Invited Article

The Faculty of Science is 90 years old*

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The first sitting of the Faculty Board of Science, as we know it today, was held on the 17th September 1915; like today it was a Friday. The Rector, Dr. Edoardo Magro was in the chair and there were three members in attendance: Professor W.F. Nixon B.Sc., Arc.Sc. (Professor of Mathematics) and two others, both future *Rectores Magnifici* of the University, Professor Roberto V. Galea L.S.&A. and Professor Themistocles Zammit C.M.G., M.D. (Professor of Chemistry). In view of the agenda for the day, the following two decisions were taken:

- (i) Henceforth there were to be two Mathematics exam papers, instead of the one as till then, in each of (a) the academic course of science, (b) the preparatory course of medicine, and (c) the preparatory course of engineering;
- (ii) Professors Temi Zammit and Robert V. Galea were elected to represent the Science Faculty on Council.

These details and others relating to the subsequent meetings of the Faculty Boards of Science can be found in a single register entitled Faculty Board of Science Minutes (1915-1956), catalogued as Vol. 444 in the University Archives (no pagination). As this register extends down to 1956 it has many an interesting detail very close to our own memory such as how, on 30 August 1950, Professor Edwin Borg Costanzi (honouring us today with his presence) makes his first appearance on the board and, forthwith, is elected to represent Faculty on Senate.

In this short presentation I have been asked by the Dean to look backward over the years to give an overview of how the various situations of Science in Malta developed to lead to that auspicious Friday 17th September 1915 that we are commemorating this morning. (The looking forward is the task of this Faculy Board.) Our Alma Mater has had a chequered career, looking back for its forked roots in the Jesuit-founded Collegium Melitense, begun in 1592, and in the School of Medicine founded by Grandmaster Nicholas Cotoner in 1676 in the Sacra Infermeria, both in Valletta. In these early precursor days, the study of the Sciences was well-nigh restricted to Mathematics, a School of which was erected in the Collegium in May 1655. Interestingly, the chair was funded by a tax on the croquet-like game of mallet, played in the Floriana walled Mall (whence the name), by leisure- and pleasure-seeking knights. The purpose as conceived by Lascaris who founded it was purely functional and the discipline thought of as 'slave and servant' of the utilitarian sciences of navigation and artillery. One can, in some sense, say that the teaching of Mathematics flourished, on and off for about a century, until the suppression of the Jesuits and their college in April 1768.

Following the unceremonious dismissal of the Jesuits, Grandmaster Pinto took immediate steps to transform their college (now his college) into the university of his dreams. To this end, he invited from abroad some of the best men in Europe of the time, including a Florentine Servite Padre Roberto Raineri Maria Costaguti, a mathematician of some repute, to be the first rector. Attached to this Pubblica Università di Studi was a Collegio d'Educazione, a kind of Junior College. According to the statutes drawn up by Costaguti himself, a full university course lasted eight years and was divided into two parts: The first three years led to the degree of Master of Arts in subjects common to all three faculties of Theology, Jurisprudence and Medicine, whereas the last five were dedicated to these three traditionally professional courses; this basic structure survived till the very recent past. The teaching of the sciences, in preparation for the course of Medicine, found its way in the curriculum of the initial three years. Worth mentioning that Botany, an essential ingredient of the course of medicine that relied heavily then on the knowledge of herbs, was closely associated with a Giardino di Botanica that flourished in St Elmo's ditch where the medicinal herbs were grown.

Maltese exponents of science at this time included: (i) Dr. Giuseppe De Marco of Cospicua, trained in the Jesuit College and in Pinto's Università, who has left us various writings, including: (a) Tratttato di Trigonometria Piana, (b) Vulgaris Arithmetica Elementaris Theoria et Praxis, and (c) Breve Compendio dell'Idrostatica. (ii) Pride of place, however, should go to Giuseppe Zahra, likewise trained at the Jesuit College, but, having clashed with the Order on political grounds during the so-called Insurrection of the Priests, he slipped out of the island to Naples where he concluded his medical training, whence he headed for St Petersburg, where he very likely came in

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contact with Euler himself, then by way of Paris and Messina, he ended up in Catania to teach Mathematics. Here as incumbent of the Chair of Geometry, he earned for himself the compliment of being *il più valido matemetico che fosse in Sicilia*; he now graces our Computer Science Building with his name.

The Order's stay in Malta came to a sad end in June 1798 when Napoleon Bonaparte summarily threw it out of the island. During a short six-day stay (13-19 June), Bonaparte revolutionized all the systems in these islands, including the educational:

- (i) fifteen primary schools were to be set up for the education of Maltese children;
- (ii) sixty boys, from the richest families, were to be sent to Paris to further their studies;
- (iii) the University was to be replaced by a Central School run by eight masters, respectively in charge of: (a) arithmetic and stereometry, (b) algebra and electricity, (c) mechanics and physics, (d) geometry and astronomy, (e) navigation, (f) chemistry, (g) oriental languages, and (h) geography.

Things augured very well for the sciences, but none of these grandiose schemes saw the light of day as by 1 September the islands were up in revolt and the French made way for the British. Even before the future of Malta was settled by treaty in 1813, the practical administration of the island was already in the hands of Alexander Ball.

It is to Ball's credit that the University began to function again very soon afterwards with three main chairs for Theology (Dogma, Morals and Canon Law), one for Medicine, one for Civil Law and three for the Faculty of Arts. These were (i) Humanities and Rhetoric, (ii) Logic and Metaphysics, and (iii) Mathematics and Physics. This last chair was given to Carlo Azzopardi. The Reverend Canon Francesco Saverio Caruana, one of the leaders of the revolt and subsequently Bishop of Malta, a mathematician of note, was first rector of this refounded University (1800-1822). He also founded the school of building and design at the University. Caruana resigned in 1822 and dictatorial Governor, so-called 'King Tom', Maitland grabbed the opportunity to set up a commission to investigate the educational system at this highest institution of learning. One practical result of this enquiry was the separation of the University from the Lyceum, physically by the construction of the Doric Gate in St Paul's Street under the Greek inscription: Propylaion tes times he mathesis.

Separate Faculty Boards for the various faculties began to be held at this time. Some information on student numbers is also available: The roll of students at the University in 1833 showed a total of 300 students of which 65 attended the Arithmetic Class. Professors had an onorarium, rather than a salary, amounting to £25 per year. Important names in science that appear in the 1820s and 30s included Dr. Cleardo Naudi, *Professore di Chimica*; the teacher of Arithmetic was Sr. Gioacchino Busuttil, *Professore di Bottanica*; P. Carlo Giacinto died in 1829 to be succeeded by Dr. Stefano Zerafa. Similarly in that same year, the chair of Mathematics had been vacant for some time by the death of Dr. Giuseppe Zammit and it was being recommended that Sr Carlo Cicogani Capelli should replace him. A Dr. Giuseppe Wettinger from Cremona, described as inventor of an aerostatic balloon, appears on the scene in the 1830s.

In a report of 1836, drawn up by two British scholars, John Austin and George Cornwall Lewis, the commissioners found a University system that was to survive to the recent past in which a six-year academic course consisted of an initial three-year course in philosophy leading to three other years in one of Theology, Law or Medicine. Intake used to take place every three years with a numerus clausus of 159 for the final three years. Students paid half-a-crown a month and total intakes from these fees in 1837 came to £149 3s. 2d., which sufficed for all the staff's salaries. Recommendations for reforms by the two gentlemen were turned down and there followed a time of turmoil which saw the toppling of two rectors in as many years. The lull that followed with the lengthy rectorship of Dr. Saverio Schembri (1854-1880) was equally fruitless and a time of stagnation. Suffice it to mention that during this whole time, Council met exactly once in November 1873. For the whole of thirty-five years there were no Arts or Science degrees. The sciences reappear again in the reforms suggested by Sigismondo Savona who insisted that Theology students should have a grounding in Mathematics and Physics. This was vigorously opposed by the Church.

The Rector Annetto A. Caruana resigned in 1896 as he could not handle the warring factions within the University. He was replaced by Napoleon Tagliaferro who came armed with a new statute. Tagliaferro was an outstanding acdemic who contributed to several branches of learning, including Mathematics, Archaeology, the Natural Sciences and the Maltese Language. He studied at the Sorbonne and his publications include a paper of 1879 on the then topical Transcendental Functions. One of his early achievements at the University was to subdivide the Faculty of Arts, till then known as the Faculty of Literature and Science, into two separate areas of study: The Arts and the Sciences, that included Engineering, Architecture and Pharmacy. The split into three faculties of Arts, Science, Engineering and Architecture belongs to the next rectorship of Edoardo Magro (1904-1920).

The first meeting of the faculty board of Science was held 90 years ago almost to the day.

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Invited Article

WHAT CHEMISTS COULD NOT SEE WITHOUT MATHEMATICS Dependence of total π -electron energy on molecular structure

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Summary. Total π -electron energy E (as computed within the Hűckel molecular orbital approximation) is a quantum chemical characteristic of unsaturated conjugated compounds whose dependence on molecular structure can be deduced and analysed by means of algebraic graph theory. It is shown that E depends - in a perplexed, but mathematically well-defined manner - on a large number of molecular structural features. The mathematical representations of these structural features are the so-called Sachs graphs. Some of these Sachs graphs correspond to familiar chemical notions: bonds, rings, Kekulé structures. Most of them, however, represent structural features whose chemical significance was not anticipated by chemists. Thus we are faced with a case of structure-property relation that could not be deduced and rationalised without the use of modern mathematical methods. In the article are outlined the basic results achieved along these lines, illustrated with concrete chemical applications.

Keywords: Total π -electron energy, molecular orbital theory, quantum chemistry, chemical graph theory

Introduction

Most chemists are of the opinion that mathematics is of little importance and of almost no value in their science, including "theoretical chemistry". The undeniable fact is that most chemist can successfully do their work or conduct their research (up to winning a Nobel prize) without utilising any form of mathematics that goes beyond simplest calculus. As a consequence, being chemist often means being ignorant in mathematics.

The aim of this article is to demonstrate that, in some cases at least, the lack of mathematical way of reasoning makes chemists blind to certain aspects of their work. We are aiming at one of the central objectives of chemistry: finding connections between molecular structure and molecular properties.

It is one of the paradigms of chemistry that molecular structure determines the (physical, chemical, pharmacological, ...) properties of the corresponding substance, provided, of course, that this substance consists of molecules. Thus, from the known molecular structure, the properties of substances should be predictable. Although much success along these lines has been achieved and much knowledge accumulated, we are

still very far from the complete solution of the problem. [In contemporary chemical literature two acronyms are often encountered: QSPR = *Quantitative Structure Property Relations* and QSAR = *Quantitative Structure Activity Relations*. Under "property" are meant the physical and chemical properties, whereas "activity" refers to pharmacological, biological, medicinal and similar properties.] In this article we consider a special problem in QSPR research, namely the finding of the (quantitative) connection between the structure of a polycyclic conjugated hydrocarbon and its total π -electron energy *E*. Although *E* cannot be directly measured, it is known to be reasonably well related to the experimentally accessible thermodynamic data (Gutman, 1992, Gutman and Polansky, 1986, Schaad and Hess, 1972, 2001).

The total π -electron energy considered here is computed by means of the tight-binding Hűckel molecular orbital (HMO) approximation and, as usual, expressed in the units of the carbon-carbon resonance integral β . Details of HMO theory are found, e. g., in the books (Coulson et al., 1978, Yates, 1978). Within the HMO model it is possible to employ the mathematical apparatus of graph spectral theory; for applications of graph spectral theory in molecular orbital theory see the books (Dias, 1993, Graovac et al., 1977) and the articles (Dias, 1987, 1992, Gutman, 2003, Gutman and Trinajstić, 1973).

For the present considerations the actual value of the parameter β is not important, except that its value is negative. We nevertheless mention that for thermochemical purposes the recommended value of β is -137.00 kJ/mol and that the heats of atomisation computed by the HMO method are accurate to 0.1%, implying that E is accurate up to $\pm 0.005 \beta$ units (Schaad and Hess, 1972). Thus, the greater is E, the higher is the thermodynamic stability of the respective compound; structural factors increasing (resp. decreasing) the value of E increase (resp. decrease) the thermodynamic stability.

Graph Theoretical Preparations

In order to be able to present the results on the structuredependence of E, we must specify a few basic notions of graph theory and graph spectral theory. More details can be found in the books (Graovac et al., 1977, Gutman and Polansky, 1986).

A conjugated hydrocarbon is represented by its molecular graph. The construction of such a graph should be evident from the example shown in Fig. 1.



Figure 1. The structural formula of biphenylene and the corresponding molecular graph G_1 . The graph G_1 has n=12 vertices and 14 edges. The vertices of G_1 represent the carbon atoms, whereas its edges represent the carbon-carbon bonds of biphenylene.

The number of vertices of a molecular graph G is denoted by n. Two vertices connected by an edge are said to be adjacent.

If the vertices of the graph G are labelled by $v_1, v_2, ..., v_n$, then the structure of G can be represented by the adjacency matrix $A = A(G) = ||A_{ij}||$. This is a square matrix of order n, whose elements A_{ij} are defined so that $A_{ij}=A_{ji}=1$ if the vertices v_i and v_j are adjacent, and $A_{ij}=0$ otherwise. For an example see Fig. 2.



Figure 2. A graph G_2 and its adjacency matrix $A(G_2)$. It can be computed (but not easily) that the characteristic polynomial of G_2 is $\Phi(G_{2},x) = x^{5} - 5x^{3} + 2x$. The solutions of the equation $x^{5} - 5x^{3}$ 2 x = 0 are $x_1 = [(5 + \sqrt{17})/2]^{1/2} = 2.13578$, $x_2 = [(5 - \sqrt{17})/2]^{1/2} = 0.66215$, $x_3 = 0$, $x_4 = -[(5 - \sqrt{17})/2]^{1/2} = -0.66215$ and $x_5 = -[(5 + \sqrt{17})/2]^{1/2} = -2.13578$. These five numbers are the eigenvalues of the graph G_2 and form the spectrum of G_2 .

The characteristic polynomial of the graph G, denoted by $\Phi(G,x)$ is equal to the determinant det(xI-A) where I is the unit matrix. It can be shown that $\Phi(G,x)$ is a polynomial in the variable x, of degree n. For an example see Fig. 2.

The numbers $x_1, x_2, ..., x_n$, obtained by solving the equation $\Phi(G,x)=0$, are the eigenvalues of the graph G. These eigenvalues form the spectrum of G. For an example see Fig. 2.

Some Results from the Theory of Total π -Electron

Energy

Anticipating that the majority of the readers of this article will not be interested in the perplexed mathematical details of the theory of total π -electron energy, and will not be willing to spend time on apprehending them, in

what follows we give only a few master formulae that the non-interested reader may skip and go straight to the next section. Those who are interested to learn the entire theory should, first of all, consult chapter 8 of the book (Gutman and Polansky, 1986).

It can be shown (Graovac et al., 1977, Gutman and Trinajstić, 1973) that, in the majority of chemically interesting cases, the total π -electron energy is related to the eigenvalues of the molecular graph as

where the summation goes over the positive-valued eigenvalues of the molecular graph. Another neat way in which Eq. (1) can be written is

$$E = \sum_{i=1}^{n} |x_i| \qquad \qquad \text{Eq. (2)}$$

the where now summation embraces all graph eigenvalues.

Thanks to the symmetric form of Eq. (2), the HMO total π -electron energy E is particularly suitable for mathematics-based investigations. The first significant result in this area was obtained by the British mathematician and theoretical chemist Charles Coulson, good 30 years before other chemists started to use graph spectral theory (Coulson, 1940). Coulson found a connection between E and the characteristic polynomial of the molecular graph, an expression that may look frightening to chemists:

$$E = \frac{1}{\pi} \int_{-\infty}^{+\infty} \left[n - \frac{ix\Phi'(G, ix)}{\Phi(G, ix)} \right] dx \qquad \text{Eq. (3)}$$

In Eq. (3), Φ' stands for the first derivative of the characteristic polynomial, and *i* for the imaginary unit, $i=\sqrt{-1}$.

A quarter of century later, the German mathematician Horst Sachs discovered the way in which the characteristic polynomial of a graph depends on its structure. His result, nowadays referred to as the Sachs theorem (Gutman, 2003), reads as follows:

$$\Phi(G, x) = x^{n} + \sum_{S} (-1)^{p(S)} 2^{c(S)} x^{n-n(S)}$$
 Eq. (4)

where the summation goes over all so-called Sachs graphs of the graph G. These Sachs graphs, essential for the present considerations, are defined as follows.

By K_2 is denoted the graph consisting of two vertices, connected by an edge. By C_n is denoted the cycle possessing *n* vertices, *n*=3,4,5,..., see Fig. 3.

Figure 3. Components of the Sachs graphs. Any Sachs graph consists of components that are
$$K_2$$
 and/or C_3 and/or C_4 and/or ... see Fig. 4.

A graph in which each component is K_2 or C_3 or C_4 or C_5 or ... is called a Sachs graph. Some of these Sachs graphs are contained in the molecular graph; examples are found in Fig. 4.



Figure 4. Examples of Sachs graphs (indicated by tick lines) contained in the biphenylene graph G_1 . The biphenylene graph contains a total of 514 Sachs graphs. Each of these graphs can be understood as representing a structural feature of the respective molecule.

