

Perchlorate Contamination of Soils Collected from the Maltese Islands

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Abstract

During the summer months, the Maltese Islands experience a large number of religious feasts, most of which are accompanied by firework activity. Between the 26th of January and the 8th of December, approximately 86 religious feasts are celebrated annually in different towns and villages in the Maltese Islands, accompanied by both aerial and ground fireworks displays. The pyrotechnical community counts several thousand enthusiasts who passionately and without any financial compensation produce fireworks. Perchlorate contamination in the environment is a worldwide problem, with high levels detected in dust fall collected from the Maltese Islands (Vella et al., 2015). During this study the levels of perchlorate in soil samples collected from 19 different locations were determined. Perchlorate was detected in 8 of 19 samples, with 3 of these samples having levels below detection limit. The levels ranged from BDL to 357 $\mu\text{g kg}^{-1}$, with a mean value of 49.9 $\mu\text{g kg}^{-1}$. The highest perchlorate concentrations were detected in soils collected from the South of the Maltese Islands, as was observed for dust samples. This was attributed to the predominant wind direction, being from the Northwest, causing the movement of contaminants from the North to the South of the Maltese Islands. These results and perchlorate levels in dust fall (Vella et al., 2015), clearly point out that the Maltese environment is contaminated with perchlorate, due to the excessive pyrotechnic activity.

Keywords: Perchlorate, soil, Maltese Islands, fireworks

Introduction

Perchlorate has recently received great attention since it is a widespread contaminant in ground, surface and drinking water, food, milk, and breast milk (Ginsberg et al., 2005; Trumpolt et al., 2005; Wolff, 1998; Sungur & Sangun, 2011; Sanchez et al., 2006). It is a key component in most of solid propellants as an oxidizer because of its safety, performance, ease of manufacture and handling. In the United States, perchlorate has been used for several decades mainly in national defence for military applications and for manufacture of solid rocket propellants. Currently, there are no other oxidisers to replace perchlorate that can be used for military performance with the same level of

safety and low environmental impact (Cunniff et al., 2006)

In the Maltese Islands, the only known anthropogenic source of perchlorate is that imported for the production of pyrotechnic articles, which are burned locally as ground and aerial production fireworks. The national territory consists of a small (316 km²) archipelago of two densely populated islands, Malta (the larger island) and Gozo located in the central Mediterranean. During the summer months, towns and villages on the islands celebrate religious feasts most of which are accompanied by prolonged firework activity. These festivals (over 85 in number) take place mainly between June and September, with aerial displays being let off at intervals during several days prior to the actual feast day on the Sunday. Since fireworks are a common feature in Maltese village feasts, the occurrence in air, dust and water of perchlorate is expected, especially during the festive season.

The chemicals in fireworks are not entirely used up in the explosion (Camilleri & Vella, 2016) and the post-explosion debris containing unreacted chemicals as well as other reaction products disperse in the environment by wind and other agents. Post-explosion debris may either settle on the ground as contaminated dust or dissolve partly in rain water to release soluble species that can enter the water table. The perchlorate ion is very soluble and quite stable in water bodies. Most studies have shown that perchlorate does not sorb to soils, except for those with a high anion exchange capacity (Urbansky & Brown, 2003). Perchlorate has been shown to be reduced by anaerobic microbial degradation, in the presence of significant amounts of organic carbon and nitrate and in the absence of oxygen (Trumpolt et al., 2005).

Widespread human exposure to perchlorate from both anthropogenic and natural sources occurs mainly through ingestion of water, dust and food. Perchlorate is a dietary goitrogen, since it interferes with the normal function of the thyroid gland. It competitively inhibits uptake of the iodide ion by the sodium-iodide symporters located in the thyroid gland (Charnley, 2008). These symporters are also located in the mammary gland and in the placenta and have a higher affinity to perchlorate than iodide ions (Wolff, 1998). At high levels perchlorate may interfere with the production of triiodothyronine (T3) and thyroxine (T4), which regulate growth, metabolic activity and development (Wolff, 1998). These thyroid hormones are required for normal growth, most importantly in foetuses and newborns where they are involved in the development of the central nervous system (brain and skeleton) and for metabolic activity in adults (Wolff, 1998).

The United States Environmental Protection Agency (US EPA) has set a reference dose (RfD) for perchlorate of 0.7 µg kg⁻¹day⁻¹, which is equivalent to 49 µg per day for a 70 kg adult (Shi et al., 2007).

In this paper, the presence of perchlorate in soils collected from different sites in the Maltese Islands is reported. Recent publications have shown the presence of perchlorate in different matrices, including dust and water samples (Vella et al., 2012; Vella et al., 2015; Pace et al. 2016): These results are novel, since the level of perchlorate in local soil samples, had not previously been determined.

