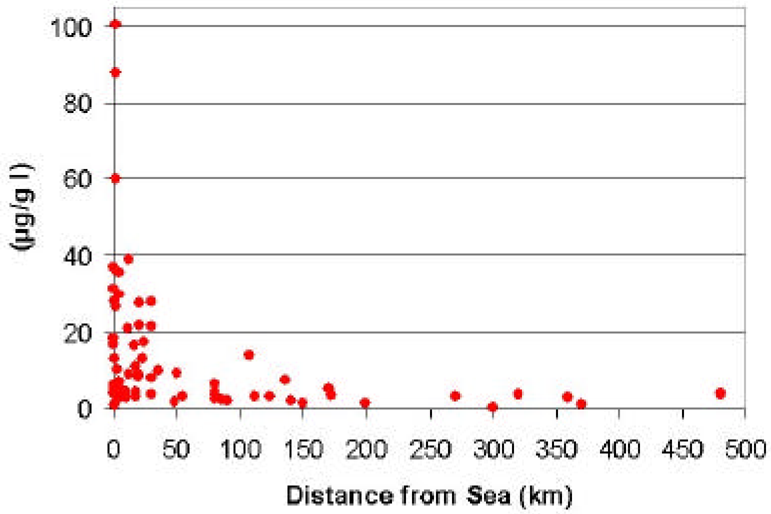


Figure 16: Total iodine in soils plotted against distance from the seacoast. Data is from a database of soil iodine results (Johnson 2003b)

The question of iodine levels in relation to altitude has not been addressed by this study. The Ounein Valley is located in the Atlas Mountains at about 1500 m. The Agadir area (Igounane) is in the foothills of the Atlas Mountains where this mountain chain meets the coast at heights 400 - 700 m. The literature is full of suggestions that high altitude (mountainous regions) can be related to iodine deficiency. This is usually based on a deficiency of iodine in the population being related to an inferred, but not proven, deficiency in the environment (e.g. Delange (1994)). The altitude effect on iodine deficiency in the environment is probably a consequence of other factors caused by high altitude such as poorly developed soils and rain shadow effects.

Some workers have considered soil parent material to be of great importance in determining the iodine status of the soil, more important than the distance from the sea (Cohen, 1985 and Anke et al, 1995). Data presented here and elsewhere do not demonstrate a simple correlation between iodine content of soils and distance from the sea coast but the majority of published data does show that a significant input of iodine to the soil will come from the atmosphere, particularly in a coastal zone 0 - 50 km (see Figure 16). It is only in recent years that the significance of iodine migration in the atmosphere through volatilisation from the plant-soil system has been recognised as an important part of the iodine cycle. Where input from other sources is low, the contribution of soil parent material will become increasingly important. A few "exotic" rock types will contribute significant iodine to a soil. Principal amongst these are organic rich shales, the Kimmeridge Shales of Dorset, England for example contain on average 17 µg/g I which is eight times higher than that expected from normal shales (see Table 11).

In the case study areas described here there are no "exotic" lithologies so the contribution of bedrock to the iodine status of the soil should be similar in both area. Unfortunately, for samples described here there is no geological information concerning the site of sample collection. However, BGS carried out a regional geochemical mapping programme to the east of the Ounein Valley producing geochemical maps for some 28 elements. This was done by collecting the -250 µm fraction of sediment from 1st and 2nd order stream beds which, because of the arid nature of the region, were dry for most of the year. The sampling density was one sample per kilometre square and the majority of analyses were done by ED-XRF. Although iodine was not an element specified in work contract, the ED-XRF produces results for a large number of elements including iodine. XRF is a poor method for determining iodine with a detection limit no better than approximately 1 µg/g. The results for the Agadir Melloul map sheet are presented here and although this is previously unpublished and not standardised data it gives a good idea of the distribution of iodine in the environment in relation to the geology. A regional geochemical map of iodine with such a high sampling density has never been produce before.

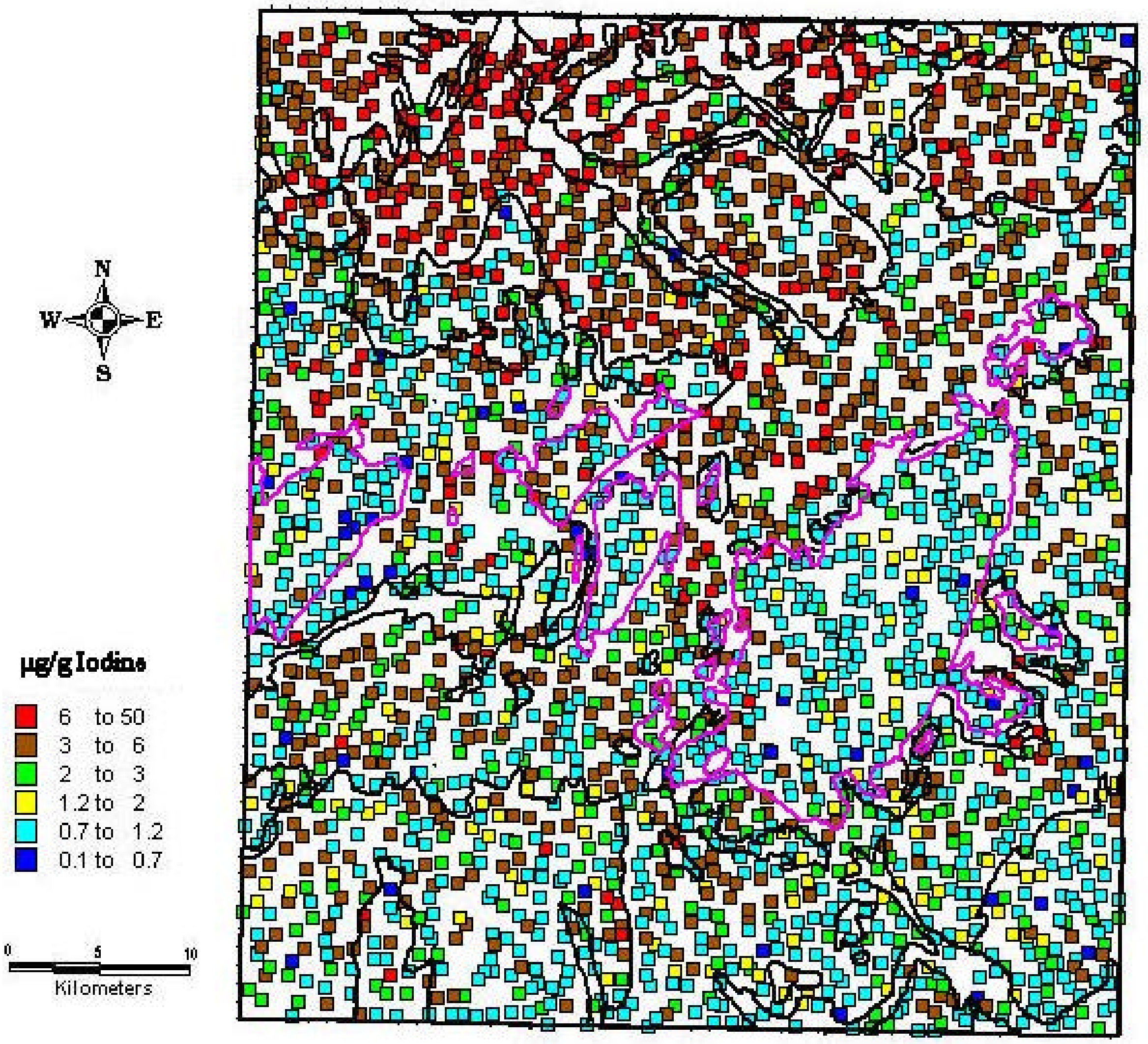


Figure 17a: A regional geochemical map of iodine in stream sediments from the Agadir Melloul map sheet. Geological linework is shown in the background. An explanation of the geology and location of the area is given in Figure 17b.

The highest iodine results are found in the north of the area and are not correlated with the geology whereas many of the major and trace elements do show a close relationship to the underlying geology (Johnson 2001b). However, there is some degree of correlation between the low iodine results and the Lower Proterozoic (indicated on Figure 17a by a purple line) where iodine levels associated with these very old metamorphic rocks are consistently low.

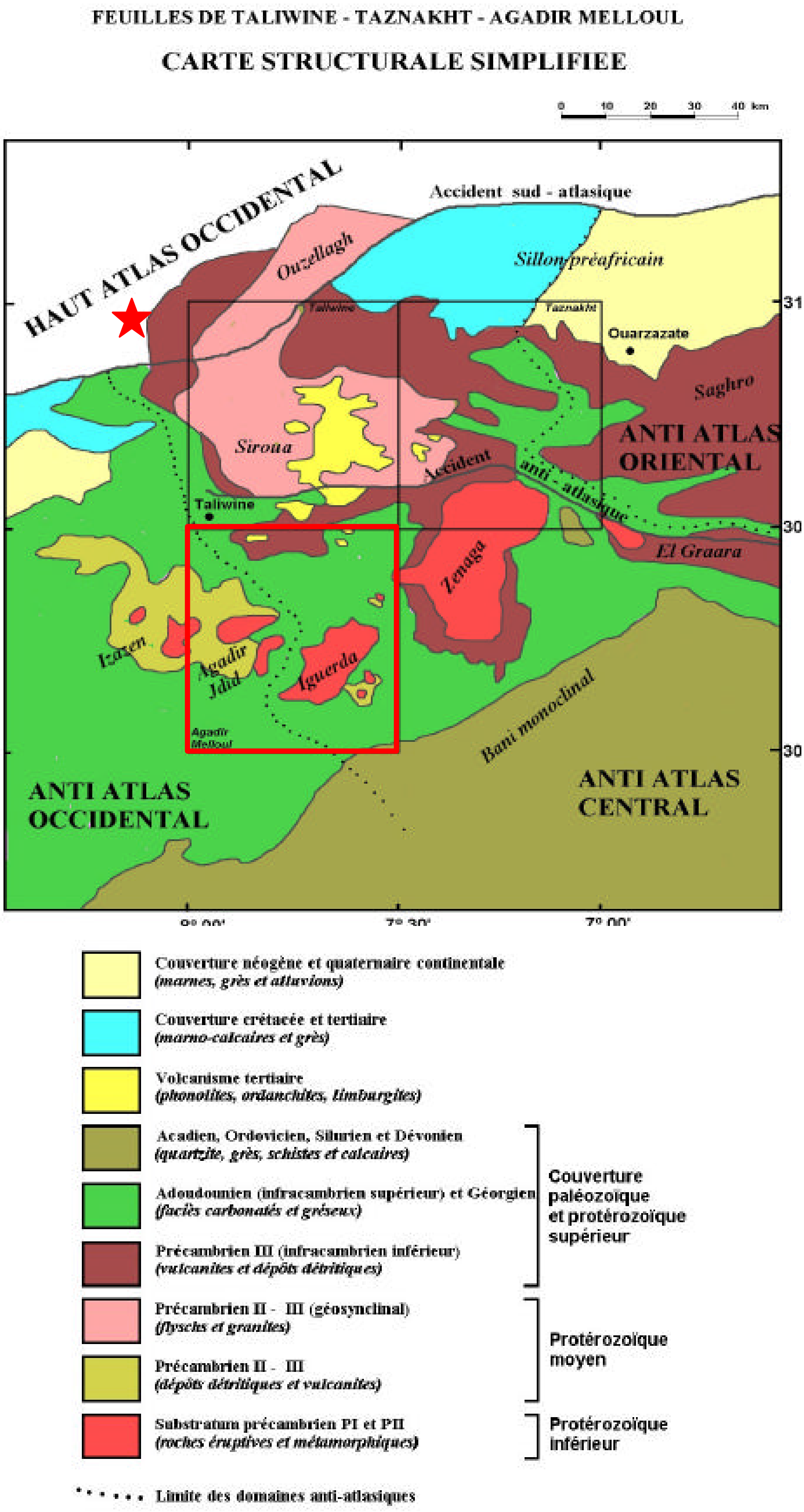


Figure 17b: A simplified geological map to explain the geological lines on Figure 17a (Agadir Melloul is indicated as a red box). The lithologies outlined with a purple line on Figure 17a represent the outline of the Protérozoïque inférieur. The location of the Ounein Valley case study area is marked with a red star (after Johnson, 2001b).