In Eq. (4), p(S), c(S) and n(S) are the number of components, cyclic components and vertices, respectively, of the Sachs graph *S*. For instance, the Sachs graphs S_1 , S_4 , S_7 and S_9 (depicted in Fig. 4), have, respectively, 1, 6, 3 and 2 components, 0, 0, 1 and 2 cyclic components, and 2, 12, 10 and 12 vertices.

When Eq. (3) and Eq. (4) are combined, one arrives at an explicit expression, connecting the total π -electron energy with molecular structure (Gutman, 1977, Gutman and Trinajstić, 1976):

$$E = \frac{1}{\pi} \int_{-\infty}^{+\infty} x^{-2} \ln \left| 1 + \sum_{S} (-1)^{p(S)} 2^{c(S)} x^{n(S)} \right| dx \qquad \text{Eq. (5)}$$

The Chemical Significance of Equation (5)

Each Sachs graph can be understood as representing a particular structural detail of the underlying molecule. Some of these structural details are those familiar to every chemist. For instance, S_1 and S_2 in Fig. 4 pertain to two distinct carbon-carbon bonds of biphenylene, S_6 corresponds to one of its six-membered rings, S_4 and S_6 can be viewed as representing two of its Kekulé structural formulae. However, most Sachs graphs have no usual chemical interpretation. For instance, hardly any non-mathematical chemist has ever thought of structural details such as S_3 (three mutually non-touching carboncarbon bonds) or S_7 (a six-membered ring and two nontouching carbon-carbon bonds, not belonging to this ring), etc. etc. Yet, all such structural details play role in determining the magnitude of the total π -electron energy, and thus are responsible for the thermodynamic stability of the respective molecule.

Eq. (5) is really awkward, but it represents the mathematically complete solution of the structuredependence problem of a molecular property, in this particular case - of the HMO total π -electron energy. There exist very few QSPR results of this kind.

What can we learn from Eq. (5)?

First: The relation between total π -electron energy and molecular structure is extremely complicated. [In our

opinion, the true relation between any molecular property and molecular structure is extremely complicated, only usually we are not aware of this fact.]

Second: Eq. (5) precisely identifies all structural details that influence the total π -electron energy. As already mentioned, some of these are familiar: bonds, rings, Kekulé structures. Most of them are exotic, never anticipated by "intuitively thinking" chemists. Eq. (5) reveals the plenitude of (relevant) information contained in a molecular structure, most of which chemist would never recognise without utilising graph spectral theory.

Third: Eq. (5) shows the precise mathematical form in which each structural feature influences the value of E. Thus from it we could make quantitative inferences. The effect of various structural details on E is far from being linear (what chemist prefer because of the simplicity of the linear mathematical expressions).

Fourth: In principle, any question concerning the structure-dependence of *E* can be answered by means of Eq. (5). In reality, we encounter serious mathematical difficulties. Therefore, research in the theory of total π -electron energy continues until the present days (Gutman et al., 2004, Zhou, 2004) and will, most probably, go on also in the foreseen future. One particular problem that has been completely resolved is the effect of cycles on *E* (Gutman, 1984, Gutman and Bosanac, 1977, Gutman et al., 1993, Gutman and Polansky, 1981). We outline the details of this topic in the subsequent section.

Applications: Effects of Cyclic Conjugation

Long time ago chemists have recognised that cyclic π electron systems exhibit very large stabilisation or destabilisation relative to their acyclic analogs. The pairs benzene vs.

hexatriene (stabilisation) and cyclobutadiene vs. butadiene (destabilisation) are textbook examples. Already in the 1930s Hűckel formulated his 4m+2 rule, claiming that monocyclic conjugated systems are stable if they possess 4m+2 (i. e., 2, 6, 10, 14, ...) π -electrons, and are unstable if the number of π -electrons is 4m (i. e., 4, 8, 12, ...). That this is an energy-based effect was demonstrated in the 1960s (Breslow and Mohácsi, 1963).

Extending the Hűckel rule to polycyclic conjugated molecules became possible only after graph theory was applied in molecular orbital theory, more precisely: after Eq. (5) was discovered.

Using the fortunate fact that the total π -electron energy depends on Sachs-graph-type structural features, and that (some) Sachs graphs consist of cycles, it was possible to express the effect of a particular cycle *C*, contained in the molecular graph *G*, on the respective *E*-value (Gutman, 1984, Gutman and Bosanac, 1977, Gutman et al., 1993, Gutman and Polansky, 1981):

$$ef(G,C) = \frac{1}{\pi} \int_{-\infty}^{+\infty} \ln \left| \frac{\Phi(G,ix)}{\Phi(G,ix) + 2\Phi(G-C,ix)} \right| dx \qquad \text{Eq. (6)}$$

In Eq. (6) *G*-*C* denotes the subgraph obtained by deleting the cycle *C* from the graph *G*. Whenever ef(G,C) is positive, the cycle *C* stabilises the molecule; negative *ef*values imply destabilisation.

In Fig. 5 are given the energy-effects of two typical polycyclic conjugated systems.



Figure 5. The energy-effects of the cycles of phenanthrene and biphenylene, expressed in the units of the HMO resonance integral β .

The examples shown in Fig. 5 illustrate some basic properties of cyclic conjugation, which - again - would not be recognised without use of mathematics.

(a) Not only rings, but also larger cycles (often ignored by chemists) have their energy contributions.

(b) The energy-effect usually decreases with increasing size of the cycle, but has a non-negligible value also for cycles of larger size.

(c) Cycles of the same size may have significantly different energy-effects.

(d) In the examples shown in Fig. 5, the 6-, 10- and 14membered cycles have a stabilising effect, and the 4-, 8and 12-membered cycles a destabilising effect. This is in full agreement with the Hűckel 4m+2 rule.

(e) However, contrary to what chemists may expect based on their "intuition", the Hűckel 4m+2 is not generally obeyed. Surprisingly, only the following result could be rigorously proven (Gutman, 1979):

(f) In all alternant polycyclic conjugated hydrocarbons, cycles of size 4, 8, 12, 16, ... always have a negative *ef*-value and thus always destabilise the respective molecule. (This is just one half of the Hűckel 4m+2 rule.)

(g) In the majority of cases, cycles of size 6, 10, 14, 18, ... have a stabilising effect. However, there exist exceptions, namely alternant polycyclic conjugated hydrocarbons in which some of the (4m+2)-membered cycles have a destabilising energy-effect and thus violate the Hűckel 4m+2 rule (Gutman and Stanković, 1994).

Although the results (f) and (g) can be stated and made understandable without any mathematical formalism, they hardly could have been deduced without use of mathematical reasoning. These results could be viewed as examples of what chemistry may gain from mathematics: Over half a century, chemists believed that a certain regularity holds and is generally valid. Only a couple of years after a couple of mathematical chemists started to apply graph theory, it could be shown that one half of the regularity is generally valid (and is thus a law on Nature), whereas the other half is not.

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Research Article

Zooming in on fullerenes

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Summary. Carbon does not appear only as diamond and graphite. Fullerenes, forming a third family of allotropes of carbon (C), exist as large stable clusters of C atoms. A trivalent polyhedron P is a cubic graph which may be embedded on a convex 3-D surface of genus zero and a fullerene, Cn, is P with twelve pentagons, the remaining faces being hexagons. We introduce the concept of nut fullerenes, so called because their skeleton is a nut graph that implies one NBO with the charge contributed by the NBO electron being shared among all the C-centres. The charge distribution over all the framework of the molecule has strong chemical consequences. We study the substructures in fullerenes and other trivalent polyhedra, that determine the presence of a NBO. Together with the symmetry group of the graph, they shed new light on singular graphs and polyhedra in particular.

The Schrödinger wave equation that yields the wave functions specifying the possible energies of a molecule is well known to most scientists. Wave equations and operators are quite complex and still a healthy area of research. Determining the electron (ε) energy levels of a Carbon (C) molecule is, however, relatively easy, owing to the Hückel Molecular Orbital (HMO) theory, for $\pi - \varepsilon$ – systems. This approximates the Schrödinger's equation leading to a simpler one $Ax = \lambda x$ where A is the adjacency 0 - 1 matrix of the molecular graph G whose structure is the same as that of the molecule with the C-centres as vertices and the σ bonds as edges. In spite of the errors in the approximations, the values of λ (termed eigenvalues of A), for the ε - energy levels of the molecule and those of the vectors x describing the \mathcal{E} -orbitals, that are surprisingly close to those obtained experimentally.

Non-bonding orbitals (NBOs) present in some molecules are characterised by the presence of the *zero* energy level $(\lambda = 0)$. The orbital vector \mathbf{x} satisfies $A\mathbf{x} = \mathbf{0}$ and is said to be a *kernel eigenvector* of \mathbf{A} or of \mathbf{G} . The number of linearly independent vectors \mathbf{x} satisfying $A\mathbf{x} = \mathbf{0}$ is said to be the *nullity* of \mathbf{A} .

Fullerenes, discovered in 1987, when an arc was passed through C vapour, form a third family of allotropes of C, in addition to graphite and diamond which were known since the reign of the alchemists. They exist as large stable clusters of C atoms, each having three σ -bonds, forming a spherical or other convex shape.

In (Yoshida *et al.*, 1997) M Yoshida, P.W. Fowler *et al* described the rarely occurring NBOs of a subfamily of fullerenes by comparing the orbital patterns to the four NBOs of the graphite sheet. In (Sciriha 1998a, 1998b), the author was motivated by the same problem for an arbitrary graph. The aim was to discover the structural features that force a graph G to be singular. The results point to subgraphs called minimal configuration (mcs) that are present in G. An algorithm constructs all possible mcs and a catalogue of the smaller mcs can be found in (Sciriha 1998a) and (Sciriha 1998b). These studies prompt us to ask which part of the molecule of a singular fullerene is responsible for a particular NBO. Are chemical mcs possible?

The characterization of the graphs with eigenvalue zero, known as singular graphs, has been a long-standing problem in the sixty-year-old history of graph theory, during which time the latter has emerged as an everexpanding prolific discipline of mathematics. Each kernel eigenvector \mathbf{x} of G is an NBO and determines a well-defined core which is the singular subgraph induced by the non-zero entries of x. Moreover, a core, corresponding to a kernel eigenvector x in a minimal basis (a basis in which the linearly independent vectors have a minimum number of non-zero entries) for the nullspace of A, "grows" into a minimal configuration (mc) by adding vertices, which form a periphery, until the nullity is reduced to one. Such a mc of nullity one is the subgraph of the singular graph responsible for the presence of the NBO x. Thus a mc consists of a core and a periphery.

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If a core happens to have nullity one, then it is a special mc called *nut graph* that needs no periphery. The search for nut molecular graphs has aroused a flurry of interest among chemists because of the strong chemical implications. Nut graphs are unique among molecules with one NBO because each C-centre is charge rich. Moreover the spin and bond-order densities are also spread over the whole π -framework and not on some substructure. We consider the constraints required for a fullerene or other trivalent polyhedron to be a nut graph.



The trivalent fullerene has a planar embedding. Euler's equation n + f = m + 2 for solids of genus zero relates the number n of C-centres (vertices) with the number mof σ -bonds (edges) and the number f of faces formed by the σ -bonds. Since 2m = 3n, we deduce that a fullerene has exactly twelve pentagons and $\left(\frac{n}{2}-10\right)$ hexagons. The smallest hypothetical fullerene is the well known twenty-vertex Platonic solid, the dodecahedron, C₂₀, consisting of twelve pentagonal faces embedded on a sphere. The nullity of C_{20} is four and it is a core so that each C-centre in a hypothetical C₂₀ molecule is chargerich. The four NBOs correspond to distinct mcs found as subgraphs. Figure 1 shows a 3-D picture and a planar embedding of C_{20} as well as G_{13} , one of the mcs. The smallest fullerene with nullity one is C_{28} :1 and the smallest nut fullerene is C_{36} :14 shown in Figure 2.



Among the large number of fullerene isomers C_n for n up to 120, there are only nine singular IP fullerenes of which C_{84} : 24 has three NBOs whereas the other eight have one NBO. None of them are nut graphs, although C_{106} and C_{114} , as examples of sporadic closed shell fullerenes, approach "nut graph" status having an energy level very close to but not exactly zero.

Although there exist nut graphs of all orders $n \ge 7$, their frequency seems to be low among graphs of low order. So it was quite surprising that among the trivalent polyhedra a considerable number were found to be nut graphs. For instance, among the 1249 trivalent polyhedra of order 18, there are 285 nut graphs.

As in many areas of science, symmetry plays an important role in revealing physical and chemical behaviour. The symmetry group of the planar embedding of a fullerene enables the vertices (C-centres) to be partitioned into orbits each containing equivalent vertices. Thus vertices in an orbit may be mapped onto each other by a transformation such as a rotation and/or a reflection, preserving adjacencies. Moreover these vertices carry the same charge. Linear algebra and symmetry help to determine easily some of the energy levels of large symmetrical fullerenes, since these are given by the eigenvalues of the much smaller orbit-orbit matrix.



The chemically realizable fullerenes known to date follow the Isolated Pentagon (IP) rule. The smallest is the Buckminster Fullerene C_{60} , which has no NBO and whose spherical structure is that adopted for the football (Figure 3). Adjacent pentagons in a fullerene structure are thought to produce too much strain to allow stability.



The fullerene C_{70} , for instance, has 5 orbits, UWXYZ, containing 10, 20, 20, 10 and 10 vertices respectively as shown in Figure 4. The 5×5 orbit-orbit matrix

$$\begin{array}{ccccc} U & \left(\begin{array}{ccccc} 1 & 2 & 0 & 0 & 0 \\ W & \left(\begin{array}{ccccc} 1 & 1 & 1 & 0 & 0 \\ 0 & 1 & 1 & 1 & 0 \\ 0 & 1 & 1 & 1 & 0 \\ Y & \left(\begin{array}{ccccc} 0 & 0 & 2 & 0 & 1 \\ 0 & 0 & 0 & 1 & 2 \end{array} \right) \end{array} \right) \text{ has eigenvalues 3, 2.414,}$$

1.414, -1.414, -1.414 which are among the \mathcal{E} -energy

levels of C_{70} . The core of C_{70} is the union of two cycles C_{20} and a mc is shown in Figure 5. The study of the NBO of C_{70} shows that the unique core may grow into distinct mcs present as subgraphs in the 70-vertex graph. These mcs may even be cospectral.



Although C_{70} has nullity one, it is not a mc but contains a mc. If as for C_{70} , the entries of the NBO x are +1, -1 and zero, then Ax = 0 requires that even an uncharged C-centre has an uncharged atom adjacent to it. Thus at least two peripheral vertices are adjacent, a situation which is not allowed by mcs. The powerful theories of groups and matrices yield results interesting to chemists. For a highly symmetrical (vertex transitive) one orbit graph, there is equidistributivity of charge from the NBO among all the C-centres. This requires an even number of σ bonds for each C-atom, thus ruling out fullerenes. It follows that trivalent polyhedra with one orbit either have no NBOs or more than one. Two non-degenerate energy levels are sufficient for multi-orbits, so that a trivalent graph with one NBO is multi-orbit.



Two interesting examples of two-orbit nut graphs are the trivalent polyhedron and the smallest nut fullerene shown in Figure 2. The entries in the kernel eigenvector are -1 and 2 for both. This demands that the structure has the motif shown in Figure 6 as a factor and that it is made up of disjoint motifs that span the structure. Thus is spanned by two motifs whereas has 6 factors. More complex nut graphs have been identified but it is unlikely that they can be synthesised in the laboratory since to date all have adjacent pentagons.

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Research Article

The Production of PV Hydrogen

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Summary. A significant drawback of direct solar and wind energy is that they are intermittent. Moreover, supply and demand peaks may not coincide, which could lead to energy shedding in specific situations. A system was investigated where solar flux was first converted to DC electrical energy using photo-voltaic (PV) cells, and then the generated electricity used to produce hydrogen by electrolysis of water.

The V-I characteristics of a PEM electrolyser were determined using laboratory DC sources. Various types of PV panel, of known efficiencies, were then connected to the electrolyser and conditions for obtaining maximum efficiency in hydrogen production were determined. With careful matching of PV output to electrolyser, efficiencies as high as 10% could be obtained. These are comparable to the best published results. The match of actual hydrogen output conditions to those best suited to storage in a metal hydride tank or to direct use in a fuel cell were investigated.

Areas of PV material required to produce quantities of hydrogen necessary for specific tasks were determined. Improvements to the hydrogen generating and storage systems were suggested.

Introduction

Malta is almost completely dependent on imported fossil fuels for its energy needs. This makes security of supply and price stability of primary concern to our economy. Developments expected over the next fifty years, as well as commitments to greenhouse gas (GHG) reductions, make it imperative that we reduce our dependence on fossil fuels.

The prime candidates for (partial) substitution of fossil fuels are solar and wind energy, which could have a combined potential to displace perhaps 15% of the primary energy currently used to generate electricity. However, inevitable fluctuations in the supply of renewable energy (RE), mismatches between supply and demand, and the difficulty of storing electrical energy prevent RE sources from achieving a total substitution of fossil fuels. But the practical degree of substitution can be improved by a flexible energy carrier, used to buffer mismatches between RE generators and overall demand.

Hydrogen is widely seen as the prime candidate for such a carrier (Dutton 2003). Of course, it has to be produced by using a primary source of energy, which may not itself be environmentally benign e.g. oxidation of CH4; but there are emission-free methods of generation, like electrolysis of water. In use hydrogen is free of harmful emissions; it can be used to generate electricity with high efficiency in a mobile or static fuel cell, or it can fuel internal combustion engines. Concern with safety has led to the evolution of procedures which make for very safe handling of hydrogen. In this work we have determined the potential of the local solar flux to produce hydrogen by electrolysis using standard PV panels and a small PEM electrolyser. Problems associated with direct use of the hydrogen in a small fuel cell and with storage at atmospheric pressure in a metal hydride tank were also investigated.