Chemicals and Reagents

Potassium perchlorate (98 + % pure) was obtained from Acros Organics. Sodium hydroxide and sulfuric acid were ANALAR grade reagents from Sigma Aldrich. Deionised water was prepared from distilled water using the Elga Purelab Classic purification system.

Field sample collection and preparation

Surface soil was sampled from 18 different localities in Malta (Figure 1). Soil samples were collected from sites 1 to 12 were collected from agricultural land, while samples from sites 13 to 19 were collected from waste land. The surface soil was sampled (top 0 – 10 cms) using an HDPE sampling bottle and the sample was transferred to a Ziploc polyethylene bag and sealed. A total of 40 g soil was sampled from each site, and this was referred to as the bulk sample. The samples were dried in an oven at 90°C for 48 hrs, after which the soil was powdered using a Kenwood coffee grinder. Any rocks or fauna present in the sample was removed using tweezers prior to drying. Approximately 4 g of sample were accurately weighed and transferred to a 200 mL conical flask, 40 mL of deionized water was added and the solution was stirred for 48 hrs. The solution was then transferred to 50 mL vial and was centrifuged for 20 minutes at high speed. The supernatant was treated with alumina to remove any soil dissolved organic matter which may interfere with the ion chromatographic system. The resulting solution was filtered using Anatop filters and analysed using the ion chromatographic method described below.

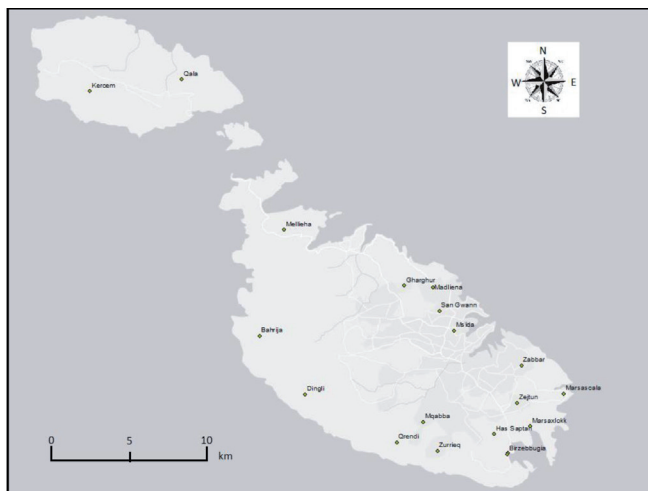


Figure 1 - Sites from which surface soil was sampled for perchlorate and chlorate analysis

In order to confirm that the extraction method is sufficient for the extraction of perchlorate from soil, samples were spiked with a known amount of perchlorate. An unspiked sample was also prepared using the same soil, to establish whether perchlorate is originally present in the sampled soil and at what concentration. The % recoveries for spiked samples ranged from 80.4 % to 104.0 %.

Chromatographic analysis

The apparatus used was a Thermo Scientific Dionex ICS 900 system equipped with a 250 mm x 4 mm analytical column (Dionex IonPac AS16) and a 50 mm x 4 mm guard column (Dionex IonPac AG16). The ICS 900 was equipped with an Anion ICE-Micromembrane Suppressor AMMS ICE-300 to reduce background conductivity and increase analyte signal. The injection volume was 700 μL with a flow rate of 0.8 mL/min: an autosampler was used. The eluent and regenerant solutions were 50 mM NaOH and 37.5 mM H_2SO_4 , respectively. Perchlorate eluted at approximately 18 minutes. The peak area in a sample was compared with that of external working standards at 28 and 11 $\mu\text{g L}^{-1}$ which standards were used to bracket the field samples. Working standards were prepared weekly from a stock solution (1.1 g L^{-1}) by serial dilution. The chromatographic method was validated using standard solutions ranging from 2 to 200 $\mu\text{g L}^{-1}$ for which the correlation coefficient r^2 was 0.999. The limit of detection for perchlorate in soils was 20 $\mu\text{g kg}^{-1}$. Samples containing perchlorate at concentrations below these levels are below detection limit. Blank runs were performed prior to sample analysis to confirm absence of carryover from previous runs or other contamination and every ten field samples were bracketed with standard perchlorate solution for quality assurance.

Results and Discussion

Perchlorate content in soils from different localities were determined. The results are shown in Table 1. Figure 1 shows the spatial distribution of perchlorate in soils in Malta and Gozo.

