



Perchlorate in dust fall and indoor dust in Malta: An effect of fireworks



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ABSTRACT

We report on the presence of perchlorate in the settleable dust of Malta, a small central Mediterranean island. Both dust fall collected directly as it precipitated from atmosphere over a period of one month and deposited indoor dust from domestic residences were studied. Perchlorate was determined by ion chromatography of water extracts of the collected dusts. Dust fall was collected from 43 towns during 2011 to 2013 and indoor dust was sampled from homes in the same localities. Perchlorate was detected in 108 of 153 samples of dust fall (71%) and in 28 of 37 indoor dust samples (76%). Detectable perchlorate in dust fall ranged from $0.52 \mu\text{g g}^{-1}$ to $561 \mu\text{g g}^{-1}$ with a median value of $6.2 \mu\text{g g}^{-1}$; in indoor dust, levels were from $0.79 \mu\text{g g}^{-1}$ to $53 \mu\text{g g}^{-1}$ with a median value of $7.8 \mu\text{g g}^{-1}$, the highest recorded anywhere to date. Statistical analysis suggested that there was no significant difference in perchlorate content of indoor dust and dust fall. Perchlorate levels in dust fall escalate during the summer in response to numerous religious feasts celebrated with fireworks and perchlorate persists at low $\mu\text{g g}^{-1}$ concentrations for several months beyond the summer festive period. In Malta, perchlorate derives exclusively from KClO_4 , imported for fireworks manufacture. Its residue in dust presents an exposure risk to the population, especially via ingestion by hand to mouth transfer. Our results suggest that wherever intensive burning of fireworks takes place, the environmental impact may be much longer lived than realised, mainly due to re-suspension and deposition of contaminated settled dust in the urban environment.

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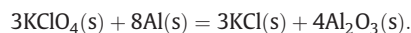
1. Introduction

The literature on the presence of perchlorate in the environment is substantial and constantly growing (Urbansky, 1998, 2002; Trumppolt et al., 2005; Gu and Coates, 2006; Sellers et al., 2007; Sijimol and Mohan, 2014): the concern over perchlorate relates to the chemical's known interference with thyroid function (Wolff, 1998; Greer et al., 2002) and the recent finding of this substance's apparent ubiquity especially in groundwater (Her et al., 2010; Sungur and Sangun, 2011; Jackson et al., 2005) and in foods (Sanchez et al., 2006; Lee et al., 2012; FDA, 2013). Most perchlorate is employed for the manufacture of solid rocket propellant and military explosives although it has various other manufacturing applications such as paints, tanning and rubber; it is also employed in pyrotechnic applications including highway flares, air bags and fireworks.

It is the use of perchlorate in fireworks that is of special interest for the Maltese Islands, a small (316 km^2) archipelago of two densely populated islands (ca. 0.4 million) in the central Mediterranean, and this is because the country has a zealous pyrotechnical community of over 1500 enthusiasts who produce fireworks as a hobby and without pecuniary interest. These skilful enthusiasts competitively display their wares in ground and aerial shows held during a summer-long period

as centre-pieces of religious festivals (known locally as *fešta*), of which over 85 are celebrated mainly between June and September. The tradition is centuries old and, if anything, fireworks are becoming even more popular: thus, since 2001, a week-long fireworks festival, unrelated to any religious *fešta*, is also being held in spring (April) and additional firework activity may continue to materialize in response to demand by tourism which is a major contributor to the European island state's economy.

Potassium perchlorate is mixed with aluminium to produce blasting powder which, upon explosion, produces solids according to the equation



The post-explosive matter is released to atmosphere as dust, in addition to unburnt potassium perchlorate and aluminium. Another composition (flash powder) also includes antimony trisulfide with aluminium as reducing agents and this adds antimony trioxide to post-explosive dust.

Dust is a significant source of human exposure to chemicals: the airborne fine particulates present an inhalation risk while coarser material which deposits as dust fall is a risk from ingestion (Christoforidis and Stamatis, 2009; Shi et al., 2011), especially for infants and children who are more prone to transferring matter from hand to mouth (Glorennec et al., 2012). Persons afflicted with pica are particularly at risk from dust ingestion. Chemicals in dust fall also represent a source

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of contamination to crops and vegetables (Smith et al., 2004; Shi et al., 2007) and are thus potential sources for consumers of these foods (Lee et al., 2012; Asami et al., 2013). Not much is known about the presence of perchlorate in dust fall. Recent work from China (Gan et al., 2014) reports perchlorate in dust collected shortly after the New Year celebrations during February–March 2013 and found values ranging from 0.132 to 5300 $\mu\text{g g}^{-1}$, but these results pertained to dust settled on window sills or building surfaces in several cities.