Electrolyser Performance

The electrolyser was a Proton Exchange Membrane type requiring de-ionised water (conductivity $<1\mu$ S/cm) and a D.C. voltage of 5V to 7V. It is rated at a maximum power of 250W at a temperature of 75°C and a pressure of 10Bar. Characteristic I-V curves of the electrolyser were obtained using a variable DC power supply. The performance was characterised by two main factors, one being the minimum voltage at which current starts to flow through the electrolyser and the other the ratio of V to I which is equivalent to the internal resistance R of the electrolyser.



Figure 1. Electrolyser degradation.

A progressive degradation in electrolyser performance was noted after some months of use. Referring to fig 1, the internal resistance of the electrolyser increased from 0.1Ω when new to 0.5Ω after 6 months of use; the V-I ratios showed that the resistance decreased to 0.29Ω when the electrolyser was heated to 60° C. The loss in electrolyser performance required a higher voltage for the same current flow, and in turn more energy for a constant rate of hydrogen production. This phenomenon of electrolyser loss in performance is well documented (Lehman and Chamberlin, 1991) in the case of an alkaline electrolyser, the degradation being attributed to loss of electrode surface and catalyst efficiency.

The current and energy efficiencies of the electrolyser were also determined at varying power densities. This was done by measuring the volume of hydrogen produced on a graduated scale and comparing its Higher Heating Value (HHV) of 146MJ/kg with the electrical energy used. The volume was 637cm³ at a pressure of approximately 40mbar as measured from the height difference between the water levels of the central water reservoir and hydrogen gas cylinder.

A series of electrolysis runs were conducted at a number of fixed values of current and their corresponding time and voltage to produce 637cm^3 of hydrogen was recorded. In all cases the electrolyser was unheated.

Voltage /V	Current /A	Time /s	Charge /C	Current eff.	Energy /kJ	Energy eff.	
4.97	5.0	352	5280.0	98.31	8747.20	88.03	
5.29	10.0	179	5370.0	96.67	9469.10	81.32	
5.79	15.0	119	5355.0	96.94	10335.15	74.50	
Table 1 Sentember 2001 Electrolycor officionay (new)							

Table 1 September 2001 Elec	ctrolyser efficiency (new).
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Voltage /V	Current /A	Time /s	Charge /C	Current eff.	Energy /kJ	Energy eff.
5.14	4.9	359	5245.0	98.97	8986.42	85.68
5.17	4.2	413	5203.8	99.75	8967.88	85.86
5.46	6.0	294	5292.0	98.09	9631.44	79.95
5.88	10.2	178	5446.8	95.30	10675.73	72.13
6.01	11.5	151	5209.5	99 64	10436.37	73 78

Table 2 December 2001 Electrolyser efficiency.



Figure 2. Electrolyser and Perspex cylinders

Hydrogen has a density of 0.0898 g/L at s.t.p. so 637cm^3 at 40mbar and 26.5°C is equal to a mass of 0.0542g or 0.0269mol H₂. As one mole theoretically requires a charge of 2Faraday, 0.0296mol requires 5191C and has an energy of 7.7kJ. Comparing the actual charge and electrical energy needed with the theoretical values provides the electrolysis efficiencies. The total charge is taken as 3 Σ It since the electrolyser has three cells in series. The time in the third column of tables 1 and 2

refers to that taken to produce 637cm^3 of H₂, the charge is the product 3Σ It and energy used is the total 3Σ VIt.

The current and energy efficiencies are taken with respect to 5191C and 7.7kJ as 100%. The current efficiency should be high (>95%), since it is a measure of the effective reactions that are occurring during electrolysis. Each electron should react with 1 H; however other unwanted reactions may occur such as those involving impurities in the electrolyte or electrodes. These reactions would consume some of the electrons involved and hence reduce the actual amount of hydrogen produced for a given charge. On the other hand, energy efficiency involves the actual energy carried by the electrons, which is a function of the voltage potential. Since each produced H₂ molecule has a specific energy, any energy excess used to perform the reaction is lost and not carried by the product; so high working voltages result in low energy efficiencies.

From tables 1 and 2 it can be deduced that within the current range used, the current efficiency is independent of the current flow but the energy efficiency decreases with increasing electrolysis current. This data implies that during lower insolation periods, such as those occurring during cloudy days, the electrolyser efficiency does not deteriorate; but actually increases as it works at a lower current density.

After a period of use, the electrolyser current efficiency was unaffected whilst a degradation in energy efficiency was experienced for a given current flow after three months. The average current efficiency from tables 1 and 2 is 97.96%. In the experimental work performed, the rate of hydrogen production was thus taken as 0.98 of that theoretically produced by the current flow. So 95719C theoretically produce 1g H₂ but in the experimental work this is taken to produce 0.98g. From data gathered during particular solar-driven production runs, the total insolation was measured using a pyranometer-integrator; the total electrical energy found by calculating $\Sigma V_t I_t$ where the time interval is set to one second; and the total charge from Σ It where V_t and I_t are the voltage and current at time t respectively and are measured by the PC monitoring system through an analogue-to-digital converter and interface with PC parallel port.

Due to the polarisation properties of the electrolyser, the



I-V behaviour for pulsed DC was investigated. Figure 3. Pulsed DC (0.5Hz) fed into the electrolyser.

From fig 2 it can be seen that the electrolyser voltage increases sharply from 4.9V to 5.8V upon application of 4A current. The current flow into the electrolyser therefore occurs over a voltage range of 5.8V to 6.2V, the average being 6V. For a continuous current flow of 4A (with no pulsing), the electrolyser voltage was approximately 6.8V. This indicated that the electrolyser was working at a lower voltage for the same current flow when pulsing was used. A gain in efficiency was being obtained since by pulsing at 4A, the working voltage was reduced by 8.8%. However, as the duty cycle was 50%, the electrolyser should be actually compared to a continuous 2A current. The voltage at a steady 2A was approximately 6V, so actually the pulsing made no real improvement in practical efficiency since the effect could be directly duplicated by working at a lower current density.

A further run was carried out using high frequency pulsing at 20kHz 50% duty cycle. The average current and voltages measured using digital multimeters, were 0.47A @ 4.8V and 1.56A @ 5.33V. These points practically lie on the continuous-DC curve obtained for the same electrolyser temperature and age. This again shows that no particular benefit in terms of energy efficiency is to be found in converting electrical to hydrogen chemical energy by using pulsed DC into the electrolyser.

PV Panels Performance

A series of PV panels were assessed by exposing them to a measured value of insolation, using a pyranometer, and then monitoring their voltage and current output on a variable load. Initial tests, carried out with the panels distant some 50m from the electrolyser, were used to determine the effects of wire resistance on peak power output and the voltage position of the peak power point. As the latter fell between 12V to 15V, direct connection to the electrolyser would lead to a serious mismatch. Matching by inserting a series resistance is inefficient; a DC-DC converter was considered but a simpler approach was taken by centre-tapping one of the panels and use of only half the number of series connected cells of each PV module. By this set-up, the working voltage and required PV area was halved, with no loss in PV efficiency.

After March 2002 the PV modules where placed on the roof of the Physics building, only 12m directly above the electrolyser laboratory. The electrical efficiency of the set of polycrystalline panels named A using this set-up was over 10% -essentially that specified by the manufacturer-while power reached 36W at 7.5V with an insolation of 948W/m² (using two parallel centre-tapped panels).

Fig 4 below shows the PP curve using the centre-tapped panels. The peak power voltage is close to that required by the electrolyser, suggesting that a high hydrogen generating efficiency should be obtained.



A set of two mono-crystalline panels (named panels B) was next tested. Their specified voltage at maximum power was 17.6V. These modules consisted of three vertical strings of cells and so that tapping of one third of the panels was relatively easy. This was expected to yield a voltage of approximately 5.9V at peak power by using a third of the module area. The peak power curve is shown in Fig.5.

Figure 5 Peak Power curve for one third tapped module B.



Module C was a mono-crystalline panel that could not be centre-tapped. Although its efficiency was quite high, the mismatch between V at PP (see Table 3) and the electrolyser working V made it unsuitable for extended use.

Module	V @ Pmax	I @ Pmax	Pmax	Insolatio n	Efficiency
	/ V	/ A	/ W	/ Wm ⁻²	/ %
С	16	3.69	59	910	11.8

Table 3 Measured performance of Module C.



Figure 6 Polycrystalline solar panels and pyranometer.

Data for hydrogen production were collected over several months using various types of PV modules working under different conditions. The working conditions, weather, average insolation and other relevant information are listed in Table 4 below.

The PV-to-electrolyser-to-fuel cell train was monitored by a PC through a parallel communications port using a mini-POD100 analogue-to-digital converter connected to the PC. After several months of data collection, a single day was then used to conduct data collection using different set-ups on the same day. For this run on the 3^{rd} July, the temperature of the electrolyser was kept at an average of 60° C and pressure above atmosphere between 0 and 0.8bar. The PV modules were always kept approximately perpendicular towards the direction of the sun and their direction adjusted through the course of the day about every half an hour.

Solar Hydrogen Production

Date	ΡV	No. of parallel	Total flux	ΣVIt	PV eff.	Electolyser	Solar H2
	type	panels				eff.	eff.
			/kJ	/kJ	/%	/%	/%
15 Nov`01	Α	2	3370.0	231.30	6.86	86.35	5.93
19 Nov`01	Α	2	4970.0	337.73	6.79	84.49	5.74
23 Nov`01	Α	2	1296.0	89.37	6.90	85.95	5.93
30 Nov`01	Α	2	907.2	59.29	6.54	84.74	5.54
4 Dec`01	Α	2	1915.5	127.02	6.63	82.17	5.45
15 Feb`02	Α	2	168.5	13.52	8.02	79.60	6.39
8 May`02	Α	2	1477.4	136.37	9.23	70.69	6.52
8 May`02	Α	2	103.7	7.57	7.30	91.57	6.69
10 May`02	Α	2	4341.6	408.88	9.42	75.69	7.13
27 May`02	Α	2	388.8	34.33	8.83	76.56	6.76
6 Jun`02	В	1	864.0	104.61	12.11	85.35	10.51
14 Jun`02	В	2	397.4	31.84	8.01	85.10	6.82
14 Jun`02	В	1	302.4	31.48	10.41	88.38	9.20
14 Jun`02	В	1	216.0	23.82	11.03	91.25	10.06
3 Jul`02	В	2	172.8	16.73	9.68	83.21	8.05
3 Jul`02	В	2	216.0	19.90	9.21	84.91	7.82
3 Jul`02	В	2	259.2	22.09	8.52	84.86	7.23
3 Jul`02	В	1	64.8	6.03	9.31	90.55	8.43
3 Jul`02	В	1	185.8	17.27	9.30	89.20	8.30
3 Jul`02	В	1	133.9	12.47	9.32	88.95	8.29
3 Jul`02	Α	1	162.0	12.38	7.64	87.73	6.70
3 Jul`02	Α	2	324.0	27.13	8.37	76.46	6.40
3 Jul`02	С	1	294.8	26.45	8.97	77.30	6.94
3 Jul`02	D	1	177.1	13.16	7.43	90.71	6.74
27 Jul`02	Α	2	5119.2	496.54	9.70	67.38	6.54

Table 5 Summary of Results from Hydrogen Production runs.

The runs conducted using panel C show the effect of the PV panel characteristics on the final solar hydrogen efficiency according to their working voltage and efficiencies described earlier. The electrolyser efficiency was always quite high as it was kept at a high temperature ($\sim 60^{\circ}$ C).

One final run was then conducted on 27th July, 2002 to reproduce the central results of the work. Data was collected continuously over a relatively long stretch of over four hours using the two centre-tapped polycrystalline panels (type A) in parallel. This PV set-up was chosen as most data available was obtained using these modules and also to provide a relatively high power hydrogen production rate. The day was expected to yield relatively good efficiencies since the sky was quite clear and maximum air temperature only reached 27°C. The maximum recorded insolation was 990W/m² at around noon solar time. The solar hydrogen efficiency was 6.54%. The electrolyser temperature was at an average of approximately 45°C so the electrolysis efficiency

could have been improved by increasing the temperature towards 65°C.

The PV efficiency was only slightly lower than the maximum ever achieved for these panels. The overall solar hydrogen efficiency was also typical for this set-up, as can be seen from a comparison with data obtained from previous runs. This shows that the solar hydrogen efficiencies claimed in this work were repeatable even after a number of months.



Figure 7 27th July, 2002: 2 centre-tapped polycrystalline panels (type A) in parallel.

Fuel Cell Performance

The fuel cell was of the PEM type made by Electrochem(FC25-02SP). It comprises a single cell having an active area of 100cm². For better gas circulation, the cell has both gas inlets and gas exhaust outlets. It also has two 250V resistance heaters that can be used to bring the fuel cell to a working temperature of approximately 60°C. Specified performance is a maximum of 25A at 0.5V. To obtain the I-V characteristics for the fuel cell, it was fed with continuous flows of hydrogen and oxygen produced from the electrolyser. The gases were allowed to vent out from the fuel cell gas outlets after circulating in the cell. This also helped to remove the water produced on the oxygenreacting side inside the fuel cell.



Figure 8 Fuel Cell and D.C. motor.

As the output voltage is very low while the current is high, a number of low resistances were used, including some wire loops across the fuel cell terminals. The values of these low resistances were calculated from the ratio of V to I. The voltage across the load was taken to be equal to that across the terminals of the cell. The recommended working temperature for the fuel cell is about 60-70°C. At this increased temperature, the opencircuit voltage, the short-circuit current and the maximum output power were all found to increase but only a slight improvement in current to voltage ratio is obtained (fig 6). A number of further runs were then conducted to determine the current and energy efficiencies of the fuel cell. The current, voltages and time were measured for the fuel cell to consume a recorded volume of hydrogen. The hydrogen was fed both through the fuel cell inlet and exhaust nozzles to form a closed gas loop, so the volume change will only reflect that consumed by the fuel cell.

Voltage /V	Current /A	Time /s	Energy /J	Charge /C	H ₂ used /mg	Energy eff.	Current eff.
0.622	1.00	600	373.20	600	8.50	37.33	73.710074
0.667	1.04	600	416.21	624	8.02	44.12	81.218274
0.513	1.78	600	547.88	1068	13.70	34.01	81.402439

Table 6 Fuel Cell efficiencies.



Fig 9 Fuel Cell I-V characteristics.

After the first run at 1A, the current efficiency was found to be lower than expected i.e. 73.7% as compared to ~95%. Hydrogen loss was suspected; so the gas inlets to the fuel cell were greased and re-tightened. The next two runs from table 5, show an improvement in current efficiency to over 81%, confirming the suspected hydrogen leak. The current efficiency was however still below the expected value, implying that some hydrogen was still being lost through leakage from the system. This was probably due to the gas connections to the fuel cell being a combination of rubber flexible pipes and brass olive seals, which would not be very secure against hydrogen diffusion.

From the last two runs, the current efficiency was found not to be a function of current flow, whereas the energy efficiency drops at increasing current as the working voltage decreases. This behaviour is similar to that of the electrolyser. The current efficiency reference is the same as that used in the electrolyser, that is 95719C to produce 1g of H_2 being 100% efficiency. The energy efficiency however, is with reference to the reversible energy of hydrogen at minimum entropy, that is, the L.H.V., being 117.624kJ/g at 25°C and 1bar. Using this factor the fuel cell efficiency can reach a maximum of 100%. If the H.H.V. of H₂ is used as the reference, then the absolute energy efficiencies of runs in table 5 would equate to 30.99%, 36.62% and 28.23% respectively. The energy efficiency drops (to 34%) when the fuel cell was operated at a higher current (1.78A). The maximum rated power of the fuel cell is at higher currents, so the efficiency is expected to decrease even further at higher power delivery. This energy efficiency is low compared to other commercial systems such as that of the DCH Technology cell delivering 12W of electrical power at 48% efficiency (Larminie and Dicks, 2002).

The fuel cell was found to be relatively simple to operate and the hydrogen side did not require to be completely scavenged of air by purging with hydrogen before the cell could provide power. However, the fuel cell occasionally became flooded with water produced on the oxygen side and from condensation of water vapour in the entering gases. This flooding dramatically reduced performance, particularly if the cell was being run low temperature. Opening the cell and manually drying out the membrane would restore the performance in such cases.

Metal Hydride Storage

The metal hydride storage tank used was ST-25-AL of Ergenics Inc., with a total weight of 25kg of which about 9.7kg are absorbing chemical and a volume of 3dm^3 . The ST-25-AL unit with Hy-Stor® 209 was designed to work at a pressure of 10bar @ 25° C and can absorb 1.2% by mass of hydrogen in the compound metal powder. The metal hydride tank was evacuated to below 50mm Hg, and then connected to the gas dryers being fed from the top of the hydrogen Perspex cylinder. Initially the tank was kept at room temperature measured as 26.5° C. The metal powder in the hydride tank combined with 2.5dm³ of H₂, but then was very reluctant to absorb any more gas even at a hydrogen gas pressure of 50mbar above atmosphere.

The cylinder was then cooled to approximately 5°C by immersing it in a bucket filled with a water-ice mixture. At this temperature, the absorption increased. This was noted from the increase of the hydrogen flow into the tank. A further 4.48dm³ were accepted inside the tank before the rate again decreased showing that the tank was unable to absorb further under those conditions.