Rock Type	Mean Iodine content (µg/g)
Igneous Rocks	
Granite	0.25
All other intrusives	0.22
Basalts	0.22
All other volcanics	0.24
Volcanic glasses	0.52
Sedimentary Rocks	
Shales	2.3
Sandstones	0.8
Limestones	2.3
Organic-rich shales	16.7

Table 11: Iodine in igneous and sedimentary rocks (after Fuge and Ander, 1998)

The preceding discussions have considered that the Ounein Valley has less iodine in the environment than the Agadir area because of its distance from the sea and that iodine levels in both areas are independent of any lithological control. But can we say the Ounein Valley is deficient in iodine? In order to answer this we need some reference points against which to measure the iodine status in the environment.

There is no accepted threshold figure for defining whether an environment is iodine deficient. The iodine status of an area is usually synonymous with the iodine status of the local population as defined by medical parameters such as thyroid size or urinary iodine levels. The results from this study can be compared with iodine analyses for soils and waters from around the world and, more specifically, with geochemical samples from other IDD regions (see Table 4 for soil total iodine results). Johnson (2003b) calculates an "average" soil iodine level to be 5 µg/g. Whilst this shows that the Ounein Valley area has less total iodine in the soil than the average, the total iodine content of a soil is a poor indicator of the iodine status of a local environment. This is because of the complexity of factors that control the iodine status of a soil creating greater variability locally and making comparison between different areas difficult unless soil types and characteristics are very similar. Furthermore, it is not the total soil iodine $I_{(tot)}$ that is the critical consideration in this discussion, it is the iodine that is available to the food chain. In this study the cold water soluble iodine $I_{(sol)}$ is taken as an indication of the bioavailable iodine and the area of high prevalence IDD has three times less "bioavailable" iodine than the no IDD area near Agadir. There is insufficient data on $I_{(sol)}$ in soils to put this in the context of other areas of the world.

The use of crops to define an area's iodine status is also problematic. Inconsistencies in reporting results, e.g. whether for wet or dry matter, inclusive or exclusive of various plant parts such as husk, stem and leaves, make worldwide comparisons difficult. This investigation shows there to be little difference in iodine content between to grains from Agadir and the vegetables from the Ounein Valley (see Figure 15) but this is probably an invalid comparison. Muramatsu et al (1995) have shown that the soil-plant transfer factor for iodine in rice (a grain crop) is very low compared to green leafy vegetables. However, the results for crop samples can enable a daily intake of iodine to be calculated (see next section).

The Chinese Atlas of Endemic Diseases and their Environments (Tan, 1989) states that in most areas of IDD the prevalence rate is negatively correlated with drinking water iodine. No threshold levels are stated but maps suggest IDD will occur at level of less than 5 µg/l I. In early studies of goitre belts in the UK Murray et al (1948) noted the correspondence with low iodine in the drinking water. They recognised that other factors, e.g. water hardness could be correlated with goitre prevalence and suggested a "non-goitrous" level for the iodine content of drinking water at >5 µg/l for hard water areas and > 3 µg/l for soft water areas. They also give examples where changes to the water supply impacted on the goitre prevalence rates. Murray et al (1948) cite the work of McClendon and Williams (1923) who used data produced from the routine examination of 2.5 million US recruits for the 1914-1918 war. Their data (Table 12) suggests that areas with > 3 µg/l I were practically goitre-free.

Iodine in Water (µg per litre)	Goitre rate (per thousand men)
0 — 0.5	15 — 30
0.5 — 2	5 — 15
3 and above	0.1

Table 12: Results from McClendon and Williams (1923) that showed the goitre rate amongst 2½ million recruits related to the iodine content of representative river waters

> ***" Using >3 µg/l I in drinking water as a threshold for defining an iodine sufficient environment, the Ounein Valley with an average of 1.6 µg/l I is clearly a region at risk from IDD, a fact clearly demonstrated by the historical high prevalence of IDD."***
>
> **BOX 5**

In other areas studied by the British Geological Survey (China - Fordyce et al, 2003 and Sri Lanka - Fordyce et al, 1998) the iodine levels of drinking water have provided an excellent indicator of the iodine status of the local population. In areas where the water is taken from surface or shallow sub-surface wells, the water results also give a good indication of the iodine status of the local environment. Water results do not tend to have the variability of results found in local soils.

Using >3 µg/l I in drinking water as a threshold for defining an iodine sufficient environment, the Ounein Valley with an average of 1.6 µg/l I is clearly a region at risk from IDD, a fact clearly demonstrated by the historical high prevalence of IDD. On the basis of the drinking water iodine content the Ounein Valley can be considered an iodine deficient environment. The drinking water results cited by Aquaron et al (1993) for the endemic goitre region of Skoura-Toundoute in the Atlas Mountains also fall well below this threshold.

4.2 HOW DOES THE LOW IODINE STATUS OF THE OUNEIN VALLEY IMPACT ON ITS INHABITANTS?

The geochemical analysis of samples from the Ounein valley would indicate:

1. Iodine in drinking waters is low and below the threshold of 3 µg/l suggested for defining iodine deficient environments.
2. Soil total iodine levels are generally low being less than the world soil average of 5 µg/g. The results are lower than the coastal area of Agadir where there is three times more "bioavailable" (water extractable) iodine.

3. Food crops contain levels of iodine comparable with those quoted for other non IDD areas of the world.
4. Iodised salt is available from markets though analyses indicate much less iodine in the salt than specified.

The sociological and nutritional investigation carried out in 1995 by Oldham et al (1998) highlighted:

5. The isolation of the region with an inadequate transportation infrastructure.
6. A poor population living a subsistence style of existence with limited access to markets selling food from far away.
7. Poor education.
8. A dietary deficiency of iodine reaching over 90% in some villages.
9. On the basis of urinary samples, out of 197 school children studied, only 3% were considered to be normal, with 42.6% recorded as having a severe iodine deficiency.

Much has been done since 1995 to improve the transport infrastructure, educating the local people about the problems of IDD and the provision of iodised salt. There is no doubt that improvement of the iodine status of the population goes hand in hand with development, primarily because people have access to more iodine rich-foods from outside their local area. Furthermore, the development alleviates poverty and people are more willing to pay for "exotic" iodine-rich foods such as sea fish.

Environmental iodine deficiency is the result of the interaction of numerous natural factors and not a consequence of social or economic conditions. Such conditions can be changed to minimise **the risks** from IDD, and in the Ounein Valley there is evidence of change over the past five years, but the environment will remain iodine-deficient.

> ***"There is no doubt that improvement of the iodine status of the population goes hand in hand with development, primarily because people have access to more iodine rich-foods from outside their local area. Furthermore, the development alleviates poverty and people are more willing to pay for "exotic" iodine-rich foods such as sea fish."***
>
> **BOX 6**

Consider how the low iodine environment impacts on the diet. Figure 18 shows the contribution of food types to the 1997 average daily intake of iodine (156 µg per day) for 15-18 year olds from the UK. Unfortunately, such detailed information is not available for the region of Morocco studied but estimates can be made from knowledge of local eating habits. A poor family living a subsistence existence would eat less food and the diet would probably consist mainly of cereal grain, vegetables, fruit and nuts. In India, for example, about 75% dietary iodine is expected from cereals (Sharma et al, 1999). There would also be no high iodine chemicals in the diet as added to manufactured foods such as the red food colouring erythrosine (Dunn, 1993). The diet would have little of the iodine rich foods shown in Figure 18, namely, fish, dairy produce and meat. Without these foods the diet would probably provide about 50 µg I per day, a fraction of the recommended 150-200 µg I per day. This estimates makes no allowance for the crops being iodine deficient and does not include intake due to salt iodisation. The contribution of iodised salt has been discussed earlier in this section and could be anything between 16 - 240 µg I per day substantially adding to the 50 µg per day calculated above.

On the question of the crops being iodine deficient, it would appear that the variation in iodine content of vegetables, grains and fruits is minimal when compared to differences with the iodine-rich foodstuffs. To illustrate this, a search of the project's database on iodine in wheat (Fiona Fordyce, unpublished) came up with 13 results from around the world between 6-227 µg/kg, a range of 221 µg/kg. Sea fish results are between 471 - 15,941 µg/kg, averaging around 2000 µg/g, i.e. ten times the variation seen in wheat iodine levels. Improving the iodine status of crops may add 5-10 µg iodine to the daily diet whereas introducing sea fish to the diet would add at least 12 µg I per day.

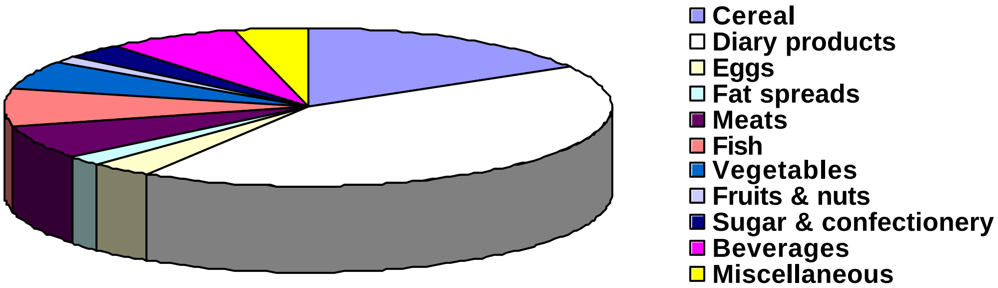


Figure 18: The contribution of food types to the average daily intake of iodine (156 µg/day) for UK 15-18 year group. (Based on data presented by Expert Group, 2002).

Jiang et al (1997) report iodine levels in wheat rising from 40 to 160 µg/kg I over a three year period of supplementing iodine in the environment through the addition of iodine to the irrigation water. A daily consumption of 200 g of wheat a day would mean an extra iodine input of 24 µg a day. If this fourfold increase in iodine crop levels could be achieved in the Ouenin Valley, then the average daily intake from food would increase by 50%.

In the absence of continued development or active programmes to supplement iodine in the diet or environment, the low iodine status of the Ounein Valley will continue to put its residents at risk for IDD.

4.3 WHAT CAN BE DONE TO IMPROVE THE IODINE STATUS OF THE OUNEIN VALLEY ENVIRONMENT?

Dunn (1993) considered the major factors in assessing dietary intake to be:

1. the natural iodine content of foods;
2. the iodine added in food processing;
3. the amount and type of food consumed;
4. iodine supplements (e.g. iodised salt);
5. other ingesta (e.g. iodine-containing medicines).

The contribution of drinking water and the atmosphere could also be added under factor 5.

The iodine added in food processing and the amount and type of food consumed are factors that become important during the course of development. These two factors are responsible for ensuring that most of the developed world has sufficient dietary iodine. Without development a population will rely on the food types grown locally and on the natural iodine content of food (factor 1). Factor 4 can be implemented to ensure that under-developed areas receive sufficient dietary intake but requires a political will to do so. This is a function very much driven by the work of organisations such as the International Council for the Control of Iodine Deficiency Disorders. This project focuses principally on factor 1.