Site	Soil Sample (Locality)	Sampling Date	Perchlorate (μgkg^{-1})	Chlorate (μgkg^{-1})
1	San Gwann	March 2013	ND	ND
2	Madliena	March 2013	36.8	(29.3)
3	Gharghur	March 2013	ND	(30.3)
4	Qrendi	March 2013	315	68.7
5	Zurrieq	March 2013	(14.9)	ND
6	Mqabba	March 2013	ND	94.4
7	Dingli	March 2013	82.1	ND
8	Bahrija	March 2013	103	(15.0)
9	Birzebbugia	March 2013	ND	ND
10	Mellieha	March 2013	(18.2)	65.5
11	Kercem	March 2013	ND	ND
12	Qala	March 2013	(4.30)	ND
13	Marsaxlokk	September 2013	(10.8)	ND
14	Zabbar	September 2013	ND	(30.6)
15	Zejtun	September 2013	(0.50)	(20.9)
16	Marsascala	September 2013	ND	ND
17	Birzebbugia	September 2013	(2.00)	83.9
18	Msida	September 2013	(3.10)	ND
19	Hal Saptan	October 2013	356.8	ND

ND - Not Detected; Values in parenthesis are below detection limit.

Table 1 - Perchlorate and chlorate concentrations ($\mu\text{g kg}^{-1}$) in soils collected from different localities during March, September and October 2013.

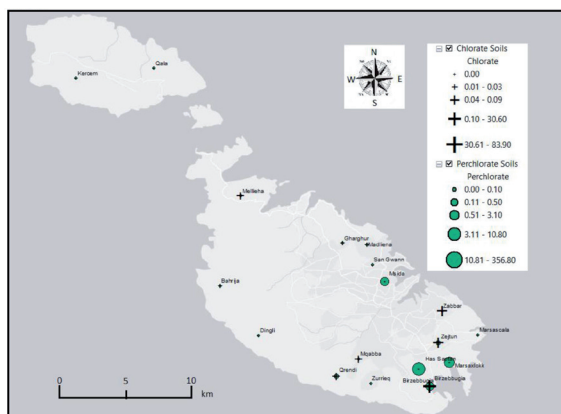


Figure 1 - Map of the Maltese Islands showing the concentrations of perchlorate for soils collected from different localities during March and September 2013 using ArcMap 10.1 Software

The highest concentration of perchlorate was observed in Hal Saptan at $357 \mu\text{g kg}^{-1}$, followed by Qrendi with a concentration of $315 \mu\text{g kg}^{-1}$. Perchlorate was detected in 8 of 19 samples, however 3 of the 8 samples had levels below the detection limit. The highest perchlorate concentrations were detected in soils collected from the South of the Maltese Islands, as was observed for dust samples. This was attributed to the predominant wind direction, being from the Northwest, causing the movement of contaminants from the North to the South of the Maltese Islands.

The concentrations of perchlorate in soils collected from the Maltese Islands were higher than those detected in soils collected from other countries. In a study carried out in Northeastern China, soils were collected during September 2010 and March 2011 (Ye et al., 2013). Fireworks and firecracker displays were held between the Spring Festival on the 2nd February 2011 and the Lantern Festival on the 17th of February 2011. For the soils collected during September 2010, perchlorate was detected in only 1 of 36 samples, presumable because perchlorate in the soil would have been washed out by the melting snow and precipitation which is very common in the Summer months (between May and September), in this part of China. All the soil samples collected during March 2011 contained detectable levels of perchlorate with concentrations ranging from 2.15 to $7.02 \mu\text{g kg}^{-1}$. The increase in perchlorate in soils collected during March, was attributed to the firework displays during February. The concentration of perchlorate in local soils ranged from BDL to $356.8 \mu\text{g kg}^{-1}$ with a mean value of $49.9 \mu\text{g kg}^{-1}$, which compares with the mean for Chinese soils of $3.87 \mu\text{g kg}^{-1}$, i.e. one tenth that of Malta. Most of the local soil samples were collected during the fireworks-free period, however perchlorate was still detected in 50 % of the samples collected during March. Even though large amounts of precipitation (356 mm) took place between the 'festa' season and collection of the samples, perchlorate was still detected in half of the samples.

During another study carried out in China, the concentration of perchlorate ranged from 0.001 to 216 mg/kg (Zhiwey et al., 2014), with higher concentrations in Northern China when compared to Southern China. Northern China is drier than Southern China, therefore the deposited perchlorate will be less mobilized in Northern China compared to Southern China, resulting in higher concentrations in dust and soils. This concentration is approximately 1000 times higher than the concentrations found in the Maltese soils. The reason for such a large difference could be due to the large consumption of fireworks in China during a short period of time, just before sampling.