The electrolyser was then given a new Perspex centre cylinder which could withstand pressures of up to 1.8bar. The metal hydride tank was evacuated and then filled with hydrogen at room temperature (14°C) and a pressure of approximately 1bar over a period of several days. A sum of 69.3dm³ hydrogen was put into the metal hydride. The tank was still absorbing hydrogen readily at 1.5bar but no further gas was delivered into the tank. Its release from the tank was next investigated.

Although it was not possible to measure the actual amount of hydrogen expelled from the tank, a stable Bunsen flame was supported for a total of 40 minutes, and 16.2dm^3 (9bar x 1.8dm^3) were still inside the tank from the total of 69.3dm^3 . This indicated that at least a large proportion of the hydrogen was combining with the metal alloy.

Discussion

The efficiencies of the PV panels (approximately between 8% and 13%) were the main determining factors in the overall hydrogen production efficiency. The electrolysis efficiency varied between 70% and 90% depending on the working voltage which is a factor of the applied PV power, electrolyser temperature, and insolation conditions. By choosing a high efficiency mono-crystalline PV panel with a suitable working voltage and heating the electrolyser to over 60° C, the solar hydrogen efficiency exceeded 10% on two occasions.

The efficiencies were compared to the insolation received by the active area of each PV module. For panel types A, B and C, these corresponded to 80%, 87% and 90% of the physical module area respectively. As efficiency was referred to the cell area, the effects of variations in the construction of the different modules were eliminated. For example, the maximum efficiency of 10.51% (Table 7) obtained using module B, would result in a solar hydrogen efficiency of 9.14% compared to total module area. The module area efficiencies must be used when designing systems involving large PV areas as the physical module areas need to be considered. An interesting observation was that just after a sudden fall and rise in insolation due to the passage of a small cloud on a sunny day, the instantaneous efficiencies were particularly high. This was due to both the PV working at a lower temperature and to the electrolyser voltage decaying to a lower value due to depolarization. The electrolyser efficiency could be increased by using low power water circulating pumps so that no gas is allowed to stay on the electrodes acting as an insulator.

All the efficiencies obtained compare well with others found in the literature. The PV panel efficiencies were similar to those quoted by the manufacturer while an electrolyser efficiency of 75% (a working voltage of ~2V per cell) is also typical. These values can be compared with those from the Schatz Energy Project (Lehman and Chamberlin, 1999): PV panels running at approximately 10% efficiency and a feed of ~6kW of electricity to the electrolyser producing about 20 standard dm³ of H₂ per minute. This equates to an electrolysis efficiency of about 70% and an overall solar hydrogen efficiency of 7%. The actual measured efficiency was about 6.5%.

This work has demonstrated that solar hydrogen production efficiencies of over 9% (to module area) can be achieved. To produce an average of 1kg of H₂ (142MJ) per day, an initial solar energy of 1.56GJ/day is needed. The daily insolation averaged over a year on a surface inclined at 36° to the horizontal in Malta is 19.1MJ/day, or 17.2MJ/day on a flat horizontal surface (Iskander and Xerri, 1996). Hence, 1kg of H₂/day corresponds to a module area requirement of 82m² inclined or 91m² horizontal. A small electric vehicle carrying 2 persons requires 0.1kWh/km (Mallia and Schembri,2002), equivalent to ~360kJ/km. As 1 kg of H₂ (L.H.V. 117.624MJ) feeding a 45% efficient fuel cell produces 52.9MJ, such a car carrying 1kg of H₂ has a range of 150km. For a household having 2 such cars each covering 50km daily, only 0.67kg of H₂ are needed, corresponding to about 60m² of module area. This is some 40% of the area occupied by a standard terrace house of 8m x 20m. However, larger electric cars, with a typical consumption of 0.25kWh/km e.g. a 1998 Peugeot 106, would need a correspondingly larger PV area. This can be compared to a modern, high efficiency small car consuming gasoline at a rate of 5.6dm^3 /100km, where traveling 100km produces ~12.5kg of CO₂.

Use of hydrogen in a household rather than a transport setting would require a different approach, as households have both direct electrical and heat energy needs. PV electricity is best used directly; so during daylight hours H_2 production should only use electrical energy surplus to household demand for direct electricity. The required amount of H_2 would be significantly reduced if daytime space/water heating requirements are met by flat plate solar heat collectors.

However, in a household using only electricity from fuel cells running on hydrogen: 1 kg of H₂ (L.H.V. 117.624MJ) in a fuel cell at 45% efficiency would produce 52.9MJ (14.7kWh) of electricity and a further 50MJ (13.9kWh) of heat energy. For an average household consuming about 10-14kWh of electricity per day, including space and water heating applications, the above quoted area producing 1kg of H₂ is adequate. In fact, if 60%-70% of the heat energy produced by the fuel cell is utilized for space/water heating, one can have a significant reduction in the area of the PV array.

Both the electrolyser and metal-hydride tank are designed to work at pressures of up to 10bar. The complete system could be designed to work at this pressure to allow metal hydride tanks to be fully utilised. Further increase in pressure would require the use of an external diaphragm compressor. Pressures of up to 200bar can be achieved allowing considerable compressed gas storage in high-pressure steel tanks. These are commonly used in commercial distribution of H_2 . A 50L tank at 200bar (1kg H_2) requires an additional energy of 1MJ for compression. This is only about 1% of the chemical energy held by the gas.

An interesting comparison could be drawn between a Fuel Cell system and an advanced battery system. Both systems have the advantage of being relatively clean in terms of emissions, high efficiency and modular so can be designed to specific requirements especially in the case of vehicles. However it is quite clear that for very large systems, the fuel cell has clear advantages over the storage battery as fuel cell systems and hydrogen storage benefit from economies of scale. This is even more so in the case of supplying electricity to an industrial building; if storage batteries are used, the amount of space and investment needed would be too high. On the other hand if a simple, quick, compact and efficient power backup is required, a battery would be a favorite although small portable fuel cells are now being built to power computer laptops and mobile phones.

Below is a table comparing the equivalent electrical energy of 15kWh contained by 1kg of hydrogen.

Storage Type	Complete System Weight to store 15kWh electricity
Lead-Acid	540 kg
Li Polymer	125kg
NiMH	253kg
Na-Ni-Cl (Zebra)	200kg
H ₂ in metal hydride	270kg
H ₂ in reinforced C at 300bar	175kg

Table 7 Comparison of system weights of electrical energy carriers

In the above table, the battery systems are for 18kWh energy storage since only 80% depth discharge can be utilized. As for the hydrogen systems, the weight includes the storage tank and fuel cell.

Conclusion

The production of hydrogen by electrolysis of water using PV panels can reach overall efficiencies of 10%. With the local solar flux, such efficiencies make possible the generation of quantities of hydrogen useful in terms of urban transport from roof areas available on a standard terrace house. However, fuel cell personal transport is not predicted to reach significant levels before at least 2020. Locally, battery-powered electric cars are likely to be operational in considerable numbers much sooner than that.

PV generation of hydrogen for use in-house would require a different approach. The electrical energy needs of the household would have first call on the PV system output, with the direct beneficial effect of displacing fossil fuel use (and GHG emissions) from the power station. Only power surplus to household needs would go to the electrolyser, with the product stored at low pressure in a metal hydride tank. Subsequent use would be strongly conditioned by device cost--a 1kW commercial fuel cell sells at \in 30,000 – 32,000.

This latter situation reflects a current conundrum in the production of hydrogen with RE on medium-to-large scale. The prime intention of RE generation is to displace fossil fuel use, an aim best achieved by using the generated electricity directly. Spare capacity for hydrogen production would require a much accelerated program of RE generation, without there being a market for large quantities of hydrogen for a number of years. Present needs are mainly met by oxidation of CH₄, a cheaper (but not cleaner) method at current prices of natural gas. The one place hydrogen production by RE would be competitive at present is where it is used as a buffer between a wind farm and a small, isolated grid-a situation quite likely to arise on Malta when wind farms are eventually set up. With a limited distribution network, the hydrogen could be used in both static and mobile applications.

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Research Article

Commercial and non-target species of deep-water trawled muddy habitats on the Maltese continental shelf.

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Summary. Prior to joining the European Union, Malta operated a 25nm Exclusive Fishing Zone that was retained as a Fisheries Conservation Zone (FCZ) following EU membership. The present study was conducted in this FCZ as part of the ongoing MEDITS trawl survey programme. Otter trawl samples were collected from muddy bottoms at depths of 100-300m. The catch from each haul was sorted into commercial and non-commercial components, and fauna were identified and counted. Samples for analyses of infauna and sediment characteristics were collected using a 0.0625m² capacity box-corer. Macrofaunal abundance data for the stations were analysed using ordination techniques (nMDS) and relationships between environmental variables and faunal assemblages were explored by superimposing individual variables on the two-dimensional nMDS plots. The analyses clearly separated the commercial species into two distinct groups of assemblages that seemed to be defined principally by depth: those from inshore and south-eastern stations (depth range 100-250m) and those from north-western stations grouping together; however, the offshore stations had a greater variability in non-target species composition, especially for infauna. For the offshore stations, geographical position seemed to be important since stations off the north-western coast of the Maltese islands grouped separately from those off south-eastern Malta.

Keywords: Fisheries Conservation Zone, trawling, fisheries, MEDITS, benthos, macrofauna, infauna, muddy bottoms, community structure.

Introduction

Prior to joining the European Union, Malta managed an Exclusive Fishing Zone that extends to 25 nautical miles from the baseline of the Maltese Islands (Fig 1). Post-EU membership, this zone was retained as a Fisheries Management Zone (FMZ). The Maltese FMZ, which covers an area of 23,600 km², has a unique stock of demersal resources that are associated with certain physical and hydrographic features. For shallow shelf resources (<200 m) within the FMZ, adult populations are believed to be isolated to some degree from adjacent populations and there is limited exchange of adult individuals (Anonymous 2001; Camilleri, 2003). Therefore, the shelf seas around Malta can be regarded as an independent management unit for demersal resources. Knowledge of the demersal fisheries resources within this area is still poor although data are now being accumulated through Maltese participation in the Mediterranean International Trawl Survey (MEDITS; since 2000) and in the FAO programme MedSudMed. The MEDITS programme, in which all the Mediterranean European Union Member States participate, was designed to characterize the bottom fisheries resources in the Mediterranean by contributing annual data on population distribution (relative and demographic structure (length abundance) distributions, maturity stages, etc.) of the resource.

In recent years, there has been an increasing interest by fisheries scientists in ecosystem-based fisheries management, where fish stocks are no longer considered in isolation but as one component of an integrated ecosystem that includes the water column and the seabed (Link, 2002; Pitkitch et al., 2004). Considered as such, management of a fish stock becomes an exercise in management of the ecosystem in such a way as to allow long-term harvesting of the resource without either causing collapse of the population to below sustainable levels, or harm to the other components of the system on which this resource depends (Gislason et al., 2000; Link, 2002). In turn, such ecosystem management requires a good knowledge of the components of the system and how they interact together and against a change background of environmental conditions. Additionally, ecosystems and their biota are often vulnerable to anthropogenic activities such as demersal towed gears, which lead to changes in the benthic environment. Bottom trawling can lead to large-scale ecological effects that include physical disruption of the seabed, degradation of associated communities, over-fishing of demersal resources, changes in the structure and functioning of marine ecosystems as a result of the depletion of populations, and energy subsidies through large amounts of fisheries by-catch and the associated discards (Hall, 1999; Kaiser & De Groot, 2000).

National and international initiatives, including the establishment of no-fishing or restricted-fishing zones, such as the Malta FMZ, and other types of marine protected areas, increase the need to quantify the benthic environment within such areas. In this context, knowledge of the commercial demersal assemblages, the

sorted into commercial and non-target species, after which the fauna were identified and counted.

Three replicate samples for infauna and sediment analyses were collected using a 0.0625m² box-corer (Khalsico). Sediment granulometry and organic carbon



benthic assemblages, the associated benthic habitats, and of their respective interactions, is essential.

At present, there is little information on the distribution of biological assemblages in relation to environmental parameters within the Maltese FMZ even if such information is essential for the management of living resources with this management unit. This paper aims to quantify the biota associated with the deep-water muddy bottoms (100 - 400m) of the Maltese islands and to investigate the spatial distribution of the biotic assemblages that these ecosystems support.

Sampling methodology

The present study was conducted in the Maltese 25 Nm FMZ as part of the ongoing MEDITS trawl survey programme. One otter trawl sample per station was collected in summer 2004 from stations located at different depths between 100m and 300m on muddy bottoms (Fig. 1). Sampling was undertaken on board the RV *Sant*` *Anna*. Each trawl haul lasted for ca. 45 minutes, depending on the depth and substratum type, and trawl speed was c. 3 knots; a semipelagic experimental trawl net (IFREMER GOC 73: width 22m; height of vertical opening, 2m; length, 40m; stretched mesh size at cod-end, 20mm) was used (Fiorentini *et al.*, 1999). The entire faunal component from each haul was

were determined according to the procedures described by Buchanan (1984).

Statistical analyses

The macrofaunal abundance data for each station were analysed using ordination techniques. A similarity matrix was constructed from the fourth-root transformed abundance data using the Bray-Curtis similarity measure; non-metric multidimensional scaling (nMDS) ordination was then applied. The SIMPER program was used to determine which species contributed most to the similarity within each grouping of stations identified *a posteriori* (Clarke & Warwick, 1994a).

Relationships between measured abiotic characteristics (depth and sediment characteristics; see Table 3) and faunal assemblages were determined using the BIOENV procedure (Clarke & Ainsworth, 1993). and by superimposing scaled individual variables onto the sample locations on the two-dimensional nMDS ordination plots (Field *et al.*, 1982; Clarke & Warwick, 1994a). All the analyses were undertaken using the PRIMER 5.22 statistical software package (Clarke & Warwick, 1994b).

Results

Examination of the nMDS ordination plot revealed that the commercial species were separated into two distinct groups of stations: the inshore + south-eastern stations and the north-western deeper stations (Fig. 2a). The inshore and south-eastern sites were dominated by Trachurus trachurus (Atlantic Horse Mackerel), Illex coindetti (Broadtail Squid) and Mullus barbatus (Red Mullet), while the north-western stations were dominated by typically deeper water species such as Aristeomorpha foliacea (Giant Red Shrimp), Nephrops norvegicus (Norway Lobster) and Galeus melastomus (Blackmouth Catshark; Table 1). From the superimposition of the environmental variables on the two dimensional nMDS ordination plots, depth appeared to correlate best with the two identified biological groupings; in general, the depth of the inshore and south-eastern stations ranged from 100-250 m while for the north-western stations it ranged from 200–350 m. The non-target species showed a similar pattern with respect to the inshore stations (Fig. 2b), but there was a greater variability for the offshore stations (Table 2). There was also a strong correlation of the offshore stations with geographical position: stations off the north-western coast were grouped together, as were those off south-eastern Malta.

The dominant non-target species in the areas studied (Table 2.) where the crinoid *Leptometra phalangium*, juveniles of *Illex coindetti* and of *Parapanaeus longirostris*, and other natantian decapods (e.g. *Plesionika heterocarpus*). The infauna had the greatest spatial variation (Fig. 2c) but nonetheless, there is evidence of a depth gradient in infaunal assemblage composition. Stations M13 and M15 had no infauna and were excluded from the plots.



Fig 2. Non-metric multidimensional scaling (nMDS) plot for the ten sampling stations based on fourth root transformed species abundance data using the Bray-Curtis similarity measure. (a) Commercial species; (b) Non-arget specioes, and (c) Infauna. Superimposed plots of scaled values of depth, mean grain size, % sand, % organic carbon are also shown.

the NW sector stations.					
	Inshore -	+ SE	NW		
Taxon	Mean abun. (ind. / km ²)	St. dev.	Mean abun. (ind. / km ²)	St. dev.	
Aristeomorpha foliacea	0	0	4569	±6310	
Trachurus trachurus	0	0	0	0	
Illex coindetii	1813	±1705	0	0	
Nephrops norvegicus	0	0	856	±524	
Mullus barbatus	606	±326	0	0	
Galeus melastomus	0	0	236	±283	
Phycis blennoides	3	±5	238	± 168	
Citharus linguatula	401	±589	0	0	
Trisopterus minutus capelanus	353	±551	0	0	
Aspitrigla cuculus	201	±222	0	0	

Table 1. Mean abundance values of the top ten commercial species from the SIMPER species list, which contributed consistently to the dissimilarity between the inshore + SE sector and the NW sector stations.

Table 2. Mean abundance values of the top ten non-target species from the SIMPER species list, which contributed consistently to the dissimilarity between the different geographical locations.

	Insh	ore	SI	.	NW		
Taxon	Mean abun. (ind. / km ²)	St. dev.	Mean abun. (ind. / km ²)	St. dev.	Mean abun. (ind. / km ²)	St. dev.	
Leptometra phalangium	0	0	10490	±14835	20	±34	
Antedon mediterranea	0	0	135	±40	0	0	
Parapenaeus longirostris (juv.)	266	±195	4289	±5825	80	±55	
Cidaris cidaris	13	±10	220	± 80	3	±6	
Latreilla elegans	26	±31	122	±173	0	0	
Sepia orbignyana	19	±18	0	0	3	±6	
Illex coindetii (juv.)	254	±138	655	±806	0	0	
Plesionika heterocarpus	0	0	0	0	207	±120	
Sergestes corniculum	0	0	0	0	196	±217	
Pasiphaea sivado	0	0	0	0	73	±67	

The correlation analyses made using the BIOENV program, all gave relatively high values of Spearman's coefficient (Table 3). For all three assemblage types, a combination of three to five abiotic variables gave the highest correlations, with depth, % gravel, % coarse silt, median particle diameter and % organic carbon being the most important.