4.3.1 Improving the natural iodine content of food

Improving the natural levels of iodine in foodstuffs necessitates an understanding of the behaviour of iodine in plants. It appears to have no role in the physiology of terrestrial plants and although not an essential element for plants it can be toxic in large concentrations resulting in Akagare disease (Yamada et al, 1999). Jopke et al (1996) cite work indicating that iodine in relatively low concentrations can also have toxic effects on some plants, e.g. leaves of tomatoes will show light spots, and will roll up and die. A direct correlation between the iodine content of plants and the total iodine of the soils on which they grow is not apparent (Simpson, 1930 and Butler et al, 1956) though there is evidence that crops grown in soils enriched with iodine will assimilate the iodine to produce iodine enriched food (Jopke et al, 1996).

The correlation between soil iodine and iodine in crops may become more apparent if investigators were to look at the bioavailable iodine in the soil and consider iodine in the context of the complete soil-plant system. The soil water and soil gas can form 50% of a soil's volume yet very few investigations have looked at this part of the soil-plant environment. In recent years studies have improved our understanding of the transfer of iodine from atmosphere to the soil-plant system and back again. Widung et al (1985) found that plants with actively growing roots produced a larger fraction of volatile inorganic iodine than the soil alone produced. Plants must therefore have an important role in the geochemical cycle of iodine.

Tracer experiments on the behaviour of radioiodine in the soil-plant-atmosphere system give an insight into the parts of the plant which might concentrate iodine. Muramatsu et al (1995) showed there was a tendency for older leaves to show higher concentrations of radioiodine than younger ones. The values for fruit, grain and beans were significantly lower than those for their leaves. Muramatsu et al (1993) reported the transfer factors of iodine for different parts of rice plants decreased in the order of: second leaf blade > first leaf blade > stem > rachis > unhulled rice > brown rice. Similarly, Moiseyev et al (1984) found I-125 concentrated more in the leaves than the grain and stems of pea plants. The chemical species of iodine volatilised from the plant is identified as methyl iodide (Muramatsu and Yoshida, 1995).

> ***"Soils from mountain ranges, such as the Himalayas, Alps and Andes, and from areas with frequent flooding, are particularly likely to be iodine-deficient. The problem is aggravated by accelerated deforestation and soil erosion. This deficiency in the soil cannot be corrected. The food grown in iodine deficient regions can never provide enough iodine to the population and livestock living there."***
>
> ***Venkatesh Mannar and Dunn (1995)***
>
> **BOX 7**

Although plants take iodine through their roots, the probable most important pathway into plants is from the atmosphere by direct absorption (Fuge, 2003). Away from coastal areas a significant part of the iodine absorbed on leaves could be iodine volatilised from the soil. The absorption of atmospheric iodine in leaves has important consequences for grazing animals. These animals effectively become concentrators of the iodine by grazing large areas of leafy plants. This is reflected in the higher iodine contents in milk and meat. The accumulation of iodine in the leaf part of plants would suggest that local residents could maximise the available local iodine by consuming more leafy vegetables.

Different crop species may have a varying capacity to take up iodine from the environment. Muramatsu et al (1995) found accumulation factors from soil to plant varied from 0.0003 to 0.016, the greatest accumulation factor being for Brassica napus (oilseed rape). (The accumulation factor represents a ratio of the iodine amount in a unit dry weight of soil and that in the plant).

Venkatesh Mannar and Dunn (1995) write that deficiency in the soil cannot be corrected (see Box 7). We believe that although it cannot be corrected it can be managed so as to maximise the available iodine and supplement what is already there with iodine added through irrigation water or fertilisers.

Addition of iodine by fertilizers

Contents of iodine in a variety of fertilizers are listed by Whitehead (1973) with levels ranging from less than 1 µg/g in common nitrogen fertilizers to 79.5 µg/g in Chilean nitrate. Phosphate fertilizers also contained relatively high levels of iodine (18.7 - 26 µg/g I), presumable derived from high iodine phosphate rocks.

Gurevich (1964) describes the use of seaweed fertilisers as a prophylactic measure against endemic goitre. Seaweed ash was demonstrated to be the best way of applying the fertiliser with a content of 11,100 µg/g (compared to 2,380, 250 and 22 µg/g for natural seaweed, seaweed compost and fish meal respectively). A country with a seacoast could make use of seaweed in its efforts to reduce the risks of IDD.

Application of Chilean nitrate or phosphate fertilisers is a means of adding to the iodine status of the soil (Itano and Yasuhiko, 1935 and Jopke et al, 1996). The affect of nitrogen fertilisers on the iodine status appears to be ambiguous (Moiseyev et al, 1984) but Alderman and Jones (1967) demonstrated that the use of such fertilizers actually reduced the iodine content of grassland, presumably due to a dilution effect caused by the rapid growth of vegetation.

Moiseyev et al (1984) also demonstrated that the introduction of organic matter to a soil can regulate the transfer of iodine from soil to plant and thus limit the amount of iodine in the food chain. Adding organic matter to a soil will fix the available iodine making it less readily available for root uptake. These workers also cite a reference from other work in the Soviet Union that showed the application of $CaCO_3$ (as ground lime) to a Sod-Podzolic clay loam lowered the iodine content in oat grain and straw by one-half. A change in the cation or anion ratios in soil solution in either direction produces a decrease in the coefficient of accumulation of iodine. Simpson (1930) reported that iodine in alkaline soils seemed to be of low availability while in acid soils it was readily available.

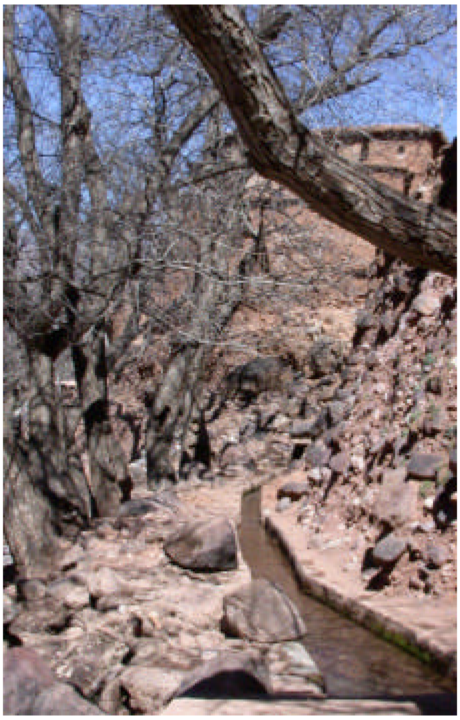
Adding iodine to the soil through the addition of fertilizer will only have a significant impact if the iodine is retained in the soil as bioavailable iodine. Too much organic matter will have the effect of fixing the iodine but this will not be made available to the food chain unless there is some process in the soil to release it. A sandy soil with no organic matter will not retain any added iodine that will be rapidly removed from the soil by volatilisation or washed away by soil water.

> ***"The investigation of the influence of iodine fertilisation with Caliche showed that plants are able to assimilate iodine. Cress showed an increase in iodine concentration to over 30 mg/kg in its dry matter. Therefore, it could be possible to offer the consumer cress or other plants as a prophylactic against iodine deficiency besides the use of iodised salt."***
>
> ***Jopke et al (1996)***
>
> **BOX 8**

In practical and economic terms, the use of iodine-rich fertilizers requires the political will to implement such a system, and it must be demonstrated to be more effective than say for example using iodised salt. It is unlikely that the people of the Ounein Valley would be willing to pay the extra cost of using iodine-rich fertilisers. The best approach may be that suggested by Jopke et al (1996) in which a regularly eaten foodstuff could be grown in pots or trays to provide a prophylactic against iodine deficiency (see Box 8). They demonstrated the production of an iodine-rich cress (30µg/g dry matter) fertilised with natural Caliche. In their experiment they used a sandy soil, a soil texture that is very characteristic of many high risk IDD areas and a soil that has little fixation potential for iodine in an unclosed system.

Addition of iodine to the water

In this project's other case study area we had the opportunity to work in an area where iodination of irrigation water had been trailed for several years (Fordyce et al, 2003). This was in the Xinjiang Province of China reported by Shaohua and Delong (2000) and discussed by Rengel et al (1999) as a possible agronomic approach for improving the iodine in crops. The iodination of irrigation water in the Xinjiang Uygur Autonomous Region increased soil, crop and animal iodine levels (Cao et al, 1994) and demonstrated this was an advantageous and cost effective method of supplying iodine to the environment. However, as the work of Fordyce et al (2003) demonstrated, there is not a long residence time for such iodine in soils that are naturally iodine deficient because they do not have any capacity to retain iodine. Any programme of irrigation water iodination should consider agricultural practices that will maximise the retention of iodine over a long period of time but not techniques that will strongly fix the iodine and make it unavailable for uptake to crops.



Photograph 6: Typical irrigation channel in the Ounein Valley (Photograph by M Strutt)

The Ounein Valley relies on irrigation to grow crops and this could be considered as a viable way to improve the iodine status of the environment. The advantage of this method over salt iodinisation is that it benefits the whole biosphere and not just people. Shaohua and Delong (2000) consider it to be a cost effective method of less than 0.12 US$ per person, the cost reducing if the effects persist over many years.

Several workers have considered other ways of adding iodine to the drinking water supply and the work of the current project concludes that the iodine in drinking water can be a significant factor in determining the iodine status of a local population.

Vigneri et al (1993) describe a project that supplemented the municipal water supply to a town in Sicily of approximately 13,000 people producing a water supply that averaged 46.5 µg/l I. Foo et al (1996) report the delivery of an average of 139 µg/l I in a village water supply in Sarawak. Both these studies comment on the cost effectiveness of this method of iodine supplementation and Foo et al note that such projects can be more rapidly implemented than salt iodisation programmes. It can be questioned whether iodine added to a municipal water supply is efficiently used as much of the water will not be used for drinking or cooking. However, if used for watering gardens and livestock it has wider benefits and not just to humans. More targeted approaches by supplementing drinking water in wells are described by Elnager et al (1997), Pichard et al (1993), and Fakhouri and Vergnaud (1994). The two former references describe the supplementation via iodine-saturated silicon matrices whilst the latter looks at the possibility of delivering iodine through wood saturated with iodine. Again, the investigators claim the methods to be cost effective and low maintenance.

It has also been noted by a number of workers, e.g. Shaohua and Delong (2000) and Fordyce et al (2003), both citing examples in China, where deeper water wells have yielded drinking water with more iodine. Seeking alternative water supplies that are richer in iodine is a further strategy that could be considered in an environment where surface waters are deficient in iodine.

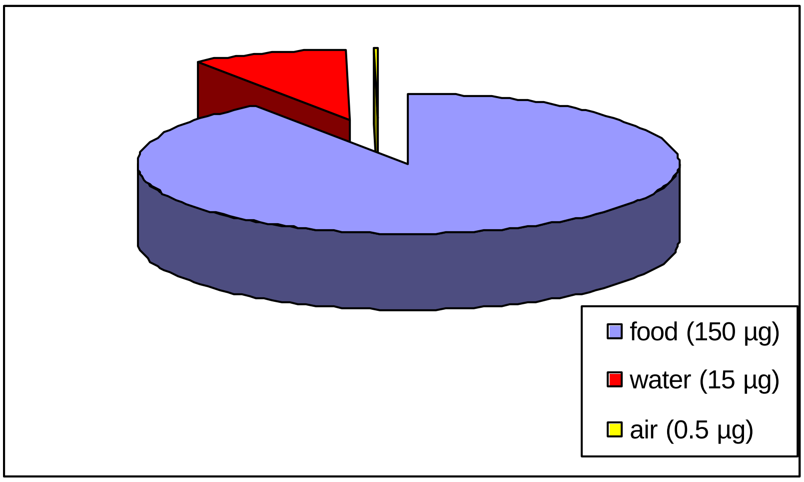


Figure 19: The relative daily contribution of iodine from air, water and food estimated for typical European diet

The importance of iodine in the drinking water to populations with iodine deficient diets is somewhat neglected though clearly an important factor (Coble, 1968). Figure 19 shows the relative proportions of iodine contributed from different sources based on a UK diet (see Figure 18), drinking water of 10 µg/l I (1.5 litres a day), and estimated inhalation of 0.5 µg/g based on atmospheric concentrations of 10-20 ng/m^3 (Nordic Project Group, 1995). The figure emphasises the small contribution of iodine inhaled from the atmosphere. Drinking water contributes about 10% of the daily iodine intake.