The levels of perchlorate and chlorate detected in soils were much lower than those detected in local dust fall samples. The mean concentrations of perchlorate and chlorate in dust fall samples collected during 2012 were 500 times and 200 times higher than those detected in soil samples respectively. The average concentration of perchlorate in dust fall was 24.1 mg kg^{-1} , compared to $49.9 \mu\text{g kg}^{-1}$ in soils. The higher concentrations of perchlorate in dust fall are expected, since, in the absence

of rain, the main method of downward transport of post-firework debris from the atmosphere is by deposition of dust. In soils the concentrations are diluted, since there are many other components present. Also, when precipitation takes place any perchlorate present in soils is expected to dissolve and will percolate into the water table. In the study carried out in China (Zhiwey et al., 2014), on perchlorate levels in dust and soils, the concentrations of perchlorate in dust were 25 times to 150 times higher than those detected in soils, as was observed locally.

A large number of studies have been carried out on perchlorate degradation in soils. During a study carried out by Tipton et al. (2003), it was shown that perchlorate can be degraded by some microorganisms in the presence of moisture, a carbon source and anaerobic conditions. In most cases the limiting factor is not the microbes but the environmental conditions (Wu et al., 2001). In another study on degradation of perchlorate in the presence of nitrate, it was shown that high nitrate concentrations interfere with perchlorate degradation in soils (Tan et al., 2004). The presence of nitrate, especially when in high concentrations as in the case of the Maltese soils, explains the persistence of perchlorate which is present in lower concentrations. However, during the study by Tipton (2003) it was shown that in soils which had previously been exposed to perchlorate, the microbes will degrade perchlorate and nitrate simultaneously.

Studies have been conducted showing that perchlorate is able to move from perchlorate-contaminated soils through the roots and accumulates in tissues and other plant organs (Sundberg et al., 2003). Plant uptake of water-soluble contaminants, such as perchlorate, occurs via passive transport by processes of diffusion and mass flow with no sufficient barriers for these contaminants. This is very worrying since perchlorate is easily transported in crops and is retained. Nowadays, there is a great deal of research being carried out with respect to uptake of perchlorate in plants, with the main reason being that these crops are used for human consumption with consequent health implications on humans. One advantage for the phytoaccumulation of perchlorate is the remediation of perchlorate from contaminated sites with many studies confirming this. Dust fall containing perchlorate may deposit on lettuce leaves, however for perchlorate to enter the plant it must enter through the roots into the transpiration stream. This means that perchlorate present in dust and soil has to dissolve in water (irrigation or precipitation), for bioconcentration to take place.

According to the National Statistics Office, the consumption of perchlorate in the Maltese Islands has decreased from 17 tonnes per annum in 2010 to about 2.5 tonnes per annum for years between 2011 and 2014. From levels of perchlorate detected in dust fall samples and from the rate of total deposition, it was calculated that the actual imported amount in 2012 of perchlorate was 90 tonnes, 36 times higher than the registered amount (Pace et al., 2016). This environmental evidence appears to provide proof that pyrotechnic manufacturing on Malta is more active than officially recognized which increases the risk to both the pyrotechnic community, and also

the health of the general population, due to negative impacts from contaminated dust, soils and water.

Conclusion

The levels of perchlorate in soil collected from 19 different localities ranged from BDL to 357 $\mu\text{g kg}^{-1}$. The highest perchlorate concentrations were observed in soils collected from Hal Saptan and Qrendi, both of which are located to the South of the Maltese Islands. The highest concentrations were detected in sites to the South of the Maltese Islands, due to the predominant Northwesterly wind. This causes the transfer of the contaminated dust and airborne particles to the South of the Maltese Islands. In most of the foreign studies it has been shown that high perchlorate concentrations were detected in breast milk, dairy milk and infant formula solutions (Borjan et al., 2011; Valentini-Blasini et al., 2007; Leung et al., 2009; Dyke et al., 2007; Kirk et al., 2005), meaning that newborns are also at a high risk from the adverse effects caused by perchlorate. Since no studies on perchlorate levels in breast milk and dairy milk have been carried out locally, the extent of the damage to these susceptible individuals is not yet known.

Since the results of this work have shown elevated levels of perchlorate in soils, it would appear prudent to consider whether there is a connection between perchlorate concentration and human health, including the local occurrence of thyroid disorders, including cancer. The precautionary principle would argue for a reduction in the intensity of firework activities, which clearly conduce to the presence of the contaminants in the environment, even if such activities may otherwise be beneficial for the development of Malta's tourism and cultural entertainment sector.

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Bio-note

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