Discussion

Two different assemblages of commercial species were identified, one in the north-western deeper waters and the other distributed inshore and to the south-east of the Maltese islands. These two areas are both trawled by local fishers. The northern areas are trawling grounds for highly prized decapod crustaceans, namely the Giant Red Shrimp (Aristeomorpha foliacea, also commonly called 'King Prawns'), the Norway Lobster (Nephrops the deep-water Pink Shrimp norvegicus), and (Parapanaeus longirostris). This area also is

characterized by other valuable but locally not commercially important decapod crustaceans such as Plesionika heterocarpus and Pasiphaea sivado. The inshore and the south-eastern areas are trawled by local fishers mainly for Red Mullet (Mullus surmuletus and Mullus barbatus), with commercial by-catches of squid (e.g. Illex coindetti; Loligo vulgaris), Poor Cod (Trisopterus minutes capelanus), Hake (Merluccius Bluemouth Rockfish merluccius), (Helicolenus dactylopterus dactylopterus) and others. The results of our analysis of the commercial catch confirm what local fishers that trawl have known for years, that is, that certain commercial species are commonly present at particular depth ranges and in particular geographical locations.

In the analysis of the non-target species, the northern stations also grouped together as for the commercial assemblage. However, the inshore and south-eastern stations, which grouped together in the commercial catch analysis, were separated in the non-target species analysis

abiotic	similarity matrices as measu	area by weighted Spearman rank correlation.
Biotic assemblage	Spearman correlation coefficient	Variable combination
Commercial	0.738	Depth, % Gravel, % Silt &Clay, Median diameter, % Organic Carbon
	0.737	Depth, % Gravel, % Silt & Clay, % Organic Carbon
	0.734	Depth, % Gravel, % Silt, % Coarse silt, % Organic Carbon
Non-target	0.772	Depth, % Coarse silt, % Organic Carbon
	0.771	Depth, % Gravel
	0.771	Depth, % Gravel, % Coarse silt, % Organic carbon
Infauna	0.674	Depth, % Sand, % Very coarse silt
	0.673	Depth, % Sand, % Very coarse silt, Median diameter
	0.673	Depth, % Sand, % Very coarse silt, % Organic carbon

Table 3. Combinations o	f the twelve variables yiel	ding the best three i	matches of biotic and
abiotic similari	ty matrices as measured b	y weighted Spearma	in rank correlation.

which may suggest a closer association with the environmental attributes across the study area. Most of the non-target species are prey items for the commercial species. The non-target organisms collected by otter bottom trawling are predominantly made up of macrobenthos. A comparison of the the commercial and the non-target components of the samples analysed shows that commercial assemblages residing in different geographical locations may be feeding on two different benthic assemblages (the non-target groups identified by the ordination analysis). Individual commercial species, especially fish, are known to have different diets in different geographic locations according to the availability of prey species within that location (Konstantinos et al., 2002). The different non-target assemblages in the inshore and south-eastern stations may be related to different levels of trawling intensity in these two areas. Non-target species, especially benthic organisms, are affected directly by bottom trawling and tend to be less mobile and have longer recovery times (Hall, 1999; Kaiser & De Groot, 2000). In contrast, the commercial catch (especially fish) are usually less sensitive, are more mobile and remain relatively unchanged in terms of their distribution with a moderate level of trawling effort. Commercial species, especially fish, tend to change their feeding behaviour from a predatory to a scavenging one in trawled areas as the fish are attracted by an increased food supply (an energy subsidy) as a result of the mechanical killing of benthic fauna (Demestre et al., 2000; Kaiser & Spencer 1994).

The stations to the SE of Malta have a high abundance of the crinoid *Leptometra phalangium* (Table 2). The

numbers recorded are an underestimate of the actual population density on the seabed as a large number of the crinoids were probably lost during hauling of the net since these animals are very small (1-3 cm) and pass easily through the net's mesh. Smith et al. (2000) also recorded a large number of Leptometra phalangium in the vicinity of a trawled area on a muddy bottom at a depth of about 200m in the eastern Mediterranean using underwater video. On the sides of the trawl lane, the crinoids were present in dense aggregations, but the animals were rarely seen in the areas with trawl marks. In trawled areas, suspension-feeders might profit from collecting and feeding on re-suspended sediments, and this might explain the dense aggregations of L. phalangium adjacent to trawling lanes; however, these fragile organisms are easily damaged, which explains why they do not occur in trawling lanes (Smith et al., 2000).

In the present study, the occurrence of large populations of *Leptometra phalangium* at the south-eastern stations may be related to the presence of trawling lanes in this area as this area may be subject to medium intensity trawling, however, this is still to be confirmed.

Overall, all the stations had a very low infaunal abundance. No fauna whatsoever were recorded from stations M13 (275m) and M15 (340m), to the northwest of the islands (the deepest stations sampled).

Conclusions

For the commercial species two distinct assemblages were found that were largely influenced by geographic location, depth and sediment characteristics. The bycatch component of trawl samples showed similar However, the inshore and south-eastern patterns. stations, which had similar commercial assemblages, had different non-target species assemblages and this may imply a different feeding regime for the commercial species of these two areas. However to confirm this hypothesis, stomach content analyses on selected commercial species needs to be made to determine if the diets of the same species from the two areas are different. The present results suggest that fishing disturbance may cause shifts in the benthic community structure that particularly affect mobile scavenging species, which are probably the most food-limited trophic group on muddy seabeds. The infauna was spatially the most variable component and different stations around the Maltese islands had different assemblages without any clear distributional patterns.

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Research Article

On the suitability of empirical models to simulate the mechanical properties of α -cristobalite

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Summary. The silicate α -cristobalite exhibits the unusual property of becoming wider when stretched and thinner when compressed, i.e. it has a negative Poisson's ratio (auxetic). Here we show that the behaviour of this silicate can be modelled through empirical simulations and that a number of force-fields can reproduce the experimentally measured single crystalline negative Poisson's ratios.

Keywords: Cristobalite, negative Poisson's ratios, auxetic

Introduction

Auxetic materials (Evans 1990, see Appendix 1), also know as 'anti-rubber' (Lakes 1987a) or 'self expanding' (Grima et al. 2000) exhibit the counterintuitive property of becoming wider when stretched and thinner when compressed, i.e., they have a negative Poisson's ratio. Auxeticity imparts many beneficial effects on the materials' macroscopic properties which make them more useful than their conventional counterparts in many practical applications. For example, auxetics exhibit an increased ability to resist indentation (Lakes and Elms 1993, Alderson 1999), have a natural ability to form dome-shaped surfaces (Evans 1991), and have an enhanced ability to absorb vibrations (Scarpa et al. 2005). These properties make products made from auxetic components superior to ones made from conventional materials (Alderson 1999).

It has long been known that negative Poisson's ratios are theoretically feasible: the theory of classical elasticity suggests that isotropic materials may exhibit Poisson's ratios within the range $-1 \le \nu \le +0.5$. However, it was generally assumed that there was little scope in studying this property as materials with negative Poisson's ratios were unlikely to be encountered in everyday life. However, in recent years, there has been a growing interest in materials exhibiting this unusual yet very useful property, especially following the report in 1987 that samples of auxetic foams had been produced from conventional ones through a simple compression/heating process (Lakes 1987b). Since then, several other auxetics have been predicted, discovered and/or manufactured including various naturally occurring auxetics such as cubic metals (Baughman et al. 1998), zeolites (Grima et

al. 2000a, Grima *et al.* 2000b) and silicates (Keskar and Chelikowsky 1992) (Yeganeh-Haeri *et al.* 1992) and man-made auxetics such as nanostructured polymers (Evans *et al.* 1991, Baughman and Galvao 1993, Grima and Evans 2000, Grima *et al.* 2005a, Grima *et al.* 2005b) liquid crystalline polymers (He *et al.* 1998, He *et al.* 2005) and microporous polymers (Caddock and Evans 1989, Alderson and Evans 1993), (Pickles *et al.* 1996) and foams (Lakes 1987b, Evans *et al.* 2005c). In all of these cases, the negative Poison's ratios can be explained in terms of models based on the geometry of the materials' nano/microstructure and the way this geometry changes as a result of uniaxially applied loads (the deformation mechanism).

This can be illustrated by considering a two-dimensional honeycomb structure deforming through hinging of the ribs forming the network. As illustrated in Figure 1, stretching of this traditional honeycomb will result in the cells getting longer in the loading direction and narrower along the transverse direction, i.e. they exhibit a positive Poisson's ratio (see Fig. 1a). Auxetic behaviour may be obtained by performing a simple modification in the honeycomb geometry to obtain a re-entrant structure. Stretching of this re-entrant honeycomb will result in opening-up of the cells which will now get longer in both the loading and transverse directions with the effect that the structure exhibits a negative Poisson's ratio (see Fig. 1b).

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Figure 1: (a) conventional and (b) auxetic hexagonal honeycombs.

Negative Poisson's ratio in α-cristobalite

An auxetic material which has attracted considerable attention is the naturally occurring silicate α -cristobalite for which auxetic behaviour for loading in certain directions was independently discovered and reported more than ten years ago by Keskar and Chelikowsky (Keskar and Chelikowsky 1992) who studied this mineral using *ab initio* modelling techniques and by Yageneh–Haeri and co-workers (Yeganeh-Haeri *et al.* 1992) who measured the single crystalline mechanical properties of α -cristobalite experimentally using Brillonium spectroscopy.

The experimental work of Yageneh–Haeri *et al.* (Yeganeh-Haeri *et al.* 1992) suggests that in single crystalline α -cristobalite, negative Poisson's ratios can be measured in the family of planes passing through the [001] direction where the most negative Poisson's ratios are found for loading at approximately $\pm 45^{\circ}$ to [001] direction. Thus, for example, as illustrated in Fig. 2a, negative Poisson's ratios can be found in the (100) plane of α -cristobalite with the most negative Poisson's ratios being measured for loading in approximately the [011] and the [011] directions.

This silicate is particularly interesting because it illustrates how nature can produce a material where the extent of the single crystalline auxeticity is so pronounced that the isotropic polycrystalline aggregate Poisson's ratios are also predicted to be negative. This is very significant as chemists could be inspired by this material in their quest for synthesising new man-made materials which exhibit negative Poisson's ratios.

In this work we examine the suitability of various empirical models to reproduce the crystal structure and mechanical properties of α -cristobalite. In particular, we will attempt to reproduce the single crystalline negative Poisson's ratios of α -cristobalite as experimentally measured by Yageneh–Haeri *et al.*

Methods used

The structural and mechanical properties of α -cristobalite were simulated using two software packages, namely:

- 1. The Open Force-Field module, OFF, within the commercially available molecular modelling package *Cerius*² (Release 3.0 and 4.1) developed by Accelrys Inc., and,
- 2. The General Utility Lattice Program, GULP (Version 1.3.2), a molecular modelling program created by Prof. Julian D. Gale, formerly of the Royal Institution of Great Britain (now at Curtin University of Technology, Australia).

Within the OFF Cerius² package, one can find several force-fields which are parameterised for simulating SiO₂ systems. These include the Universal (Rappe et al. 1992); Burchart (de Vos Burchart 1992); BKS (van der Beest et al. 1990); CVFF (MSI 1997) and COMPASS (Sun et al. 1998) force-fields which were used in this study. These force-fields differ from each other in the formulation of their energy expression, were for example, in the case of the BKS force-field, the energy expression is composed solely from non-bonding Van der Waals (VDW) and Coulombic terms (i.e. the system is treated solely as an 'ionic' system) whilst in the case of the Burchart force-field, in addition to the VDW and Coulombic non-bond terms, one also encounters simple bonding terms, for example, a Morse term for 1-2 connected atoms (bond lengths) and the harmonic term for 1-3 connected atoms (a Urey-Bradley term to describe the bond-angles). The other $Cerius^2$ force-fields used, i.e. the Universal, CVFF and COMPASS force-fields have even more complex energy expressions, which, for example include torsion terms and/or cross-terms.

The GULP package offers the added advantage over the Cerius²-OFF that it permits the inclusion of atom polarisability through the use of the core-shell model. Various GULP compatible force-fields (or 'libraries of potentials') have been developed, some of which have been used in this study as they were reported to be suitable for modelling of zeolites and silicates. In GULP, a polarisable atom is represented by a positive core coupled with a negative mass-less shell where in a nonpolar atom, the centre of the shell coincides with the centre of the core whilst in polar atoms, the shell is offset from the core with the result that one side of the 'atom' appears as 'positive' whilst another side appears as 'negative'. An energy expression constructed from a GULP library is generally made up from non-bond terms (Coulombic and VDW), simple bond terms (typically describing bond lengths and/or angles) and the implementation of the Core-Shell model.

In this particular study, the libraries of potential used were the **Catlow 1992** library (Sanders *et al.* 1984; Jackson & Catlow 1988; Schroder *et al.* 1992; Gale & Henson, 1994; Jentys & Catlow 1993; Lewis *et al.* 1995; den Ouden *et al.* 1990); the **Parker 1992** library (Sanders *et al.* 1984; Baram & Parker 1996); the **Sauer 1997** library (Sierka & Sauer 1997; Sauer *et al.* 1998), and the **Sastre 2003** library (Sastre & Gale 2003) and the **Glass** library (Blonski and Garofalini 1997) These libraries have all been parametrised for SiO₂ systems.

In the simulations, the unit cell of α -cristobalite was aligned relative to the global *XYZ*-coordinate system in such a way that the [100], [010] and [001] directions were aligned parallel to the *X*, *Y* and *Z*-axes respectively[†].

In Cerius², for all simulations, the energy expressions were set up using the default force-field parameters and settings. (In the case of the Universal force-field, the charges used were calculated using the Charge Equilibration procedure developed by Rappé and Goddard (Rappe and Goddard 1991) since this force-field does not contain any information on the atomic charges.) Non-bond interactions were summed up using the Ewald method (Ewald 1921) and the energies of these systems were minimised to the default *Cerius*² high convergence criteria which include a condition that the RMS gradient must be less than 0.001 kcal mol⁻¹ Å⁻¹. No constraints on the shape and size of the unit cell were applied during the minimisations. For each force-field, the single crystalline mechanical properties were obtained by simulating the 6x6 stiffness matrix C of the minimised systems which can be calculated from the second derivative of the energy expression, E, since:

$$c_{ij} = \frac{1}{V} \frac{\partial^2 E}{\partial \varepsilon_i \partial \varepsilon_j} \qquad i, j = 1, 2, ..., 6$$

where *V* is the volume of the unit cell, ε_1 , ε_2 and ε_3 are the strains in the *X*, *Y* and *Z* directions respectively whilst ε_4 , ε_5 and ε_6 are the shear strains in the *YZ*, *XZ* and *XY*-planes respectively. The on-axes Poisson's ratios were then calculated from the terms of the compliance matrix **S**=**C**⁻¹ since, for example:

$$v_{yz} = -\frac{\varepsilon_z}{\varepsilon_y} = -\frac{s_{32}}{s_{22}} \quad \& \quad v_{zy} = -\frac{\varepsilon_y}{\varepsilon_z} = -\frac{s_{23}}{s_{33}}$$

The off-axes mechanical properties were then obtained using standard transformation of axes techniques (Nye 1957).

A similar procedure was carried out with GULP, where once again the default GULP settings for energy minimisation and calculation of the stiffness matrices was used. In particular, the Ewald summation was also used to sum up the non-bond interactions and minimisations were stopped after the GULP high convergence criteria were satisfied (i.e. 10⁻¹⁰ fractional units were imposed for function, gradient and parameter tolerances).

Results and Discussion

The stiffness matrices as simulated by the various $Cerius^2$ -OFF and GULP models are shown in Table 1 whilst a graphical comparison of the simulated and the experimental crystal structure and Poisson's ratios in the

(100) plane are shown in Figure 2. These are followed by a comparison of the simulated lattice parameters and various mechanical properties (see Table 2 and Figure 3).