In an iodine deficient environment with food providing only 50 µg iodine per day and the water supply just 5 µg, the relative proportions remain the same. However, if the water is naturally enriched in iodine (say from a deep water source) or if the water is supplemented with iodine so levels are 50 - 80 µg/l instead of 3 µg/l, then the daily contribution of drinking water iodine will rise to be 1.5 - 3 times greater than that supplied in food.

Management of Environmental Iodine

Measures to manage the local iodine balance more efficiently include: changing the crops grown; using grazing livestock to concentrate iodine; improving the soil's ability to fix the iodine; making the soil's iodine more bioavailable without losing it through volatilisation; finding alternative more iodine-rich water supplies; and preventing removal of iodine by flooding. The more efficient management of environmental iodine is discussed in Johnson (2003c).

The preceding sections show that there are cost effective ways of supplementing the levels of iodine in the environment and the Ounein Valley could benefit from such supplementation. These techniques can be used in conjunction with medical intervention to reduce the risks of a population exposed to IDD and without hope of short-term rapid economic development. Scientists can demonstrate the effectiveness of such methods, but it remains for the politicians to have the will to implement them and tackle such endemic problems for which there are clear solutions.

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APPENDIX A: Sample Site Information

1. Locational Information

Map Sheet			Collectors		Site			Soil	Water	Crop	Latitude	Longitude	
Name	**Number**	**Date**	**1**	**2**	**Code**	**No.**	**Dup.**	**S**	**W**	**V**	**°N**	**°W**	**Weather**
Talat-N-Ya'Qoub	NH-29-XVI-4d	18/03/2002	MHS	MM	MR	0001		✓	✓	✓	30.87009	008.20115	6
Talat-N-Ya'Qoub	NH-29-XVI-4d	20/03/2002	MHS	MM	MR	0003		✓			30.88224	008.19008	7
Talat-N-Ya'Qoub	NH-29-XVI-4d	20/03/2002	MHS	MM	MR	0004		✓	✓	✓	30.89801	008.18365	7
Agadir	NH-29-XV-1d	24/03/2002	MHS	MM	MR	0005		✓			30.45870	009.54174	8
Talat-N-Ya'Qoub	NH-29-XVI-4d	21/03/2002	MHS	MM	MR	0007		✓			30.87115	008.15931	7
Agadir	NH-29-XV-1d	24/03/2002	MHS	MM	MR	0008		✓			30.44723	009.54144	8
		24/03/2002	AS			0009		✓			30.57636	009.16973	8
Agadir	NH-29-XV-1d	24/03/2002	MHS	MM	MR	0013	0035		✓		30.48276	009.54592	8
Talat-N-Ya'Qoub	NH-29-XVI-4d	19/03/2002	MHS	MM	MR	0015		✓			30.90952	008.15030	6
Talat-N-Ya'Qoub	NH-29-XVI-4d	20/03/2002	MHS		MR	0016		✓			30.86875	008.18268	7
Talat-N-Ya'Qoub	NH-29-XVI-4d	20/03/2002	MHS	MM	MR	0017		✓	✓	✓	30.88480	008.19723	7
Talat-N-Ya'Qoub	NH-29-XVI-4d	18/03/2002	MHS		MR	0018			✓		30.86951	008.18658	6
Talat-N-Ya'Qoub	NH-29-XVI-4d	20/03/2002	MHS	MM	MR	0019		✓	✓		30.83374	008.20096	7
Ghabat Admine		25/03/2002	MHS		MR	0020		✓		✓	30.49564	009.49147	8
Agadir	NH-29-XV-1d	23/03/2002	MHS		MR	0021	0095	✓		✓	30.48784	009.50401	8
Agadir	NH-29-XV-1d	24/03/2002	MHS	MM	MR	0023		✓			30.49647	009.53595	8
		24/03/2002	AS		MR	0024		✓			30.65295	008.51265	8
Agadir	NH-29-XV-1d	24/03/2002	MHS	MM	MR	0025		✓			30.43530	009.54746	8
Talat-N-Ya'Qoub	NH-29-XVI-4d	19/03/2002	MHS	MM	MR	0026		✓			30.90443	008.15046	6
Talat-N-Ya'Qoub	NH-29-XVI-4d	20/03/2002	MHS		MR	0028		✓	✓	✓	30.83287	008.20402	7
	NH-29-XV-1d	25/03/2002	MHS	MM	MR	0029		✓			30.43513	009.58456	8
Talat-N-Ya'Qoub	NH-29-XVI-4d	19/03/2002	MHS	MM	MR	0032		✓		✓	30.86141	008.10698	6
Ghabat Admine		25/03/2002	MHS		MR	0033	0050		✓		30.49579	009.49385	8
Talat-N-Ya'Qoub	NH-29-XVI-4d	21/03/2002	MHS	MM	MR	0034		✓			30.87701	008.18108	7
Agadir	NH-29-XV-1d	24/03/2002	MHS	MM	MR	0035	0013		✓		30.48276	009.54592	8
Agadir	NH-29-XV-1d	24/03/2002	MHS	MM	MR	0036		✓			30.49194	009.53583	8
Talat-N-Ya'Qoub	NH-29-XVI-4d	20/03/2002	MHS	MM	MR	0037		✓			30.88644	008.20696	7
Talat-N-Ya'Qoub	NH-29-XVI-4d	21/03/2002	MHS	MM	MR	0038		✓	✓	✓	30.86079	008.15679	7
Talat-N-Ya'Qoub	NH-29-XVI-4d	20/03/2002	MHS	MM	MR	0039	0019	✓	✓		30.83374	008.20096	7
Agadir	NH-29-XV-1d	23/03/2002	MHS	MM	MR	0040			✓		30.49611	009.49500	8
Talat-N-Ya'Qoub	NH-29-XVI-4d	19/03/2002	MHS	MM	MR	0041		✓			30.85714	008.10712	6
Ghabat Admine		25/03/2002	MHS		MR	0042		✓			30.49718	009.49516	8
	NH-29-XV-1d	25/03/2002	MHS	MM	MR	0043		✓			30.43134	009.61991	8
	NH-29-XV-1d	25/03/2002	MHS	MM	MR	0044		✓			30.43336	009.56648	8
Talat-N-Ya'Qoub	NH-29-XVI-4d	19/03/2002	MHS	MM	MR	0045		✓	✓	✓	30.88441	008.13748	6
Talat-N-Ya'Qoub	NH-29-XVI-4d	19/03/2002	MHS	MM	MR	0046		✓			30.86025	008.10249	6
		24/03/2002	AS		MR	0047		✓			30.71200	008.14500	8
Agadir	NH-29-XV-1d	23/03/2002	MHS	MM	MR	0048		✓			30.48276	009.54874	8
Talat-N-Ya'Qoub	NH-29-XVI-4d	19/03/2002	MHS	MM	MR	0049			✓		30.85990	008.09983	6
Ghabat Admine		25/03/2002	MHS		MR	0050	0033		✓		30.49579	009.49385	8

Agadir	NH-29-XV-1d	23/03/2002	MHS	MM	MR	0051		✓			30.48310	009.54203	8
Agadir	NH-29-XV-1d	24/03/2002	MHS	MM	MR	0052		✓			30.45538	009.53398	8
Talat-N-Ya'Qoub	NH-29-XVI-4d	20/03/2002	MHS	MM	MR	0054		✓			30.82983	008.20639	7
Talat-N-Ya'Qoub	NH-29-XVI-4d	19/03/2002	MHS	MM	MR	0056		✓	✓	✓	30.90524	008.14883	6
Agadir	NH-29-XV-1d	23/03/2002	AS		MR	0057		✓			30.46081	009.53030	8
Ghabat Admine		25/03/2002	MHS		MR	0058		✓			30.49404	009.49245	8
Agadir	NH-29-XV-1d	24/03/2002	MHS	MM	MR	0059		✓			30.48068	009.52491	8
Agadir	NH-29-XV-1d	24/03/2002	MHS	MM	MR	0060		✓		✓	30.45156	009.53908	8
Agadir	NH-29-XV-1d	23/03/2002	MHS	MM	MR	0061		✓		✓	30.48576	009.54583	8
Talat-N-Ya'Qoub	NH-29-XVI-4d	20/03/2002	MHS	MM	MR	0062		✓			30.83648	008.19919	7
Agadir	NH-29-XV-1d	24/03/2002	MHS	MM	MR	0064			✓		30.46678	009.52768	8
Talat-N-Ya'Qoub	NH-29-XVI-4d	20/03/2002	MHS	MM	MR	0065		✓			30.88635	008.20319	7
Agadir	NH-29-XV-1d	24/03/2002	MHS	MM	MR	0066		✓		✓	30.46640	009.52907	8
Talat-N-Ya'Qoub	NH-29-XVI-4d	21/03/2002	MHS	MM	MR	0067		✓			30.85820	008.16352	7
Talat-N-Ya'Qoub	NH-29-XVI-4d	20/03/2002	MHS	MM	MR	0069	0090	✓			30.89557	008.18446	7
Agadir	NH-29-XV-1d	24/03/2002	MHS	MM	MR	0070			✓		30.48253	009.52618	8
Agadir	NH-29-XV-1d	23/03/2002	AS		MR	0071		✓			30.46356	009.53080	8
Talat-N-Ya'Qoub	NH-29-XVI-4d	20/03/2002	MHS	MM	MR	0072			✓		30.88568	008.19946	7
		25/03/2002	MHS	MM	MR	0073		✓			30.43059	009.61355	8
Agadir	NH-29-XV-1d	24/03/2002	MHS	MM	MR	0074	0097	✓			30.49425	009.53397	8
		24/03/2002	AS		MR	0077		✓			30.62324	008.99953	8
Agadir	NH-29-XV-1d	24/03/2002	MHS	MM	MR	0079			✓		30.46128	009.53242	8
Talat-N-Ya'Qoub	NH-29-XVI-4d	20/03/2002	MHS	MM	MR	0080		✓			30.86655	008.18811	7
		25/03/2002	MHS	AS	MR	0082		✓			30.57862	009.35108	8
Agadir	NH-29-XV-1d	23/03/2002	MHS	MM	MR	0083		✓	✓	✓	30.49593	009.50106	8
Agadir	NH-29-XV-1d	23/03/2002	MHS	MM	MR	0084		✓			30.48556	009.50631	8
		24/03/2002	AS		MR	0085		✓			30.40937	009.43228	8
Agadir	NH-29-XV-1d	24/03/2002	MHS	MM	MR	0088		✓			30.46394	009.52600	8
Agadir	NH-29-XV-1d	24/03/2002	MHS	MM	MR	0089		✓			30.42213	009.61024	7
Talat-N-Ya'Qoub	NH-29-XVI-4d	20/03/2002	MHS	MM	MR	0090	0069	✓			30.89557	008.18446	7
Talat-N-Ya'Qoub	NH-29-XVI-4d	21/03/2002	MHS	MM	MR	0091		✓			30.85884	008.16065	7
Agadir	NH-29-XV-1d	23/03/2002	MHS		MR	0093		✓			30.48896	009.50214	8
Talat-N-Ya'Qoub	NH-29-XVI-4d	19/03/2002	MHS	MM	MR	0094		✓			30.88227	008.14213	6
Agadir	NH-29-XV-1d	23/03/2002	MHS		MR	0095	0021	✓		✓	30.48784	009.50401	8
Agadir	NH-29-XV-1d	24/03/2002	MHS	MM	MR	0096		✓			30.44064	009.54384	8
Agadir	NH-29-XV-1d	24/03/2002	MHS	MM	MR	0097	0074	✓		✓	30.49425	009.53397	8
Talat-N-Ya'Qoub	NH-29-XVI-4d	19/03/2002	MHS	MM	MR	0098		✓			30.88254	008.14544	6
Talat-N-Ya'Qoub	NH-29-XVI-4d	20/03/2002	MHS	MM	MR	0099		✓			30.98281	008.18489	7
		24/03/2002	AS		MR	0100		✓			30.75896	008.31875	8