In this paper, we present new data which reports on perchlorate in dust fall collected directly as it precipitates from atmosphere; the period of observation was moreover extended to include several months during which very little or no pyrotechnic activity takes place and this with a view to understand better the duration and extent of exposure of the islanders to perchlorate. To our knowledge, most previous investigations have considered dust collected from surfaces shortly following temporally and spatially proximate firework activity. The chemical composition of the dust was determined in order to shed light on its origin. We also present data on perchlorate in indoor dust and compare our results with a recently published first report on similar information from twelve countries (Wan et al., 2015). The implications of our findings to human health are discussed.

2. Materials and methods

2.1. Chemicals and reagents

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

2.2. Field sample collection and preparation

Dust fall was collected from a total of 43 sites from both the main island of Malta and the smaller island of Gozo (Fig. 1), 38 sites of which were sampled during September and October 2011 and 17 sites during March, May, July, August, October and December 2012 and February 2013. Dust fall was collected in four Beatson jars of 10 cm diameter which were exposed for about 30 days on rooftops of houses, away from walls. After collection, the jars were capped and stored at room temperature pending analysis. Any rain water which collected together with dust in the jar was evaporated in an oven and the deposit analysed as described for the dry dusts. Settled indoor dust was collected in

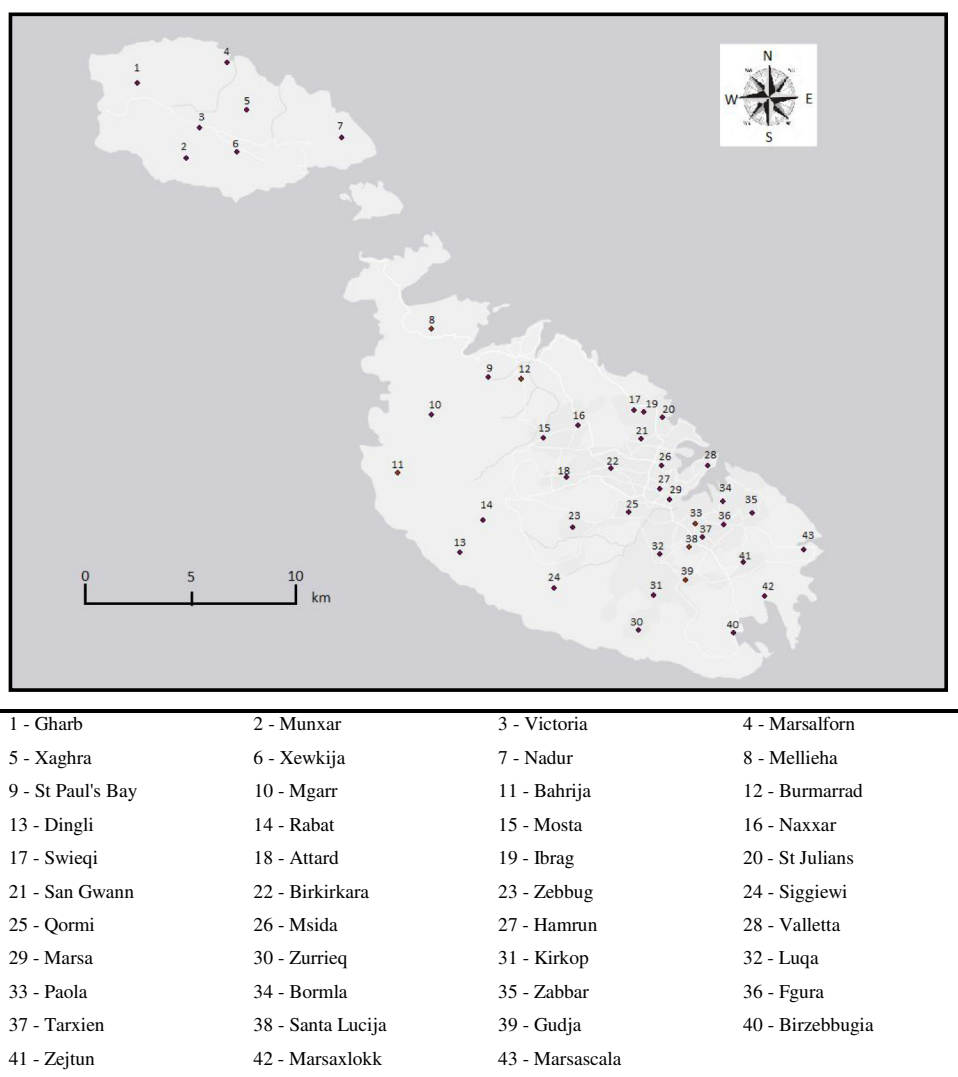


Fig. 1. Map of the Maltese Islands showing the localities from which dust fall was collected during September 2011 to February 2013.

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