	Ex	peri	men	tal		Syn	ımet	ry re	qui	reme	ents
(59.4	3.8	-4.4	0.0	0.0	0.0	(••	• ·)	-		
3.8	59.4	-4.4	0.0	0.0	0.0				N		
-4.4	-4.4	42.4	0.0	0.0	0.0		•		• NO	n-zero	value
0.0	0.0	0.0	67.2	0.0	0.0		•		· Ze	ro valu	ie
0.0	0.0	0.0	0.0	67.2	0.0		_ ヽ				
0.0	0.0	0.0	0.0	0.0	25.7)			• •			
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(000	U.		r As	6	0.0.)			CVI	ГГ		
90.0	05.0	-4.5	0.0	0.0	0.0	(146.7	14.9	-12.0	0.0	0.0	0.0
11./	95.9	-4.3	0.0	0.0	0.0	14.9	146.7	-12.0	0.0	0.0	0.0
-4.3	-4.5	49.9	0.0	0.0	0.0	-12.0	-12.0	68.2	0.0	0.0	0.0
0.0	0.0	0.0	54.8	0.0 5.1.0	0.0	0.0	0.0	0.0	79.5	0.0	0.0
0.0	0.0	0.0	0.0	54.8	25.1	0.0	0.0	0.0	0.0	79.5	0.0
(0.0	0.0	0.0	0.0	0.0	35.1)	0.0	0.0	0.0	0.0	0.0	52.2
						`					
	1	Bura	hart	t				BK	S		
						(70.4	11.7	4.3	0.1	-0.1	-0.1)
104.0	21.1	1.3	0.0	0.0	0.0	11.7	69.8	4.1	0.0	0.0	0.1
21.1	104.0	1.3	0.0	0.0	0.0	4.3	4.1	47.2	-0.1	-0.1	0.0
1.3	1.3	45.6	0.0	0.0	0.0	0.1	0.0	-0.1	71.4	0.0	0.0
0.0	0.0	0.0	59.5	0.0	0.0	-0.1	0.0	-0.1	0.0	71.5	0.0
0.0	0.0	0.0	0.0	59.6	0.0	-0.1	0.1	0.0	0.0	0.0	24.6
0.0	0.0	0.0	0.0	0.0	31.4)	()
	1	FT •					C		100		
	,	Univ	ersa	I		(C	atiow	7 19 9	2	
/						(74.3	4.4	9.6	0.0	0.0	0.0
298.42	40.44	26.70	0.0	0.0	0.0	4.4	74.3	9.6	0.0	0.0	0.0
26.70	26.70	169.50	0.0	0.0	0.0	9.6	9.6	69.2	0.0	0.0	0.0
0.0	0.0	0.0	118.65	0.0	0.0	0.0	0.0	0.0	/4./	0.0	0.0
0.0	0.0	0.0	0.0	118.65	0.0	0.0	0.0	0.0	0.0	/4./	20.0
0.0	0.0	0.0	0.0	0.0	89.03)	(0.0	0.0	0.0	0.0	0.0 2	50.0)
			10	•			G		100	_	
	Pa	arke	r 199	92			S	auer	199	7	
(74.3	3 4.4	9.6	0.0	0.0	0.0	(77.02	4.00			0.0	
4.4	74.3	9.6	0.0	0.0	0.0	1.83	4.09	23.21	0.0	0.0	0.0
9.6	9.6	69.2	0.0	0.0	0.0	23.21	23.21	70.62	0.0	0.0	0.0
0.0	0.0	0.0	74.7	0.0	0.0	0.0	0.0	0.0	68.40	0.0	0.0
0.0	0.0	0.0	0.0	/4./	0.0	0.0	0.0	0.0	0.0	68.40	0.0
(0.0	0.0	0.0	0.0	0.0	30.0)	0.0	0.0	0.0	0.0	0.0	21.45)
	S	astro	e 200)3				Gla	ISS		
61.81	1.64	17.73	0.0	0.0	0.0	(240.82	23 71	68.28	0.0	0.0	00)
1.64	61.81	17.73	0.0	0.0	0.0	23.71	240.82	68.28	0.0	0.0	0.0
17.73	17.73	60.80	0.0	0.0	0.0	68.28	68.28	165.77	0.0	0.0	0.0
0.0	0.0	0.0	63.96	0.0	0.0	0.0	0.0	0.0	113.42	0.0	0.0
0.0	0.0	0.0	0.0	63.96	0.0	0.0	0.0	0.0	0.0	113.42	52.05
0.0	0.0	0.0	0.0	0.0	18.75)	0.0	0.0	0.0	0.0	0.0	52.05)

Table 1: The stiffness matrices ($\mathbf{C}=[c_{ij}]$) obtained for α -cristobalite using the various force-fields in this study, and the symmetry requirements for α -cristobalite (Nye 1957).

[†] Note that for non cuboidal unit cells, the software packages *Cerius*² and GULP orient the unit cells in a different manner. In a particular, in *Cerius*², the cells are aligned in such a way that the [001] direction is aligned parallel to the Z-axis and the (100) plane is aligned parallel to the YZ-plane whilst in GULP, the [100] direction is aligned with the X-axis and the (001) plane is aligned parallel to the XY-plan. Since α -cristobalite has a cuboidal unit cells, this difference in alignment will not affect the way that the crystal is algned in the XYZ-global coordinate system.



(c) Simulated with GULP



Figure 2: A graphical comparison of the simulated and experimentally determined crystal structure of α -cristobalite in the (100) plane and the Poisson's ratios in the (100) for loading in a direction in the same plane.

	Latti	ce Paramet	ers	rs Single o in the on-av		alline Poisson's ratios 0)-plane (YZ plane) 45° off-axis		Single crystalline Young's moduli		Polycrystalline aggregate	
	<i>a, b</i> (Å)	с (Å)	α, β, γ (deg.)	V_{yz}	ν_{zy}	$(45^{\circ})^{v_{yz}}$	$(45^{\circ})^{\nu_{zy}}$	E_{x}, E_{y} (GPa)	Ez (GPa)	v_{max}	ν_{min}
Experimental	4.978	6.948	90.000	-0.098	-0.070	-0.497	-0.497	58.75	41.79	-0.211	-0.115
COMPASS	5.050	6.842	90.000	-0.077	-0.043	-0.280	-0.280	94.19	49.42	-0.080	-0.004
CVFF	4.965	6.619	90.000	-0.160	-0.074	-0.317	-0.317	143.49	66.43	-0.127	-0.026
Burchart	4.978	6.684	90.000	0.020	0.011	-0.305	-0.305	**	45.62	-0.039	0.072
BKS	4.889	6.528	90.000	0.073	0.050	-0.417	-0.417	*	46.86	-0.074	0.026
Universal	4.635	6.068	90.000	0.138	0.079	-0.007	-0.007	289.75	165.29	0.092	0.125
Catlow 1992	4.971	7.009	90.000	0.132	0.122	-0.303	-0.303	72.85	66.91	-0.034	0.025
Parker 1992	4.970	7.008	90.000	0.132	0.122	-0.303	-0.303	72.81	66.89	-0.035	0.025
Sauer 1997	4.979	7.095	90.000	0.345	0.283	-0.198	-0.198	70.02	57.46	0.071	0.148
Sastre 2003	5.001	7.138	90.000	0.310	0.279	-0.256	-0.256	56.42	50.89	0.026	0.120
Glass	5.289	7.432	90.000	0.420	0.258	0.024	0.024	212.61	130.52	0.176	0.210

Table 2: The lattice parameters, the on-axis and 45° off axes single crystalline Poisson's ratios, the Young's moduli and the Polycrystalline aggregate values. * In the case of the BKS force-field $E_x \neq E_y$ and the specific values are $E_x = 27.81$ GPa and $E_y = 60.89$ GPa. ** In the case of the Burchart library, the values were: $E_x = 99.94$ GPa and $E_y = 99.87$ GPa.



Figure 3: A graphical comparison of the differences (or % differences) between simulated and experimentally determined properties of various structural and mechanical properties of α -cristobalite. The upper and lower boundaries of the Poisson's ratios are also shown.

These results and comparisons show very clearly that the there is no single force-field or library that can reproduce <u>all</u> the experimental properties to a high degree of accuracy but there are a number of force-fields which can successfully reproduce all the general features of this silicate.

In particular, referring to Figure 2, we may see that all the models used (except for the Glass library) produce a structure of α -cristobalite which is very similar to one obtained experimentally from X-Ray data. Furthermore, referring to Table 2 and Figure 3a it may be deduced that with the exception of the Universal force-field and to a lesser extent the BKS force-field (*Cerius*² force-fields) and the Glass library (a GULP library), all models can successfully reproduce the lattice parameters of α cristobalite within ±5%. In this respect, the models which best reproduce the structural parameters (i.e. the crystal structure and lattice parameters) are the Catlow and Parker libraries (GULP libraries).

A comparison of the stiffness matrices in Table 1 suggests that all force-fields predict a stiffness matrix for α -cristobalite which is of the form expected for a system with a tetragonal symmetry (α -cristobalite has a P4₁2₁2 symmetry). In fact, the only force-field where the matrix deviated slightly from the expected form was the BKS force-field and this may be due to the formulation of the BKS force-field, which, unlike the other force-fields used, contains only the non-bond terms, i.e., it does not take covalent character into consideration. However, it should be noted that the values of the terms in the stiffness matrices as simulated by the different models are very different from each other and different from the experimentally obtained matrix. This suggests that the different models do not predict the 'stiffness' of the material very accurately and precisely. Nevertheless, referring to Figure 2, it is very significant to note despite the differences in the actual values of the matrix terms, all the models correctly predict that the Poisson's ratios in the (100) plane of α -cristobalite are most auxetic for loading at approximately 45° to the major axes (i.e. approximately the [011] and $\begin{bmatrix} 0\overline{1}\overline{1} \end{bmatrix}$ directions).

Furthermore, referring to Figure 2, Table 2 and Figure 3, one may observe, that with the exception of the Glass model, all models predict that α -cristobalite exhibits auxetic behaviour to some extent or another since all models (with the exception of the Glass library) correctly predict that α -cristobalite is auxetic in the (100) plane for loading at approximately 45° to the major axes.

It can also be observed that the COMPASS and CVFF force-fields (*Cerius*² force-fields) are extremely suitable for modelling the Poisson's ratios of α -cristobalite, since:

- These force-fields correctly predict that αcristobalite is auxetic for loading in any direction in the (100) plane;
- They correctly predict that the polycrystalline aggregate are expected to be negative;

 The CVFF force-field predicts polycrystalline aggregate values for the Poisson's ratios which are very similar to those predicted by experimental data whilst the COMPASS forcefield predicts lattice parameters and Young's moduli which are very similar predicted by experimental data.

All this is very significant as it shows that it is possible to use empirical simulations to study the Poisson's ratios of single crystalline materials, including those which exhibit the unusual property of having a negative Poisson's ratio. In fact, the simulations suggest that in such cases, the simulations generally predict values of the Poisson's ratios which are close to those measured experimentally. Secondly, these simulations show that in such studies, it is very important to use more than one force-field to study such materials, and rather than discussing the 'exact' values of mechanical properties as smilulated by some particular force-field, it is more useful to discuss 'trends' were different force-fields provide similar results. For example, in this case, despite the fact that the different models gave different values for the elastic constants, they correctly and consistently predicted that α -cristobalite exhibits auxetic bahaviour, particularly in the (100) plane when loading at approximately 45° to the major axes.

Finally, the simulations suggest that in the case of α cristobalite, it is not essential to include the effect of atom polarisability to be able to correctly describe the structural and mechanical properties. In fact, the simulations suggest that the best force-fields which can reproduce the auxetic behaviour of α -cristobalite are the CVFF and COMPASS force-field which unlike the GULP models, are unable to represent atom polarisability.

Conclusion

It has been showed that empirical simulations can successfully reproduce the structural and mechanical properties of α -cristobalite and that the quality of the simulated properties depenend primarily on the forcefield used. In particular, it has been shown that the *Cerius*² force-fields CVFF and COMPASS are particularly suitable for simulating the properties of this silicate. All this is very significant as it suggests that empirical simulations can be successfully used to study α -cristobalite in more detail in an attempt to understand more clearly the way how nature can achieve the very usual property of a negative Poisson's ratio. It is hoped that through such studies, scientists and engineers will be one step closer to obtain materials and structures which expand when stretched by mimicing the behaviour of this naturally occurring auxetic.

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Appendix 1*

The term 'auxetic' derives from the Greek word αυξετοσ (auxetos) meaning 'that may be increased', referring to the width and volume increase when stretched (Evans et al. 1991). In modern Greek, we also find the word αυξάνω (auxano) meaning 'to increase'. Since no equivalent word is available in the Maltese language to describe systems which experience a width increase when stretched, we propose that in Maltese, systems which expand when uniaxiually stretched will be termed 'awksetiku' (singular masculine), 'awksetika' (singular femine) or 'awksetiči' (plural). Thus for example, the terms 'an auxetic material', 'an auxetic structure', 'auxetic materials' and 'auxetic structures' will translate to 'materjal awksetiku', 'struttura awksetika', 'materjali awksetiči' and 'strutturi awksetiči' respectively.

(*) The contribution of Professor Oliver Friggieri, Professor of Maltese, University of Malta is gratefully acknowledged.

Appendix 2

The isotropic polycrystalline values of the Poisson's ratios relate to an idealised scenario where the crystal domains in a sample of α -cristobalite are arranged in such a way that the resulting material is isotropic, in which case the maximum and minimum values of the polycrystalline Poisson's ratios may be calculated using:

$$v^{\max} = \frac{3K^{\text{Voigt}} - 2G^{\text{Reuss}}}{6K^{\text{Voigt}} + 2G^{\text{Reuss}}} \& v^{\min} = \frac{3K^{\text{Reuss}} - 2G^{\text{Voigt}}}{6K^{\text{Reuss}} + 2G^{\text{Voigt}}}$$

where K^{Voigt} and G^{Voigt} are the greatest possible bulk and shear polycrystalline moduli respectively as estimated using the Voigt method (Voigt 1928, Hill 1952), i.e.:

$$K_V = \frac{A+2B}{3} \& G_V = \frac{A-B+3C}{5}$$

where:

$$A = \frac{1}{3} (c_{11} + c_{22} + c_{33}), \quad B = \frac{1}{3} (c_{23} + c_{31} + c_{12})$$
$$C = \frac{1}{3} (c_{44} + c_{55} + c_{66})$$

whilst K^{Reuss} and G^{Reuss} are the lowest possible polycrystalline bulk and shear moduli respectively as estimated using the Reuss method (Reuss & Angew 1929, Hill 1952), i.e.:

$$K_R = \frac{1}{3a+6b} \& G_R = \frac{5}{4a-4b+3c}$$

where:

$$a = \frac{1}{3} (s_{11} + s_{22} + s_{33}), \ b = \frac{1}{3} (s_{23} + s_{31} + s_{12})$$
$$c = \frac{1}{3} (s_{44} + s_{55} + s_{66})$$

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The Renewable Energy Potential of the Maltese Islands

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Summary. The potential of renewable energies is presented for the territory of the Republic of Malta. These are in the main sun, wind and biogas. Taking the base year 2003 for comparing the percentage contribution of electricity generated from renewables to that generated from fossil-fuelled power stations, it was found that rooftop solar photovoltaic systems could produce 9.1%, onshore wind farms could offset 5.4% and the offshore wind potential lies in the region of 3.4%. Energy from waste could contribute another 5.6%, while widespread solar water heating in domestic buildings could offset 4.8%. Economic analysis of applying renewable energy power systems under the present constraints is carried out. A range of barriers to the use of renewable energy devices is described. The currently available incentives are listed and a number of measures that could be implemented to allow widespread applications of renewable energies are suggested

Keywords: renewable energy, potential, widespread, barriers, incentives, islands.

The Solar Potential

Since 1993, solar radiation has been continuously monitored at the Institute for Energy Technology (IET) of the University of Malta. This is the only site in Malta that is currently operating in this field; but the only long term data available is that taken by the Royal Air Force at Qrendi over the period 1958-1972.

Figure 1 shows the mean daily global horizontal solar radiation for each month over Malta in kWh/m²/day. It is clear that the peak radiation occurs in summer and reaches a maximum of almost 8 kWh/m²/day, while in winter it drops to a minimum of 2.5 kWh/m²/day. This data compares favourably with other sites around the Mediterranean region and southern Europe (Palz 1984, Yousif 2005).



Figure 1: Long term mean daily global horizontal solar radiation for different sites in southern Europe and the Mediterranean. Several studies on solar radiation potential in Malta have been carried out (Akiwale 2003 and Scerri 1982). A summary description of the weather conditions is shown in Table 1 (Akiwale 2003) where, G = Global horizontal solar radiation;

 $H_0 = Extraterrestrial radiation;$

 $G/H_0 = Clearness Index.$

Sky Description	Range	Occurrence (%)
Cloudy	G/H ₀ <0.2	2.9
Partly Cloudy	0.2 <g h<sub="">0<0.6</g>	34.5
Clear	0.6 <g h<sub="">0<0.75</g>	61.9
Very Clear	G/H ₀ >0.75	0.7

 Table 1:
 Summary description of the Clearness Index of the sky conditions over Malta.

It follows that more than 62% of the year enjoys an abundance of sunshine, while only 11 days (3%) may be considered as very cloudy days.

Performance Of Solar Photovoltaic (PV) Systems

Since 1996, IET has carried out performance tests on a number of grid-connected solar photovoltaic (PV) systems. One of the main conclusions reached was that a typical stationary grid-connected PV array, inclined at 30° to the horizontal and facing the true geographic

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South would produce a daily mean electric output of 3.6 kWh/kWp of solar module capacity (Ribeiro, Yousif 2004).

Potential Of Power Generation From Grid-Connected PV Systems

The fact that Malta enjoys an abundance of sunshine and mild temperatures, coupled with other factors such as the existence of flat roofs as the standard way of building and the recent trend of increased power consumption in summer due to air conditioning, all favour the application of solar photovoltaics on a wide scale.

In order to reach a realistic assessment that reflects the potential of solar PV applications, one has to appreciate the fact the solar PV systems would ideally be decentralised rather than large ground-based systems, due to the scarcity of suitable land. Hence, one would consider the availability of rooftop areas in domestic, industrial and public buildings. The commercial sector in Malta may be excluded, as most of the establishments do not have their own rooftop. There is also some potential for façade cladding and building integration of photovoltaics, but this could not be quantified at this stage.

a. Domestic Buildings

The categories of local households as identified in 2003 are given in Table 2 (National Statistics Office 2005).