Samplers: MHS - Strutt; AS - Stewart and MM - Mounir

Weather: 6 - Heavy rain within 48 hours; 7 - Heavy rain within 2-7 days and 8 - no rain within 1 week

2. Soil Information

Site No	Contamination					Land use		Clast Geology								Notes
	1	2	3	4	5	1	2	1	2	3	4	5	6	7	8	
1	A0	G1				AR	PA	3D00	3L00	1JB0	1JD0					SOIL FROM FIELDS OF VEG CULTIVATED FOR AREA POPULATION OF TOUG-AL-KHIR.
2																Control Sample - Replicate of MRS21
3						AR		3D00	3L00	4200	1EA0	1JB0				50m N OF E/W PISTE BETWEEN TOUG-AL-KHIR & LARB'A-N-TANTARYA. LTBR/RD SOL
4	G1	A0				AR		3D00	4200							BEANS & CARROTS 50m S OF SITE. LTBr SOIL. AB LST CLASTS
5	D0					AR		3D00	4200	4201						V. SPARSE WHEAT IN FIELD OVERLOOKING, SE & W-E OUED (DRY) SOIL HIGHLY CLASTIC. 150m ABOVE PISTE & ACCESS TO QUARRY
7						AR		3D00	3L00	1JD0	1JE0	1EC0				WHEAT TERRACE 30m S OUED SW AFOURIGH (APPROX 1km)
8	D0					AR		4200	4201							WHEAT FIELD WITH ARGANE TREES. 15m E OF OUED c. 600m E IRHIL-OU-DERDOUR AND DOWNSLOPE FROM IT
9						AR										100m FROM HOUSE. KITCHEN GARDEN IN TREES WITH MAIZE. NO CONTAMINATION
11																Control Sample - Replicate of MRS39
12																Control Sample - Replicate of MRS69
14																Control Sample - Replicate of MRS74
15						AR		3D00	1J00							INTEBEDDED TUFFS, ASH, BRECCIAS. WHEAT TERRACE TO W OF OUED VALLEY. DEEPLY INCISED INTO 45 DEGREE DIPPING VOLCS
16	D0	A0				AR		1000	3D00							MISC. VOLCANIC EXTRUSIVECLASTS. WHEAT & MNR ONIONS. BETWEEN TOUQ-AL-KHIR & SOUK AT ADOUZ
17	D0	A0				AR		3D00	3L00							BEANS AND CARROTS COLLECTED WITH SOIL ON TERRACE BELOW LARB'A-N-TAMTARGA.WATER IN IRRIGATION CHANNELNEXT TO FIELD
19																Duplicate of MRS39
20	A0					AR		4200	4201	3D00	4500					WHEAT/BARLEY FIELD (Barley collected) C.100m SE OF TAHOTKOKT. 50m n PISTE
21						AR		4200	3D00							BARLEY FIELD 300m W OF SCHOOL AT IGOUNANE. BARLEY & SOIL COLLECTED
22																Reference Material
23						AR		4200	4300	3D00						BARLEY FIELD ON RIDGE TO SE AIT ALI AND NW TIT MELLOUL
24						AR										WHEATFIELD WITH GOAT DUNG
25	D0					RG		4200	4201							AREA OF ROUGH GRAZING AT MOUTH OF OUED VALLEY. GREAT DEAL OF DOMESTIC WASTE/SHANTY/ROAD BUILD
26	D0					AR		1J00	3D00	1ABH						FIELD OF WHEAT NEXT TO PISTE AND 150M E OF SCHOOL. ALSO c.200M W OF N/S STREAM. AB. FELSITE BOULDERS ON COLLINE TO W. INTRUSINE BODY IN VOLCANIC SEDS
27																Reference Material

28	D0					AR		3D00	3L00	2I00						COLLECTED LEGUMES OF BROADBEANS AND WHITE CARROT. TERRACE FIELD 20M W OF N/S STREAM S ANZI WATER FROM SEEP W-E. WATER COLLECTED 50M UPSTREAM OF PISTE FROM ANZI TOWARDS S
29	C0	A0	D0	B3		RG		4200	4201							GREEN AREA WITH HOUSING, AVAILABILITY OF SOIL IN AREA LIMITED. ROUGH BROWNFIELD
32	D0					AR		3D00	3L00	3700						CARROTS COLLECTED IN LOWER TERRACE OF 2. LOWER ABANDONED WITH BROADBEANS, UPPER WITH WHEAT.
34	A0	D0				AR										TERRACE OF WHEAT SE (200m) PISTE FROM TARROUDANT TO TIZI-N-TEST. 400m N SOUQ LARB'AT ADOUZ
36	A0					AR		4200	3D00							WHEAT FIELD c.200m W OF SCHOOL AT TIT MELLOUL. BR SOIL HIGHLY CLASTIC
37	D0	A0	B1	G1		AR		4200	3D00	2I00	2H00	3L00				TERRACE OF WHEAT TO W (400m) MOSQUE AT TAWRIRT. DOMESTIC AND FARM WASTE AROUND EDGES. OLIVE GROVE AROUND FIELD.
38	D0	A0				AR		3D00	3L00							WATER COLLECTED AT SPRING/SEEP USED AS VILLAGE POTABLE AND IRRIGATION SUPPLY. BEANS AND CARROTS COLLECTED 75m BELOW SPRING (TO NW IN TERRACED FIELD). SOIL LTBR SASI
39	A0					AR		3D00	3L00							TERRACE BELOW SCHOOL AT ANZI. SET ASIDE? WATER COURSE IRRIGATION CHANNEL FROM SOURCE ON HILLSIDE c. 200m ABOVE AND NE OF SITE
41						AR		3D00	2I00	3L00						SMALL WHEAT TERRACE TO WEST OF TAKOUCHT, SMALL FIRE IN CORNER OF FIELD (REMAINS OF)
42	A0					AR		4200	4201	3D00	QTZ					200M N SCHOOL AT TAHOTKOKT. ON SLOPE DOWN TOWARDS SCHOOL. SPARSE WHEAT. HIGHLY CLASTIC RD/BR SOIL
43	D0	A0				RG		4200	4201	3D00	3L00					OVERLOOKING AGADIR PORT. ON STEEP SLOPE ABOVE JUNCTION BETWEEN ROAD TO CITY & MARRAKECH TO ESSOURIA HIGHWAY.
44	H0	D0	A0			RG		4200	4201							AREA OF SCRUB c.250m N MAIN E-W ROUTE (N OF AGADIR) BETWEEN PORT & MARRAKECH/OUARZAZATE
45	A0					AR		3D00	3L00							ABOVE VILLAGE OF AFOURIGH. CARROTS COLLECTED, SOIL FROM FIELD OF VEG AND WATER IN IRRIGATION CHANNEL 30m E OF SITE
46	A0	G1	D0			AR		3D00	1EA0	1000	1JB0	1JF0				SMALL FIELD OF ONIONS (IMMATURE). TERRACE. LTBR.RD SOIL
47	G1	D0				AR										WHEAT FIELD, PLASTIC BOTTLES LOCALLY, SHEEP DUNG, 50M FROM ROAD AND OVERHEAD CABLES.
48						AR		4200	4201	4300	3D00					BARLEY FIELD 150m E OF CLIFF LINE (META-SEDS) c.300m W OF AIT OUIZ
51						AR										BARLEY FIELD, THIN SOIL, HIGHLY CLASTIC c.600m E OF AIT OUIZ
52						AR		4200	4201	3D00						WHEAT FIELD SE OF NE-SW OUED, 600m S OF AIT AHMED, AHGAN TREES
54	D0	E0				AR		3D00	1JF0	1JE0	1JB0	1EC0	1JA0			2ND TERRACE ABOVE N/S STREAM. IMMATURE BEANS (NO FRUIT)

56	A0	D0				AR		3D00	1000	1J00						VEGETABLE FIELD TO E OF SCHOOL SW OF TAMDGHOUST. CARROTS COLLECTED. BEANS LOCALLY. ABUNDANT IMMATURE WHEAT
57						AR										WHEAT FIELD, HOLLOW BY STREAM BED, NO CONTAMINATION SEEN
58	E0	D0				AR		4200	4201							20m SW OF OUED (N-S FROM VILLAGE OF TAHOTKOKT) APPROX 150m S 0F E END OF VILLAGE
59						AR		4201	3D00							SMALL WHEAT FIELD AT FOOT OF VALLEY (DRY) RUNNING NNE-SSW FROM TAKOUIT-OU-MZIL
60	A0					AR		4200	4201							BARLEY FIELD SSW AIT AHMED.20m W OF OUED 150m E N/S PISTE. BARLEY COLLECTED
61						AR		4200	4300	3D00						IN FIELD OF BARLEY (COLLECTED) N OF AIT OUIZ LTBR/RD SOIL. HIGHLY CLASTIC
62						AR		1JB0	1JD0	1JE0	1JF0	1EC0				c.800M S ANZI. TERRACE TO E c.30M UPSLOPE OF STREAM (N/S) FROM ANZI. FALLOW. LTBR SOIL.
65	A0					AR		3D00	1000							EXTRUSIVE VOLCANICS AND FINE GRAINED INTRUSIVES. BARLEY FIELD TERRACE ABOVE SCHOOL NEAR TAWRIRT
66						AR		4201	4200	4300						WHEAT AND MNR BARLEY, FIELD c. 500m E OF AIT AHMED & 350m N OF E-W OUED
67	D0					AR		3D00	3L00	1JE0	2I00	1EC0	1JD0			TERRACES OF MISC. CROPS. ONION, BEANS, WHEAT, HERBS. WELL 20m N OF SITE (WATER 2m DEPTH) ON EDGE OF SMALL E/W VALLEY (DRY). ALMOND, GRENEDINE TREES.
69	D0	A0				AR		4200								TERRACE 30M ABOVE W END OF TAQOURDMI. WHEAT. ABUNDANT LST LOCALLY. ALSO LST CONGLOMERATE.
71						AR										WHEATFIELD. NO OBVIOUS CONTAMINATION, 80M FROM BUILDING.
73	C0	D0	H0	B3	A0	RG		4200	4201							"VERDANT" AREA NW AGADIR, E OF AGADIR PORT. CAMEL GRAZING. OCCASSIONAL LARGE SLABS OF CONCRETE
74	D0					AR		4200	3D00							FIELD FACING S FROM TIT MELLOUL.
77						AR										WHEAT TERRACES. WADI EDGE, 50m FROM DRY STREAM BED
80	D0					AR		1000								ABUNDANT CLASTS OF MISC VOLCANIC EXTRUSIVES. FIELD OF WHEAT.
81																Control Sample - Replicate of MRS97
82						AR		3D00	1000	4200						MISC VOLCANICS, MNR LST, FIELD S OF OUED (W-E). BARLY. 200M W N/S MARRAKECH TO AGADIR MOUNTAIN ROAD. RD/BR SOIL
83	E0	A0				AR		4200	3D00							WELL WATER, FIELDS LOCALLY WITH WHEAT & BARLEY. WATER IRON RICH, PARTICULATE. FILTER BR/RD AFTER COLLECTION
84						AR		3D00	4200	3L00						WHEAT FIELD Cc. 600m W SCHOOL AT AGOUNANE. SOIL COLLECTED.LTBR SILTY SOIL
85						AR										OPEN AND EXPOSED HILL TOP. BARLEY FIELD 500m FROM MAIN ROAD
86																Control Sample - Replicate of MRS90
87																Control Sample - Replicate of MRS19

88						AR		3D00	4200	4201	3L00					50m S E/W PISTE BETWEEN AIT AHMED AND IMOULA 600m E AIT AHMED SPARSE WHEAT
89	A0	D0				RE										AGADIR BEACH SAND SAMPLE
90																Duplicate of MRS69
91	D0					AR		3D00	3L00	2I00	1EA0	1EC0	1JB0	1JA0	3700	TERRACED FIELDS FACING W c.500M W AGARDANE. ONIONS (NOT COLLECTED) LOCAL KNOWLEDGE SAYS HIGH INSTANCE OF GOITRE HERE. NOT WITNESSED.
92																Control Sample - Replicate of MRS95
93						AR		4200								WHEAT FIELD E SCHOOL AT IGOUNANE. 100m E SCHOOL & PISTE
94						AR		3D00	1JB0	1JF0	3L00					WHEAT TERRACE FACING S OVER SLOPE TO OUED RD/BR SOIL AFOURIGH
95																Duplicate of MRS21
96	D0	A0				AR		4200	4201							WHEAT FIELD 100m E OF N/S OUED & PISTE. PISTE BELOW CLIFF LINE (BELOW IRHIL-OU-DERDOUR)
97																Duplicate of MRS74
98						AR		3D00	1JC0	1JB0	1JF0	1EC0				WHEAT FIELD SW OF AFOURIGH
99	E0	D0				AR		3L00	3D00	4200	1AA0					WHEAT FIELD TERRACE SE (100m) FROM PISTE AND SCHOOL IN TAQOURDMI
100						AR										WHEAT FIELD NO CONTAMINATION

Codes are based on the BGS Geochemical Survey Programme field cards. The codes used are as folllows:

Contamination:

A0	metal
B1	pottery
B3	brick
C0	glass
D0	plastic
E0	rubber
G1	farm effluent
H0	bulk industrial waste

Land Use:

AR	arable
PA	pasture
RG	rough grazing
RE	recreational

Rock types:

1000	igneous	1J00	igneous extrusive
2100	schist	1JA0	agglomerate
3700	conglomerate	1JB0	breccia
4200	limestone	1JC0	lapilli tuff
4201	fossiliferous lmst	1JD0	tuff
4300	dolomite	1JE0	ash
4500	chert	1JF0	welded tuff
1AA0	granite	2H00	slate
1ABH	felsite	3D00	sandstone
1EA0	gabbro	3L00	siltstone
1EC0	basalt		

3. Water Information

Site		Latitude	Longitude	Stream				
No.	Dup	°N	°W	Order	size	flow	Notes	Village Name
1		30.87009	008.20115	Well			WATER FROM PUMPED WELL FOR IRRIGATION. SAME AS FOR PUBLIC SUPPLY	ADOUZ
4		30.89801	008.18365	1	1	3	SEEPAGE FILLING BARRAGE USED FOR IRRIGATION & LOCAL POTABLE SUPPLY - 2 ROUTES - ONE FROM WELL TO VILLAGE, ONE FROM FIELDS.	TAQOURDMI
13	35	30.48276	009.54592	Well			NON-POTABLE (BUT THE KIDS DRINK IT). WELL BEHIND SCHOOL (10mS) AT AIT OUIZ	AIT OUIZ
17		30.88480	008.19723	1	3	4	WATER IN IRRIGATION CHANNELNEXT TO FIELD	LARB'A-N-TANTARYA
18		30.86951	008.18658	Tap			POTABLE VILLAGE SUPPLY FROM TAP IN GUEST RESIDENCE AT TOUG-AL-KHIR (ADOUZ)	ADOUZ
19		30.83374	008.20096	1	3	4	TERRACE BELOW SCHOOL AT ANZI. SET ASIDE? WATER COURSE IRRIGATION CHANNEL FROM SOURCE ON HILLSIDE c. 200m ABOVE AND NE OF SITE	ANZI
28		30.83287	008.20402	1	3	1	WATER FROM SEEP W-E. WATER COLLECTED 50M UPSTREAM OF PISTE FROM ANZI TOWARDS S	ANZI
33	50	30.49579	009.49385	Well			DUPLICATE WATER SAMPLE COLLECTED AT TAHATKOKT. WELL c.150M S SCHOOL. WATER POTABLE (APPARENTLY) AND FOR WASHING CLOTHES. HUMAN WASTE AROUND WELL.	TAHOTKOKT
35	13	30.48276	009.54592	Well			NON-POTABLE (BUT THE KIDS DRINK IT). WELL BEHIND SCHOOL (10mS) AT AIT OUIZ	AIT OUIZ
38		30.86079	008.15679	1	1	3	WATER COLLECTED AT SPRING/SEEP USED AS VILLAGE POTABLE AND IRRIGATION SUPPLY	AGARDANE
39	19	30.83374	008.20096	1	3	4	TERRACE BELOW SCHOOL AT ANZI. SET ASIDE? WATER COURSE IRRIGATION CHANNEL FROM SOURCE ON HILLSIDE c. 200m ABOVE AND NE OF SITE	ANZI
40		30.49611	009.49500	Well			IN SCHOOL PLAYGROUND. WELL WATER. FAR FROM CLEAR APPARENTLY POTABLE. SEDIMENT WITH SMALL INSECTS. FILTER RED/BROWN FOLLOWING COLLECTION	TAHOTKOKT
45		30.88441	008.13748	1	3	4	ABOVE VILLAGE OF AFOURIGH. WATER IN IRRIGATION CHANNEL 30m E OF SOIL SITE	AFOURIGH
49		30.85990	008.09983	1	3	3	IN IRRIGATION CHANNEL FROM LOCAL SOURCE. TIN CANS, BATTERIES & PLASTIC ABUNDANT AROUND SOURCE.	TAKOUCHT
50	33	30.49579	009.49385	Well			WATER SAMPLE COLLECTED AT TAHOTKOKT WELL 150M S SCHOOL	TAHOTKOKT
56		30.90524	008.14883	2	4	4	100M DOWNSTREAM OF SOURCE	TAMDGHOUST
64		30.46678	009.52768	Rainfall			WELL/RESERVOIR c.150m E MR0066. TADPOLES AND WORMS IN STORAGE TANK 10m E. WATER CLEAR. NO PRE-FILTER NEEDED. WATER COLLECTED FROM RAINFALL RUNOFF	AIT AHMED
70		30.48253	009.52618	Well			WELL S & 30M FROM DWELLING. WELL SUNK INTO LOCAL ROCK OUTCROP. WATER CLEARER THAN TIT MELLOUL BUT SAME SOURCE. POTABLE AND IRRIGATION WATER	TIT MELLOUL
72		30.88568	008.19946	Well			WELL SUPPLYING POTABLE WATER FOR LOCAL POPULATION OF LARB'A-N-TAMTARGA	LARB'A-N-TAMTARGA
79		30.46128	009.53242	Rainfall			WATER (POTABLE & FOR IRRIGATION RARELY) FROM WATER TOWER TAP AT AIT AHMED	AIT AHMED
83		30.49593	009.50106	Well			WELL WATER, FIELDS LOCALLY WITH WHEAT & BARLEY. WATER IRON RICH, PARTICULATE. FILTER BR/RD AFTER COLLECTION	IGOUNANE
97	74	30.49425	009.53397	Well			WATER FROM WELL POTABLE (NOT DUPLICATED)	TIT MELLOUL

stream codes:

size	flow
1 seepage or spring	1 dry with no surface drainage
3 land drain	3 low flow
4 small stream	4 moderate flow

4. Crop Information

SiteNo	Latitude	Longitude	Crop
1	30.87009	008.20115	potato
4B	30.89801	008.18365	bean
4C	30.89801	008.18365	carrot
17B	30.88480	008.19723	bean
17C	30.88480	008.19723	carrot
20	30.49564	009.49147	barley
21	30.48784	009.50401	barley
28B	30.83287	008.20402	bean
28C	30.83287	008.20402	carrot
32	30.86141	008.10698	carrot
38B	30.86079	008.15679	bean
38C	30.86079	008.15679	carrot
45	30.88441	008.13748	carrot
56	30.90524	008.14883	carrot
60	30.45156	009.53908	barley
61	30.48576	009.54583	barley
66	30.46640	009.52907	wheat
83	30.49593	009.50106	barley
95	30.48784	009.50401	barley
97	30.49425	009.53397	barley

When more than one crop type was collected from a field site has suffix of B = bean and C = carrot.

APPENDIX B: Field Methods of Analysis

The following analyses were done on the water samples on location in Morocco the evening after each water sample was collected.

pH and Temperature

(a) Remove the protective cap from the pH electrode and check that no air bubbles are trapped in the bulb at the end of the electrode. If air is present in the bulb, shake the electrode like a thermometer to remove the air. Connect the electrode and the temperature probe to the portable pH/Eh meter. Rinse the electrode and probe thoroughly with deionised water and dry them.

(b) Switch on the meter holding the on/off button for a few seconds until the LCD display appears.

(c) To calibrate the meter press the CAL button. The meter is now expecting the 4.01 calibration buffer solution. The first buffer solution measured during calibration is usually 7.01 therefore use the up arrow button to flick through the buffer solution options until 7.01 is selected. The meter is now ready to begin the calibration.

(d) Place the pH electrode and the temperature probe in the first buffer (7.01) and wait for the reading to stabilise. The meter initially indicates that the reading is NOT READY and will flash a READY signal when the reading has stabilised. Once the READY signal has appeared and the reading is stable press the CFM (confirm) button. Record the pH and temperature readings.

(e) The meter automatically expects the second buffer solution. Use the up and down arrow buttons to flick through the buffer solution options until the correct solution is selected (usually 4.01 for acid samples or 1.01 for alkaline samples). The meter is now ready to continue the calibration.

(f) Rinse the electrode and temperature probe thoroughly in deionised water and dry them. Place the electrode and probe in the second buffer solution and wait for the READY signal before pressing the CFM (confirm) button. Note the pH reading. The calibration is now complete and the meter automatically switches to pH measurement mode.

(g) To check the calibration, rinse the electrode and probe in deionised water, dry and return to the first buffer solution. The reading should stabilised around 7.01.

(h) Rinse the electrode and temperature probe thoroughly in deionised water and dry them before measuring the first sample. Rinse the electrode and probe with some of the sample water in-between measuring each sample.

(i) Store the pH electrode with the protective cap containing pH electrode storage solution over the end. Do not allow it to dry out. Care must be taken to avoid damage to the bulb at the end of the electrode.

(j) If the electrode performance is not satisfactory on calibration try shaking it to remove any air from the bulb.

Redox Potential

(a) Remove the protective cap from the redox (Eh) electrode and uncover the filling hole. Fill the electrode using Orion filling solution 90-00-11 to just below the filling hole. Empty the solution to waste by pushing the cap and body together and refill with solution ensuring that no bubbles are trapped around the electrode base. Connect the electrode and the temperature probe to the pH/Eh meter. Rinse the electrode and probe in deionised water and dry them.