The *effective* number of dwellings that may be considered as providing roof space for installing PV systems is also included in the Table based on the following facts and constraints:

- Terraced, semi-detached, fully detached and farm houses as well as maisonettes would have a factor of 1 for calculating their effective rooftop availability;
- Ground floor tenement may have a factor of 0.5 as these dwellings may or may not have other floors on top of them;
- Apartments/Flats are on average built in blocks of 3 storeys. Hence, a factor of 0.3 may be applied for the effective rooftop area;
- Other parameters that could affect the availability of roof space for the installation of photovoltaic systems may be summarised as follows:
 - Use of solar water heating systems;
 - Satellite dishes and television antennas;
 - Water storage tanks;
 - Unusable areas due to shading.

It is essential to take into consideration the aesthetics of buildings. Moreover, legislation stipulates that retrofits should be placed away from façades and the existence of 1 metre-high perimeter walls at roof level would further reduce the area available for solar photovoltaics. Hence, a realistic *utilisation* factor of 30% may be introduced to cater for these additional constraints.

Type of Dwelling	Number	Effective
	Number	Number

Total	127.970	104.357
Other	680	0
Apartments	23,810	7,937
Maisonette	20,010	20,010
Ground Floor	14,120	7,060
Farmhouse	1,110	1,110
Fully-Detached	1,490	1,490
Semi-Detached	2,770	2,770
Terraced	63,980	63,980
Terraced	63 980	63 980

Table 2: Distribution of Households by Type of Main Dwelling.

Taking a conservative average roof plan area of 80 m² per household and considering that a factor of 0.6 would be used to cater for spacing between the different rows of solar modules to avoid shading, the effective potential for each roof would accommodate a 2 kWp PV system. The overall potential for photovoltaic installations would then amount to 213 MWp that is capable of producing an annual mean output of 280,000 MWh.

Considering the high capital cost of installing PV systems, a realistic scenario could be a 1.2 kWp per roof, costing around Lm 3,500 (8,000 \in). In this case, the potential would be 125 MWp that produces a mean annual output of 164,250 MWh.

b. Industrial Zones

Eight industrial zones have been identified in Malta and Gozo. The majority of the buildings have flat rooftops with minimum shading of one building on another. Based on available survey sheets (Malta Environment and Planning Authority (MEPA) 1988 and 1994), the roof areas were calculated for each zone as shown in Table 3.

Zone	Area (000 m ²)	Reference Year
Bulebel	152.5	1994
Hal Far	76.7	1988
Kordin	46.6	1988
Marsa	149.5	1988
Mosta Technopark	28	1988
Mriehel	57.5	1994
San Gwann	86	1988
Xewkija	24	1988
TOTAL	620.8	

Table 3: Rooftop areas in industrial zones.

In many cases, cooling towers and other appliances would be installed on the roof. Hence, assuming that 50% of the roof areas are available and taking into consideration spacing between modules to avoid shading, one would conclude that the potential area available amounts to 186,000 m². It follows that this area would be sufficient to install at least 26 MWp of solar modules rated at 12% efficiency and inclined at 30° to the horizontal. The estimated annual energy output would then amount to 34,164 MWh.

c. Public Buildings

i. Schools and University

A demonstration solar photovoltaic system may be easily fit on the flat rooftops of schools. A realistic first stage introduction of 5 kWp systems could be feasible. Smaller systems of 2 kWp may be placed on the English Language schools and other educational centres, due to their limited space. The available roofs at the University of Malta could accommodate 63 kWp (Yousif, Scerri 1996).

Table 4 lists the number of schools and educational centres available in Malta (Ministry of Education, Youth and Employment 2005). Hence, the total installed capacity would amount to 1.44 MWp or an electricity production of 1,896 MWh per annum.

School	State	Church	Private
Primary	77	30	15
Secondary	37	20	9
Tertiary	23	3	3
Special	6	0	0
English	0	0	42
Language			
Others	0	0	87

Table 4: Listing of Number of Schools and Educational Centres in Malta.

ii. Hospitals and Retirement Homes

There are four public and two private hospitals having substantial roof areas, with another large public hospital coming into operation in mid-2007. A number of three-star hotels and some church hospitals have also been converted to retirement homes. The overall potential for installing PV systems on these rooftops could amount to 600 kWp or a generating output of 788 MWh per annum.

iii. Hotels

In Malta there are 120 established hotels (Malta Tourism Authority (MTA) 2005), that would each accommodate a 5 kWp PV system without encroaching on space needed for other machinery that may be installed on rooftops. This would result in a potential of 600 kWp or an equivalent production of 788 MWh per annum.

Hence, the overall potential of rooftop solar PV systems amount to 153.64 MWp with the bulk contribution coming from the domestic sector. The resulting output would reach 201,883 MWh per annum, which is equivalent to about 9.1% of the total electricity generated from the power stations in 2003 (Enemalta 2004).

The Wind Resource

(1) Introduction

Wind characteristics depend upon numerous factors such as topography, site elevation above sea level, surface roughness and location exposure to any prevailing winds. Wind speed increases with height above ground level at the specific site itself, calling for wind speed measurements at a height representative of a wind turbine hub height. Based upon current wind turbine technology, the first 100 m of the lower atmospheric boundary layer is the prime area of interest.

(2) Background

Wind data was collected at different heights above ground level at a number of locations on the central Mediterranean Maltese Archipelago and analysed in a series of research studies (Farrugia 1998 and IET 2005).

In order to evaluate the local wind resource potential in a tangible manner, wind records gathered at one of these



sites have been analysed. *Bahrija* (Site 3) is located on the south western coastal escarpment of the main island of Malta as shown in Figure 2. Other onshore prospective sites are numbered as appearing in the text. Figure 2: Schematic showing the location of *Bahrija* on the main island of Malta (indicated by a cross) and other onshore prospective sites.

The wind monitoring equipment was installed on a 45metre lattice-type communications mast with effective anemometer heights of 10 and 45 m above ground level. Wind direction was monitored at 10 m above ground level. The data analysed covered 36 consecutive calendar months commencing in March 2002.

(3) Wind Characteristics

An analysis of the mean monthly wind speeds over the discussed time frame exhibited trends similar to those displayed at other locations around the islands i.e. higher wind speeds during the colder season and lower than average wind speeds during the hotter months (Farrugia 1998 and Darmanin 1995).

These characteristics become particularly important when evaluated with respect to the electricity generation potential of wind turbines as illustrated in Figure 3, which shows the theoretical monthly average energy yield for a typical medium-size wind turbine subject to site-specific wind conditions at *Bahrija* over a 12-month time frame.



Figure 3: Mean monthly wind speeds and mean monthly theoretical energy yield for a medium-size wind turbine at *Bahrija*, 45 m above ground level.

The marked prevalence of winds blowing from the north westerly sector is evident in the wind direction frequency distribution at this site, which once again substantiates results from other locations (Farrugia 1998 and Darmanin 1995).

(4) The Wind Resource Potential and Other Indicators

Site mean wind speed and average power density are two frequently-encountered indicators of location wind resource potential. In the case of Bahrija, the range of values listed in Table 5 is based upon measured records at 10 m and 45 m above ground level. Wind speeds at other levels have been calculated using the Power Law and a site-specific wind shear exponent of 0.18. Calculated values for mean wind speed and average power density were derived, by assuming a standard air density of 1.225 kg/m3 and a Rayleigh distribution.

Height Above Ground Level	Mean Wind Speed [m/s]	Average Power Density [W/m ²]
<u>[m]</u> 10	5.0 - 5.5	150 - 200
30	6.5 - 7.0	300 - 350
45	7.0 - 7.5	350 - 400
50	7.0 - 7.5	400 - 450
1 5 16 1		1 141 0 1100

 Table 5: Mean wind speeds and power densities for different heights at *Bahrija*.

Research (Manwell et al. 2003) suggests that sites having average power densities of 300 to 400 W/m² at 50 m above ground level are suitable for wind energy development with turbines having high towers (e.g. 50 m hub height) and that sites having average power densities ranging between 400 to 500 W/m² or more are considered suitable for most wind turbine applications.

The Potential for Wind Power Generation

(1) The Onshore Wind Power Generation Potential

Locations exposed to the prevailing winds, having high elevations above mean sea level and enjoying comparable roughness characteristics to those of *Bahrija* could have winds of similar quality. Generally, such areas are expected to lie south west of imaginary lines running across the two main islands as depicted in Figure 2. These areas are also less urbanised making them more suitable for wind generation technologies. Candidate sites falling within a category similar to that of *Bahrija* are *Marfa Ridge* (Site 1), *Mellieha Ridge* (Site 2) and an expanse of land running south of the village of *Dingli* (Site 4). Sites expected to have a lower potential are also included namely *Hal Far* (Site 5) and *Delimara* (Site 6). A number of these locations have been addressed in various studies (^aBorg 2000 and Farrugia, Miles 2003). Other research work (Farrugia, Scerri 1999 and Leddin 2003) estimated the onshore wind resource potential using correlation techniques as well as mathematical models.

In this analysis the wind data measured at 45 m above ground level as specified was used as input to the Wind Atlas Analysis and Application Program (WA^SP) (Landbergh et al. 1987-2004), in order to generate wind resource maps for the islands. If areas expected to have average power densities of 300 W/m² or higher as depicted by the orthographic projections are taken as a baseline condition for wind power generation suitability, the cumulative area of land available for such a technology amounts to a circa 153 km^2 for the three main islands. This estimate is referred to as the theoretical area available for wind power generation technologies as it does not take technical, social and environmental constraints into consideration. Other research (European Wind Energy Association (EWEA) 2005), assumed that only 4% of the total theoretical area would eventually be accessible for wind power generation as a result of practical constraints. Applying such a proviso in the Maltese context results in a cumulative practical land area of about 6 km².

Wind farm array design is very important in determining optimised machine performance. Studies (Manwell et al. 2003) have indicated that the downwind - with respect to any prevailing winds - spacing between wind turbines is typically between 8 and 10 rotor diameters, whereas the crosswind spacing is 5 rotor diameters. If a crosswind spacing of 5 rotor diameters and a downwind spacing of 9 rotor diameters are assumed, then the area required by an average-sized machine (1 MW wind turbine with a 55 m rotor diameter) is 0.136 km², leading to an indicative installed capacity of 7.4 MW/km². Utilising the *practical* land area as defined previously implies that the potential for onshore wind generation could reach some 45 MW. Assuming wind turbine capacity factors of 25% to 30% (EWEA 2005) leads to the conclusion that the total energy generated would supply from 4.5% to 5.4% (Farrugia 2005) of the total annual electricity generated by Enemalta Corporation in 2003 (Enemalta 2004).

(2) The Offshore Wind Power Generation Potential

On a small island archipelago crosscutting issues, particularly those of a social and environmental nature, would limit the penetration levels of onshore wind generation facilities. Developments in the international wind energy sector over the past decade or so have seen this technology also going offshore. Sea depth, the wind resource and the site-to-shore distance are key factors that affect offshore wind project technical feasibility. The wind resource off the coast is more attractive due to lower surface roughness, resulting in higher wind speeds closer to sea level. Likewise, lower turbulence intensities also contribute towards higher energy yields when compared to machines operating onshore (Harrison 2000).

A number of areas have been identified that could be of interest for the offshore installation of wind machines (Farrugia and Scerri 2000), as depicted in Figure 4. An area off the north coast of Gozo (Site A), Sikka l-Bajda (Site B), an area offshore from Marfa Ridge (Site C), an area off the coast between Salina Bay and St. George's Bay (Site D), Sikka tal-Munxar (Site E), Benghajsa Reef (Site F) and Hamrija Bank (Site G) are the outstanding shallow zones, categorised as areas having sea depths of 20 m or less (The Hydrographic Office 1983) and are considered attractive for multi-megawatt wind turbine installations. Hurd Bank lies slightly more than 15 km off the north eastern Maltese coast but sea depths are in the 35 to 50 m range and the area is not evaluated in this study. The main offshore areas as identified and having sea depths of 20 m or less cumulatively account for 13.5 km^2 of marine space.

Sikka *l-Bajda* (Site B) is possibly the only truly offshore reef in Maltese coastal waters having appreciable dimensions. Lying 1.5 km off the north eastern extremity of *Marfa Ridge*, this reef has an approximate area of some 2 km² (Farrugia et al. 2002). In the case of offshore installations, if 7.9 MW/km² (for a 2MW turbine with a 75 m rotor diameter) is taken as a realistic measure for installed capacity, one such wind farm could generate from 1.6% to 1.9% of the total electricity generated in 2003.



Figure 4: Schematic showing the Maltese Islands and some of the shallow areas around the coast having sea depths of 20 m or less as identified in the coastal zone.

If a second reef such as *Sikka tal-Munxar* (Site E) is also considered, the marine space could support an installed capacity of about 14 MW, having an equivalent electrical energy yield of 1.4% to 1.6% of the annual electricity generated by the fossil fuelled power plants on the islands in 2003.

It follows that the practical onshore and offshore wind resource potential could supplement almost 9% of the country's electricity generation.

Potential of Electricity Production from Waste

Three sources of methane (CH₄) are considered in the Greenhouse Gas (GHG) Inventory (Government of Malta 2004). The sewage treatment plant at *Sant' Antnin* produces a considerable amount of sludge, originally intended to go into the compost being produced on site. However, due to the presence of heavy metals, the sludge is not being used for this purpose.

A second source is animal waste from pigs, cattle and poultry, a fraction of which is applied to agricultural land as manure (cattle and poultry), while the rest (pig slurry) is disposed of into the sewage system.

A third source resides in the organic component of municipal solid waste, which is being deposited in a landfill at present.

For the year 2000 it was estimated that some 15 Gg of methane was produced from solid and liquid waste treatment and from animal husbandry. With proper treatment of the whole of the material available, one could reach 20 Gg of CH_4 per annum. This represents 1.11 x 10⁹ MJ over a year, equivalent to 308,333 MWh_{th} and, in a 40% efficiency turbine, 123,333 MWh_e representing some 5.6% of total electricity generated in 2003.

Potential of Solar Water Heating Technologies

In a recent evaluation of the currently installed solar thermal applications in Malta, based on partially available information and correlation with statistical data of different types of installed solar water heaters in Malta, it was estimated that the currently installed area is in the region of 15,000 m² (10.5 MW_{th}) of flat plate collectors and 132 m² (92.4 kW_{th}) of evacuated tube collectors (European Solar Thermal Industry Federation (ESTIF) 2005). The cumulative installed areas currently cover only 8% of the potential of solar systems in houses (^cBorg et al. 2005).

Solar thermal applications do not produce electric power but rather offset electricity generation from fossil-fuelled power plants, as the main source for heating water for domestic use is electricity. By adopting the same number of *effective* roofs as that for the PV system analysis shown in Table 2, knowing that only 70% of those dwellings are inhabited at the moment and assuming that each household would have a 150-litre flat-plate solar system (each having a 2.5 m² collector), one would reach to a potential of 182,625 m². Knowing that the mean global horizontal solar radiation is 5 kWh/m²/day and assuming an overall system efficiency and a utilisation factor of 40% and 80% respectively, it would be possible to offset 106,653 MWh per year, which is equivalent to 4.8% of the total electricity generated in 2003.

Economics Of Selected Resources

(1) Photovoltaic Systems

In the case of PV installations, the typical capital, installation and commissioning costs for small systems (1 - 3 kWp) in Malta would be Lm 3/Wp (7 €/Wp) installed. The life cycle costing, based on 4% net discount factor and a 20-year lifetime span, could then be calculated to be between 14.5 and 17 cents (34 - 39 € cent) per kWh produced from the solar PV system. With the 2006 state Budget subsidy of 20% of capital cost capped at Lm 500 $(1,150 \in)$, the cost of electricity would drop to about 28 to 37 € cent per kWh. At present the power utility, Enemalta Corporation, applies net metering, provided that the generated PV electricity is below the total consumption within the billing period. Under these circumstances, a small PV system would have a payback time just within its 20-year lifetime only if it was restricted to 1kWp, so making optimum use of the state subsidy and all electric output is sold to Enemalta at a preferential rate of 12 cents (28 € cent), as compared to the present peak rate of 6.2 cents (14 \in cents). One may then conclude that, under the current market prices of PV systems, a decent payback period of 10 years may be achieved in Malta only if the selling price of PV electricity to Enemalta is set at 22 cents (50 € cent)/kWh or the state's subsidy on capital is increased to 70%.

(2) Wind Energy

Studies (EWEA 2005) have estimated the approximate costs for onshore wind-generated energy as a function of wind regime based upon a new onshore 850 to 1,500 kW capacity turbine, investment costs ranging between 900 and 1,100 \notin /kW, O&M costs of about 1.2 \notin cents/kWh over the turbine's 20-year lifetime and an annual discount rate of 7.5% (2003 calculations). At sites having low wind speeds (average wind speed of 5.4 m/s at 50 m a.g.l.) the cost of electricity ranges from about 6 to 8 \notin cents/kWh. At good coastal sites (average wind speed of about 6.9 m/s), the cost of energy ranges from approximately 4 to 5 \notin cents/kWh.

In the case of offshore wind development, costs derived (BWEA 2000) from limited experience typically stood at an indicative level of 1,600 ϵ/kW for near-shore installations. This is approximately 60% higher than the mid-range cost of onshore machines at 1,000 ϵ/kW installed.

Arguably, the cost of wind energy in the local context, with its specific conditions, may be expected to be higher than that on mainland Europe. Constraints on wind turbine size, the small grid and logistics are some aspects that will contribute to higher overall costs.