(b) Switch on the meter holding the on/off button for a few seconds until the LCD display appears.

(c) Select the redox measurement function by pressing the RANGE button, mV will appear on the display.

(d) To check the electrode performance, place the electrode and probe in Zobelles solution. The value should settle between 200 and 250 mV, depending on the temperature.

(e) Rinse the electrode and temperature probe thoroughly in deionised water and dry them before measuring the first sample. Rinse the electrode and probe with some of the sample water in-between measuring each sample.

(f) The readings obtained require correction to redox potential relative to the standard hydrogen electrode according to the formula: Corrected Eh = Measured Eh + (224 - Temperature °C)

(g) Prior to storage the electrode should be emptied and rinsed with deionised water. Store the electrode dry with the protective cap in place. A small amount of electrode storage solution should be added to the cap before storage.

Total Alkalinity

(a) Select a sulphuric acid cartridge 1.6N or 0.16N according to the expected alkalinity of the samples.

(b) Fit the cartridge to the hand held digital titrator and push the titrator piston down until it meets the top of the cartridge. Remove the cap from the cartridge and fit a feeder straw into the end of the cartridge. Wind the large wheel on the titrator until all the air is removed from the cartridge and the straw and a drop of acid leaves the end of the straw. Wipe the end of the straw to remove excess acid. Reset the titrator scale to zero by winding the small wheel to the left of the scale forwards.

(c) Rinse the measuring cylinder and conical flask with deionised water prior to rinsing them with a small amount of the first sample. Using the measuring cylinder, measure 100 ml of the first sample into the conical flask.

(d) Make sure the lid is securely tightened on the sample bottle in-between each stage of the measurements to reduce degassing of the samples.

(e) Add a few (two) drops of bromocresol green indicator using a small pipette.

(f) Add the acid using the large wheel on the titrator until the solution changes from blue to green-yellow and note the reading on the titrator scale when this occurs.

(g) When the 0.16N cartridge is used the readings should be multiplied by 0.1.

(h) The reading is the total alkalinity expressed as mg/l $CaCO_3$.

(i) The titrator should be reset to zero and the conical flask and measuring cylinder rinsed in a small amount of the next sample prior to the next measurement.

(j) Titrations should be carried out as quickly as possible to reduce degassing effects.

Conductivity

(a) Remove the plastic cover from the conductivity probe and rinse the probe and the cover in deionised water. Dry the probe and the cover and replace the cover. Connect the conductivity probe to the conductivity meter.

(b) Switch on the meter and place the probe in the 12.88 mS. calibration buffer solution making sure the solution covers the probe up to the join between the probe and the cover. The holes in the cover must be immersed in the solution.

(c) Shake the probe in the solution to remove any air bubbles trapped between the probe and the cover. This is important as the probe measures conductivity in the volume of liquid defined by the cover therefore air trapped in the cover will affect the readings.

(d) Press the CAL button and the 1413 µS indicator will be lit on the LCD display. Press the BUF button to change to the 12.88 mS calibration.

(e) When the reading is stable and the calibration is within +/- 15% of the ideal value the BUF indicator on the display stops flashing and the CON indicator appears on the display. When the CON indicator appears press the CFM (confirm) button. The meter is now calibrated and will automatically return to measurement mode. To quit from calibration mode at any time press the CAL button.

(f) Remove the plastic cover from the probe, rinse with deionised water and dry the probe and the cover prior to measuring each sample. Remember to cover the probe with sample up to the join between the cover and the probe and to remove air by shaking the probe.

(g) The probe and cover should be rinsed in deionised water and dried before storage.

(h) If the meter is difficult to calibrate try shaking the probe to remove air trapped under the cover.

APPENDIX C: Iodine Analytical Methods

DETERMINATION OF IODINE IN GEOLOGICAL AND BIOLOGICAL SAMPLES BY ICP-MS

Instrumentation

The ICP-MS instrument used in this work was a VG Elemental PQ-2+ in conjunction with a Gilson autosampler. The system is controlled by a Dell Optiplex computer through dedicated ICP-MS software. The ICP RF forward power used is 1350 W. Coolant, auxiliary and injector gas flow rates are set at 13.5, 0.9 and 0.95 l min^{-1} respectively. Data were acquired in peak jumping mode using 3 x 30 s acquisitions.

Theory of ICP-MS

An ICP-MS instrument consists of an inductively coupled plasma, which provides a source of positively charged ions, and a quadrupole mass spectrometer, which detects these ions, linked by an interface. Liquid samples are passed through a nebuliser, and the resulting sample aerosol and argon mixture passes through a water-cooled spray chamber, to remove the larger droplets, before injection into the central channel of the ICP torch. At the high temperatures of the ICP (in excess of 6000°C) the sample is desolvated and substantially ionised.

The positively charged elemental ions are extracted from the plasma into the vacuum system of the mass spectrometer. The ions pass through a sampling orifice of 1 mm diameter into a mechanically pumped vacuum system, where a supersonic jet forms. The central section of this jet is extracted through the skimmer orifice of 0.7 mm diameter and then focussed by a series of electrostatic ion lenses into the quadrupole mass analyser. DC and RF voltages are applied to opposite pairs of the four rods of the quadrupole. These voltages are varied such that only ions of a given mass:charge ratio will have a stable path through the rods and emerge from the other end. By varying the DC and RF voltages rapidly, the mass spectrometer is able to sweep across the mass range from 0 to 300 mass units in less than a second.

The ions transmitted by the quadrupole are detected using an electron multiplier. Counts for a particular mass are accumulated for a number of sweeps across the mass range and are proportional to the concentration of that element being aspirated. The response at any mass is calibrated against standards containing a known concentration of the element of interest.

Analytical Method

An element menu containing isotopes of the elements of interest was compiled. Iodine is monoisotopic with a natural abundance of 100%, therefore ^{127}I was used for the determination of iodine. Calibration standards containing iodine at 0, 0.05, 0.1, 0.2, 0.5, 1, 5, 10, 25 and 50 µg l^{-1}

were prepared by dilution from 1000 µg l^{-1} KI (BDH, Aristar). A 50 µg l^{-1} iodine check solution was included at regular intervals throughout the analysis run and used to correct for changes in sensitivity. All standard solutions were prepared in 1% TMAH (Tetramethyl Ammonium Hydroxide) and contained 50 µgl^{-1} Sb as an internal standard. Antimony was chosen in preference to conventional elements such as indium because of its superior stability in alkaline media. Raw data was transferred to an Excel spreadsheet and corrected for matrix suppression (using Sb as the internal standard), sample dilution and reagent blanks.

Sample Preparation

Water samples were diluted to 1% TMAH, by the addition of 0.2 ml of 25% TMAH and 0.05 ml of 5 mgl^{-1} Sb internal standard (50 µgl^{-1}) to 4.75 ml of water sample. The water samples were then aspirated directly into the ICP.

For solid samples, 5ml of 5% TMAH was added to 0.1 g of soil or 0.25 g of biological material, mixed thoroughly and heated in an oven at 70°C for 3 hours. After cooling, 5 ml of deionised water was added and the solutions centrifuged at 2,500 rpm for 20 minutes. The final solution containing 1% TMAH and 50 µgl^{-1} Sb was analysed by ICP-MS.

To investigate iodine solubility from soils, 25 ml of deionised water was added to 2.5 g of soil and shaken for 15 minutes. The samples were immediately centrifuged at 2,500 rpm for 10 minutes. An aliquot of the soluble fraction (20 ml) was transferred to a 30 ml nalgene bottle, to which 0.8 ml of 25% TMAH was added to give a final solution in 1% TMAH for storage.

Data Quality

The accuracy and precision of the method were assessed using geological and biological reference materials (Tables 1 and 2).

Chinese reference soils		Replicates	ICP-MS (TMAH)	Certified value	Literature values
GSS-1	(Dark brown)	6	1.7 ± 0.3	1.9 ± 0.4	1.6 – 2.3
GSS-2	(Chestnut)	27	1.3 ± 0.2	1.8 ± 0.2	1.3 – 1.9
GSS-3	(Yellow-brown)	8	1.0 ± 0.2	1.3 ± 0.4	1.2 – 1.4
GSS-4	(Limy)	10	8.5 ± 0.9	9.4 ± 1.2	7.9 – 10.4
GSS-6	(Yellow-red)	16	20.1 ± 1.2	19.4 ± 1.0	18.9 – 22.9

Table 1: Iodine concentrations (mgkg^{-1}) for geological reference materials.

Biological reference materials	Replicates	ICP-MS (TMAH)	Certified value	Literature values
SRM 1573a (Tomato leaves)	7	0.60 ± 0.10	(0.85)	
BCR 129 (Hay powder)	3	0.13 ± 0.01	0.17 ± 0.02	0.16 – 0.18
BCR 151 (Milk powder)	4	4.94 ± 0.06	5.35 ± 0.14	5.10 – 6.40
GSV-4 (Tea)	4	0.14 ± 0.04	(0.11)	
GBW 09101 (Human hair)	5	0.62 ± 0.10	(0.88)	

Table 2: Iodine concentrations (mgkg^{-1}) for biological reference materials.

Given that many of the reference materials only have indicative iodine concentrations or wide variances on the certified mean value, the ICP-MS methodology compared favourably with other reported data.

Independent QC solutions at 50 µg l^{1} were also included in the analytical runs and were within our normal control limits of ± 5%. Recoveries from spiked soil samples were between 92 and 98%.

Dr M J Watts

ICP-MS Section

20 August 2002

APPENDIX D: List BGS analytical reports

Soils - BGS analytical Report Number 10284/1

Report Number:	10284/1	Customer Ref/Order No:	IR 00812
Report Date:	6 June 2002	Sample(s) received on:	17 April 2002
Issue Status:	Intermediate	Analysis commenced on:	17 April 2002

Sample Details

All samples were received in good condition and prepared as per your instruction sheet. The samples for iodine analysis were extracted in TMAH by heating 0.1 g of sample with 5 ml of 5% TMAH at 70°C for 3 hours before diluting to 2.5% TMAH and centrifugation. The samples were analysed by ICP-MS against calibration standards containing the same proportion of TMAH.

The samples will be returned to you when all the analysis requested has been completed.

Analysis Details

Determinands	Test Method	Notes
Iodine	ICP-MS	
pH	Potentiometric electrode	
Loss on ignition at 450°C	Gravimetric analysis	

Because the method for iodine is relatively new, there are no QC charts for the method. However, a number of reference materials were analysed alongside the samples and these were used to assess the accuracy of the determinations. Between 1 and 2 mg/kg iodine the recoveries were better than 70%; this increased to 80-86% at 9 mg/kg and 108% at 20 mg/kg I. Given the uncertainty of the reference values, these recoveries were considered to be acceptable.

Because of limitations with the current software used for reporting data, the number of significant figures quoted in the attached table may not be representative of the actual uncertainty. Data should be considered accurate to no more than three significant figures.

This report is issued under intermediate status. All the analyses requested initially have been completed, and these are issued with full compliance of data verification. We await your instructions for the determination of selected samples for CEC and cold water extractable iodine.

Report authorised by: …… ……………. Date: …6 June 2002….

Ms Jennifer M Cook
ICP-MS Section Manager

LIMS ID	**CUSTOMER ID**		**pH**	**% LOI**	**Iodine**
					mg/kg
10284-0001	MRS1		7.49	4.92	1.39
10284-0002	MRS2	Replicate of MRS21	7.64	3.30	2.48
10284-0003	MRS3		7.34	3.25	2.58
10284-0004	MRS4		7.61	7.80	2.39
10284-0005	MRS5		7.74	3.70	2.13
10284-0006	MRS7		7.70	1.59	0.47
10284-0007	MRS8		7.69	2.51	1.41
10284-0008	MRS9		7.89	5.24	1.68
10284-0009	MRS11	Replicate of MRS39	7.68	3.30	1.18
10284-0010	MRS12	Replicate of MRS69	7.63	7.02	1.87
10284-0011	MRS14	Replicate of MRS74	7.68	4.00	4.39
10284-0012	MRS15		7.46	7.02	1.03
10284-0013	MRS16		7.55	3.07	1.62
10284-0014	MRS17		7.58	7.03	2.15
10284-0015	MRS19		6.50	3.79	1.35
10284-0016	MRS20		7.50	4.33	1.22
10284-0017	MRS21		7.08	3.45	2.40
10284-0018	MRS22	Standard	n/a	n/a	1.32
10284-0019	MRS23		7.53	4.60	3.06
10284-0020	MRS24		7.57	1.51	0.40
10284-0021	MRS25		7.56	4.68	4.48
10284-0022	MRS26		7.48	1.55	0.32
10284-0023	MRS27	Standard	n/a	n/a	1.36
10284-0024	MRS28		7.77	4.88	1.30
10284-0025	MRS29		7.88	1.74	2.33
10284-0026	MRS32		7.79	7.28	2.40
10284-0027	MRS34		7.56	3.34	2.05
10284-0028	MRS36		7.57	3.47	3.92
10284-0029	MRS37		7.57	6.43	1.94
10284-0030	MRS38		8.09	4.81	0.81
10284-0031	MRS39		7.70	3.50	1.16
10284-0032	MRS41		7.71	3.10	1.14
10284-0033	MRS42		7.64	3.57	1.40
10284-0034	MRS43		7.64	6.63	6.38
10284-0035	MRS44		7.48	4.13	4.63
10284-0036	MRS45		7.84	3.45	0.77
10284-0037	MRS46		7.29	6.91	3.12
10284-0038	MRS47		6.99	4.73	1.37
10284-0039	MRS48		7.49	5.95	4.17
10284-0040	MRS51		7.56	5.56	4.06
10284-0041	MRS52		7.58	4.15	1.74
10284-0042	MRS54		7.67	3.75	0.79
10284-0043	MRS56		7.81	7.05	1.33
10284-0044	MRS57		7.58	3.42	2.25
10284-0045	MRS58		7.59	2.96	1.17
10284-0046	MRS59		7.54	4.96	4.07
10284-0047	MRS60		7.51	3.74	2.00

10284-0049	MRS62		7.45	3.51	0.87
10284-0050	MRS65		7.55	6.58	1.87
10284-0051	MRS66		7.54	4.04	3.36
10284-0052	MRS67		7.56	3.42	2.31
10284-0053	MRS69		7.52	6.93	1.86
10284-0054	MRS71		7.53	4.73	7.14
10284-0055	MRS73		7.91	3.36	1.36
10284-0056	MRS74		7.42	4.21	4.08
10284-0057	MRS77		7.61	3.55	1.09
10284-0058	MRS80		7.66	3.50	1.21
10284-0059	MRS81	Replicate of MRS97	7.54	4.06	4.25
10284-0060	MRS82		7.55	2.29	0.45
10284-0061	MRS83		7.59	4.02	2.64
10284-0062	MRS84		7.47	4.32	2.21
10284-0063	MRS85		7.42	3.09	2.35
10284-0064	MRS86	Replicate of MRS90	7.51	7.39	1.83
10284-0065	MRS87	Replicate of MRS19	7.58	3.59	1.29
10284-0066	MRS88		7.55	4.02	2.42
10284-0067	MRS89		7.87	0.66	0.59
10284-0068	MRS90		7.50	7.18	1.83
10284-0069	MRS91		7.79	2.50	0.67
10284-0070	MRS92	Replicate of MRS95	7.50	3.33	2.33
10284-0071	MRS93		7.65	1.76	0.88
10284-0072	MRS94		7.57	4.97	1.86
10284-0073	MRS95		7.43	3.43	2.36
10284-0074	MRS96		7.28	2.05	1.23
10284-0075	MRS97		7.50	4.18	3.98
10284-0076	MRS98		7.30	2.23	0.62
10284-0077	MRS99		7.21	3.09	1.23
10284-0078	MRS100		7.24	3.08	1.19

Soils - BGS analytical Report Number 10284/1

Updated with additional water-extractable iodine results.

Raw data presented in **Table 5** in the main text.

Waters - BGS analytical Report Number 10280/1

Report Number:	10280/1	Customer Ref/Order No:	IR 00811
Report Date:	28 June 2002	Sample(s) received on:	15 April 2002
Issue Status:	Complete	Analysis commenced on:	02 May 2002

Sample Details

All samples were received preserved with 1 pellet of NaOH. 1% TMAH was added to all samples before analysis by ICP-MS against calibration standards containing the same proportion of TMAH.

Unless previously agreed otherwise in writing, samples will be retained for three months from the date of issue of this report prior to disposal. Please contact the Laboratory if you wish to make alternative arrangements.

Analysis Details

Determinands	Test Method	Notes
Iodine	ICP-MS	

Because the method for iodine is relatively new, there are no QC charts for the method and we do not possess a water reference material certified for iodine. However, a soil reference material GSS2 was analysed alongside the samples and gave value of 1.45 mg/kg against the reference value of 1.8 mg/kg. Given the uncertainty of the reference value, this recovery was considered to be acceptable as it was consistent with previous measurements.

Because of limitations with the current software used for reporting data, the number of significant figures quoted in the attached table may not be representative of the actual uncertainty. Data should be considered accurate to no more than three significant figures.

This report is issued under complete status. All analyses requested have been completed and results are issued with full compliance of data verification.

Report authorised by: ………………………………………   Date: ……28th June 2002

Ms Jennifer M Cook
ICP-MS Section Manager

CUSTOMER ID		**LAB ID**	**Iodine**
			µg/l
MRW 1	Talat-N-Ya'Qoub	10280-0001	2.8
MRW 4	Talat-N-Ya'Qoub	10280-0002	0.8
MRW 10	Blank	10280-0003	2.1
MRW 13	Agadir	10280-0004	3.1
MRW 17	Talat-N-Ya'Qoub	10280-0005	1.1
MRW 18	Talat-N-Ya'Qoub	10280-0006	0.5
MRW 19	Duplicate of MRW39	10280-0007	1.1
MRW 28	Talat-N-Ya'Qoub	10280-0008	1.1
MRW 33	Duplicate of MRW50	10280-0009	20.8
MRW 35	Duplicate of MRW13	10280-0010	3.1
MRW 38	Talat-N-Ya'Qoub	10280-0011	2.3
MRW 39	Talat-N-Ya'Qoub	10280-0012	1.2
MRW 40	Agadir	10280-0013	13.2
MRW 45	Talat-N-Ya'Qoub	10280-0014	1.9
MRW 49	Talat-N-Ya'Qoub	10280-0015	2.0
MRW 50	Ghabat Admine	10280-0016	20.7
MRW 56	Talat-N-Ya'Qoub	10280-0017	1.5
MRW 64	Agadir	10280-0018	14.4
MRW 70	Agadir	10280-0019	35.2
MRW 72	Talat-N-Ya'Qoub	10280-0020	2.5
MRW 75	Blank	10280-0021	2.1
MRW 79	Agadir	10280-0022	22.4
MRW 83	Agadir	10280-0023	12.3
MRW 97	Agadir	10280-0024	20.9

Crop Samples - BGS analytical Report Number 10285/1

Report Number:	10285/1	Customer Ref/Order No:	IR 00813
Report Date:	7 June 2002	Sample(s) received on:	17 April 2002
Issue Status:	Complete	Analysis commenced on:	17 April 2002

Sample Details

All samples were received in good condition. They were freeze dried and blended as instructed. The samples for iodine analysis were extracted in TMAH by heating 0.25 g of sample with 5 ml of 5% TMAH at 70°C for 3 hours before diluting to 2.5% TMAH and centrifugation. The samples were analysed by ICP-MS against calibration standards containing the same proportion of TMAH.
The excess powders will be returned to you.

Analysis Details

Determinands	Test Method	Notes
Iodine	ICP-MS	

Because the method for iodine is relatively new, there are no QC charts for the method. However, a number of reference materials were analysed alongside the samples and these were used to assess the accuracy of the determinations. Recoveries for SRM1573 (Tomato leaves), BCR129 (Hay powder) and GSV4 (Tea) were 61%, 84% and 100% respectively. Given the uncertainty of the reference values, these recoveries were considered to be acceptable.

Because of limitations with the current software used for reporting data, the number of significant figures quoted in the attached table may not be representative of the actual uncertainty. Data should be considered accurate to no more than three significant figures.

This report is issued under complete status. All analyses requested have been completed and results are issued with full compliance of data verification.

Report authorised by: ………………………………………. Date: ……7 June 2002….

Ms Jennifer M Cook, ICP-MS Section Manager

CUSTOMER ID		Sample ID	Iodine
			mg/kg
MRV1	potato	10285-0001	<0.01
MRV4B	bean	10285-0002	<0.01
MRV4C	carrot	10285-0003	0.02
MRV17B	bean	10285-0004	0.01
MRV17C	carrot	10285-0005	0.03
MRV20	barley	10285-0006	0.02
MRV21	barley	10285-0007	0.01
MRV22	Standard	10285-0008	0.49
MRV28B	bean	10285-0009	<0.01
MRV28C	carrot	10285-0010	0.02
MRV32	carrot	10285-0011	0.03
MRV38B	bean	10285-0012	0.01
MRV38C	carrot	10285-0013	0.03
MRV45	carrot	10285-0014	0.03
MRV56	carrot	10285-0015	0.02
MRV60	barley	10285-0016	0.02
MRV61	barley	10285-0017	<0.01
MRV66	wheat	10285-0018	0.04
MRV83	barley	10285-0019	0.02
MRV95	barley	10285-0020	0.01
MRV97	barley	10285-0021	0.02

Salt Samples - BGS analytical Report Number 10300/1

Report Number:	10300/1	Customer Ref/Order No:	IR 00814
Report Date:	7 June 2002	Sample(s) received on:	17 April 2002
Issue Status:	Complete	Analysis commenced on:	17 April 2002

Sample Details

All samples were received in good condition. The samples analysed as received by dissolving 0.1 g in 20 ml of 1% TMAH. The samples were analysed by ICP-MS against calibration standards containing the same proportion of TMAH.
The excess sample will be returned to you.

Analysis Details

Determinands	Test Method	Notes
Iodine	ICP-MS	

Because the method for iodine is relatively new, there are no QC charts for the method. However, a number of reference materials were analysed alongside the samples and these were used to assess the accuracy of the determinations, although none of them were close in composition to the samples of salt. Recoveries for SRM1573 (Tomato leaves), BCR129 (Hay powder) and GSV4 (Tea) were 61%, 84% and 100% respectively. Given the uncertainty of the reference values, these recoveries were considered to be acceptable.

Because of limitations with the current software used for reporting data, the number of significant figures quoted in the attached table may not be representative of the actual uncertainty. Data should be considered accurate to no more than three significant figures.

This report is issued under complete status. All analyses requested have been completed and results are issued with full compliance of data verification.

Report authorised by: ………………………………………. Date: …7th June 2002

Ms Jennifer M Cook
ICP-MS Section Manager

CUSTOMER ID	**Sample ID**	**Iodine**
		mg/kg
Salt 1	10300-0001	12.0
Salt 2	10300-0002	0.14
Salt 3	10300-0003	3.24