(3) Domestic Solar Water Heaters

Domestic Solar Water Heating systems fare now much better than before, as government is offering a subsidy of Lm 100 (230 \in) for first-time buyers. The daily consumption of hot water by a family of four persons between autumn and spring (9 months) may be conservatively estimated to be 80 litres at 60 °C, requiring about 1,000 kWh_{thermal}. Hence, the life cycle costing may be calculated to be 5.2 cents (12 \in cents)/kWh as compared to 6.5 cents (15 \in cents)/kWh, if electric heating is used instead. The payback period would then be about 4.5 years which is lower than the expected lifetime of a typical solar water heater of 10 years. Without government subsidy the payback period would rise to 7 years.

(4) Energy Generation from Waste

Confining ourselves to existing plans to convert the methane content of landfill gas to electricity to be transmitted to the grid through a 1km. cable, an efficiency of 40% would yield a unit cost of 0.65 cents ($1.5 \in \text{cent}$). O & M, which must include gas purification prior to burning, would add 0.2 cents ($0.5 \in \text{cent}$); gas collection and power transmission losses, and safe disposal of small amounts of hazardous waste from gas purification would add some 0.08 cents ($0.2 \in \text{cent}$). Total unit cost would then lie in the range $2.5 - 3.5 \in \text{cent}$. Real costs, which must include initial waste collection as well as landfill engineering costs would probably bring the cost close to 4.3 cents ($10 \in \text{cent}$) per kWh generated.

Barriers and Incentives

The major physical barrier to widespread use of renewable energy (RE) is the fact that all such sources have a low energy intensity per unit area. The very limited land area (316 km²), around 21% of which is built-up, and a high population density (1,273 persons per km²), set tight limits on the potential from land-based RE generators.

The inclusion of sea areas suitable for offshore wind generators increases potential but puts up installation and other costs. In the case of PV and SWH installations, the general presence of flat house roofs normally used for a variety of domestic purposes ranging from drying clothes to roof gardening, does provide space for small installations, basically serving one household. On a larger scale there is area available as factory roof and on top of major public and private buildings.

The original Structure Plan (SP) (MEPA 1992) was written well before RE appeared on the local planners' horizon; so there was no mention of RE installations in the section on "Utilities". The current Utilities Topic Paper, part of the on-going SP revision, does give RE some mention. But apart from an initial and continued absence of planning policies, other factors have worked against RE development. There is as yet no national energy policy and still less a policy for RE development. Local interest in promoting energy conservation and use of RE has been confined to academics and a few individuals and firms outside the University — very far from the critical mass required for a good RE take off.

Information on RE devices has not been easily available to the general public and to small firms and commercial establishments with limited human resources, whereas the advertising and information apparatus for conventional devices is very well developed. Capital costs have also proved to be a powerful deterrent; but cost has a strong relative element.

Long years of subsidy on electricity prices from transport fuel sales tax have engendered strong expectations in the public mind that such a service is a low cost one. As a result, public or private investment in energy conservation and renewable energy has suffered from low social esteem, in marked contrast to the private car market, for instance. A short amortization period and a rapid money return is also expected from RE products.

On the other hand, energy-saving and RE technologies, quite apart from prices on European markets, are locally over-priced due to import duties (now diminished or removed on the basis of EU internal market rules), valueadded tax, and high dealer mark-ups arising from low volume sales by too many importers in a small market. The combination of high prices and low electricity unit costs makes for long pay-back times and reinforces a general tendency to minimize capital cost even if this entails comparatively high running costs.

In the case of domestic water heating, there was a switch from gas to electricity between 1985 and 1995 (census years). By the latter year there was some public interest in the purchase of SWH, but in 20% of the cases, inadequate technical backup leading to poor performance has generated low level of customer satisfaction (^bBorg 2004). The common social habit of asking for advice from one's friends rather than from technical experts reinforces customer dissatisfaction (Sudhakara Painuly 2004).

Preoccupation with satisfying public demand for low priced electricity has discouraged firm action in the RE field. The wholly state-owned provider – Enemalta – has been plagued by low investment leading to low productivity and inefficient conversion. Fragmented ministerial responsibility led to disjointed and sometimes even counter productive measures.

The prospect and now the reality of EU entry is ushering in a sea change. An energy regulator—the Malta Resources Authority (MRA) - has been set up; Enemalta has renounced its generating and fuel importation monopoly, but retained ownership of the electricity distribution network. Perhaps more important from an efficiency point of view, the finances of the various divisions of Enemalta have been unbundled, so that each must now operate profitably. This should drive Enemalta towards unsubsidised tariffs, reflecting the real costs of generation.

(1) Solar Water Heaters

In fact planning policy treating SWH falls under Part 13 of Development Control Policy and Design Guidance (MEPA 2005). The "guidance" is a little uneven, appearing to treat SWH rather leniently in comparison to PV. There are also some technical lacunae, as in the suggestion that siting the storage tank within adjoining washrooms can mitigate adverse visual impacts from SWH. Meanwhile the first incentives for RE use have appeared. Since June 2003, Enemalta has offered a waiver of the installation fee of electricity meters amounting to Lm 70 (161 €) for new customers, provided that a SWH system is installed on the premises beforehand (Enemalta 2005). Government has conceded a once-only payment of 25% of CIF value, up to Lm 100 (230 €) of a solar system for households (Department of Information 2005).

It is probable that other events may prove more important in promoting widespread use of SWH. Prices for SWH models have been coming down quite perceptibly; good quality evacuated tube absorbers are currently selling at around Lm 500 (1,150 €) for a 150 litre system. On the other hand, a more "educated" public is now evaluating costs, maintenance and installation more critically, which should lead to a higher customer satisfaction, signally lacking to date. Yet, what may eventually turn out to have provided the strongest push is the surcharge (17%) on electricity and water bills included in the 2005 National Budget, which was trebled just before the 2006 Budget. Domestic hot water, almost completely supplied by electric immersion heaters, accounts for 25%-35% of the annual electricity consumption. As the surcharge is tied to movements in the total fuel bill for generation, it is unlikely to disappear or even decrease appreciably in the short-to-medium term. This could lead to households looking more closely at SWH, as these would now have payback times of 3-4 years, well short of the SWH lifetime.

(2) Photovoltaic Systems

Planning policy for PV systems also falls under Part 13 of Development Control Policy and Design Guidance (MEPA 2005). The PV modules must not "have a significant visual impact". Such a statement could act as a disincentive to prospective developers. While the guidelines say that "solar voltaic cells can be incorporated...in the form of simple panels or even cladding", to date there has not been any proposal for building-integrated PV systems.

As far as PV is concerned, a formal protocol for mains connection has been worked out between MRA and Enemalta Corporation. The 2006 Budget offered a 20% on capital costs of the installation, capped at Lm 500 (1,150 \in). A system below 3.7 kWp needs only to be registered at MRA, while an authorisation would be required for larger systems. Provided the PV power generated does not exceed total household consumption

over a billing period, Enemalta accepts net metering. Generated units in excess of household consumption over a billing period are paid at 3 cent (7.3 \in cent).

(3) Wind Turbines

Wind turbines have not yet been the subject of serious planning legislation. In the MEPA Design Guidance, they are declared to be "encumbered by physical constraints, which are predominantly related to visual intrusion". An existing proposal for a wind farm on *Marfa Ridge* has raised mixed reactions — all unofficial, as MEPA has not given any ruling on the proposal — ranging from visual intrusion to high noise levels and disruption of migratory bird routes to radar interference. In the specific setting of the Gozo and Comino Local Plan (MEPA 2001), wind turbines – other than very small ones on individual farmhouses – are banished to at least 100 m offshore.

The restriction to offshore raises further barriers: intrusion into areas of shallow water staked-out by other economic activities: increased construction and connection costs; increased cost of work directed to solutions of problems associated with the interaction of a wind farm with a small grid (Fsadni, Mallia 2006). The scale and cost of a wind farm will almost certainly require private investment, with its inevitable demand for an attractive rate of return (Meilak 2004). It is unlikely that anyone would invest in any wind farm until such problems are resolved. And they cannot be finally resolved without trials with a land-based wind farm of modest dimensions.

Elements of a Renewable Energy Policy

The present shortcomings in the approach to RE use suggest various lines of action, preferably within the framework of a National Energy Policy. That Policy will condition planning regulations for both large and smallscale applications. For instance, new or amended building regulations, similar to those adopted by several Spanish cities (ESTEC 2005) could be designed to stimulate the solar thermal market, whereby solar heating caters for a significant percentage of the thermal load in buildings. Actual incentives could be tied to installed area of absorber, a method that has been very successful in Germany. It is important that such measures drive home the point that SWH, with their lower cost and high conversion efficiency (ESTIF 2005) are the best prospect for rapid take-up, with a significant displacement of generated electricity.

The installation of PV poses a different set of problems. At present its more "glamorous" image compared to SWH cannot gainsay high capital cost and low efficiency (15%). As initial demand is likely to come from systems to be incorporated in existing structures, sensible planning parameters are required, keeping in mind available forms and costs of PV. There are then the further considerations of incentives on the two levels of capital cost and feed-in tariffs. To date we have none of the first and little of the second.

Germany has run a number of "PV-roof" programmes, which involved a 70% capital offset and a feed-in tariff of 90% of that for fossil-fuel units. At the close of the last programme at the end of 2003, capital grants were abolished but the feed-in tariffs were pushed up to the range $45-62 \in \text{cent/kWh}$ (some 3 to 4 times the average rate for fossil fuel units), leading to a strong surge in the installation of PV systems, to actual shortages of silicon in the latter half of 2004 and to a total installed capacity of 794 MWp (Systemes Solaires 2005) by the end of that year. The UK and Italy, both new comers to the PV market, have provided capital cost offsets of 50-70% and 'net-metering' i.e. barter of units.

As far as wind energy is concerned, there is not a single commercial installation of any size feeding energy into the grid. There is lack of policy, planning, legal and technical instruments in this area. In this particular situation, these elements would need to be integrated into a coherent whole, which will do justice to each element.

The methods used in Germany, the European country with the highest installed wind turbine capacity, bear looking at. Wind turbines were described as facilities for public electricity supply, and as such could be erected in open country (Knight 1997). Apart from a well-funded R&D programme, grants up to 25% of initial investment (capped at 46,000 \notin per turbine) were provided, together with a \notin 4/kWh premium on units fed to the grid. Germany had an installed capacity of 16,000 MW at the end of 2004 (Grotz, Fouqet 2005).

The U.K. has devoted the major share of its RE effort to wind energy. Two Non-Fossil Fuel Obligation (NFFO) orders issued in 1990 and 1991 were intended specifically for wind energy, with the rates of €c 8.7/kWh and €c 16/kWh being set for the two years (against 4-6 € cent/kWh for fossil fuel generation). The cut-off year of 1998 was subsequently removed, and in the year 2000 NFFO orders were replaced by Renewable Obligation Certificates (ROC). At the end of 2003, wind customers were paying 9.6 € cent/kWh. Planning issues were usually decided at the local level, but there were cases where local decisions, generally negative ones, were overturned by the Secretary of State for the Environment (Elliot 1997). Recently one major offshore farm has come into operation, bringing the total installed capacity to 890 MW. A large number of sites off the east coast of the U.K. have been leased as wind farm sites.

Italy had 1100 MW of installed wind power at the end of 2004. Grants amounting to 30-40% of eligible costs were provided, but there was a long process before selling prices were fixed in 1998 at around 10 \in cent/kWh for the first 8 years of operation. In 2003, customers were paying 13 \in cent/kWh. The multi-tiered Italian administrative set-up has led to disagreements about siting and size of wind farms. But in late 2004, four private companies were granted permits to set up a

63 MW wind farm in Troia, in northern Puglia. All forty-two 1.5 MW turbines were expected to be operational by the start of 2007.

Incentives and Measures

A number of possible measures intended to increase the take-up of renewable energy devices were published (Yousif, Scerri 1996 and Fsadni 1994). These, together with other initiatives are presented below:

- Publication of the National Energy Policy;
- Setting a national renewable energy target and a National Plan (Short, Medium and Long-term) to attain it;
- Formation of a technical body to certify the quality of imported or locally manufactured renewable energy systems, according to the national and international operating standards;
- Fiscal incentives for installing renewable energy systems;
- Formation of a Renewable Energy Fund that is supplemented by a "renewables or carbon/pollution surcharge" on transport fuels;
- Use of the Renewable Energy Fund to subsidize public RE projects in schools, hospitals, etc.
- Allowing grid-interfacing of all RE electricity generating systems;
- Provision of soft loans for installing RE gridconnected systems;
- Purchasing of extra power produced by RE systems by Enemalta at preferential rates, bearing in mind that the total effect on Enemalta's financial situation would be negligible due to the small percentage of renewables in the energy mix;
- Encouraging the local manufacturing of components that may be required for RE systems;
- Training in RE installations to ensure effective implementation and to create new jobs;
- Setting up of a monitoring entity that would ensure the adequate performance of RE systems, collate information on the state of affairs of RE applications and development in Malta and propose measures to boost their effectiveness.

Conclusions

An island scenario with limited land area and a small isolated grid favours the application of as wide a mix of RE technologies as possible. This would serve two distinct purposes. The first is to attenuate the effects of variability and intermittency of RE sources; and the second is to obtain as good a match as possible between supply and demand. In the Malta case, the cumulative contribution of solar, wind and biomass to power production could reach 24% of the total electricity generated in 2003. Furthermore, solar water heating could save an additional 4.8%.

It is high time that immediate and effective measures are taken at all levels to kick-start use of these energy sources that have remained practically untouched to date. Such measures should be accompanied by a determined drive for increased energy efficiency, which will itself enhance the RE contribution. The spiralling costs of fossil fuels as well as the current levels of pollution and greenhouse gas emissions make such a course of action imperative.

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Research Article

Gelatin nanoparticle production: an in-process study using size exclusion chromatography

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Summary. Gelatin is a good candidate for nanoparticle preparation. An in-process study of an earlier method was performed by characterizing the gelatin species present in solution at various production stages. Gelatin nanoparticles were prepared as described by Farrugia and Groves (1999). Samples from various production stages were analysed by size-exclusion HPLC. Addition of ethanol to the initial gelatin solution removed all but the low molecular weight species. Ultrafiltration was effective at separating and purifying nanoparticles. The glutaraldehyde-metabisulfite addition byproduct present in the first ultrafiltrate was practically absent in the third ultrafiltrate and in the filtered nanoparticle and control preparations. Also, ultrafiltration of gelatin solutions removed species of low to intermediate molecular weights, leaving higher molecular weight species in the retentate. The residual soluble species following desolvation were not present in the final nanoparticle dispersion. Both the nanoparticle filtrates and the ultrafiltrate washings exhibited insignificant concentrations of eluted gelatin species. The chromatogram of a water control taken through the production process was superimposable on that of the filtered nanoparticle dispersion, indicating that soluble gelatin species present post-desolvation were absent following cross-linking and neutralisation. A possible explanation is that the glutaraldehyde crosslinked the residual soluble gelatin onto the surface of existing nanoparticles.

Keywords: Gelatin nanoparticles, size-exclusion chromatography, purification

Introduction

Over the past three decades, considerable research interest has arisen worldwide in the development of new colloidal drug delivery systems. The ideal colloidal delivery system would transport the associated drug to its desired site of action and then release it at an optimum rate. The carrier itself should be non-toxic and able to be degraded in vivo so that it does not accumulate indefinitely in the tissues. The colloidal preparation also needs to be pharmaceutically acceptable with regards to stability and ease of administration. Nanoparticulate colloidal drug carriers can be used to improve the therapeutic index of both established and new drugs by modifying their distribution, and thus increasing their efficacy and reducing their toxicity. This can be achieved because the drug distribution then follows that of the carrier, rather than depending on the physicochemical properties of the drug itself (Barratt, 2000). Gelatin, a natural macromolecule, is widely used in biotechnological and biomedical applications. Thus, it is a good contender for the preparation of nanoparticles for the purpose of controlled release applications of drugs

(Akin and Hasirci, 1995), and methods for reproducibly preparing nanoparticles from gelatin have been described (Marty et al., 1978; Yoshioka et al., 1981; El-Samaligy and Rohdewald, 1983; Kreuter, 1983; Farrugia and Groves, 1999). The objective of this study was to carry out in-process development of the method developed by Farrugia and Groves (1999) by characterizing the molecular weights of the species present in solution at various stages of the production using size exclusion HPLC.

Materials and Methodology

Materials: All chemicals were of analytical reagent grade quality. Gelatin, bovine skin, lime-cured (Type B), with a bloom strength of 225, glutaraldehyde 25% w/w and sodium metabisulfite were purchased from Sigma-Aldrich Company. Absolute ethanol, sodium dihydrogenphosphate and disodium hydrogenphosphate were purchased from BDH Chemicals, sodium hydroxide was purchased from Merck Ltd., and sodium chloride was purchased from Timstar Laboratory Suppliers.

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Methodology:

(a) Size-exclusion chromatography: The HPLC system (Shimadzu SCL-10Avp) consisted of a pump system and a tuneable absorbance detector set at 205 nm. The mobile of 0.05 dm⁻³ phase consisted mol sodium mol dihydrogenphosphate, 0.05 dm⁻³ disodium hydrogenphosphate and 0.15 mol dm⁻³ sodium chloride. The mobile phase was maintained at 29°C. Samples for analyses were filtered through 0.2-µm Whatman Anotop 10 membrane filters and analysed on an Ultrahydrogel Linear 7.8 x 300 mm size exclusion column (Waters Corporation), with an Ultrahydrogel Guard Column, at a flow rate of 0.3 mL/min.

(b) Production and analysis of the gelatin nanoparticles: Gelatin nanoparticles were prepared as described in Farrugia and Groves (1999). Briefly, a 1% w/w B225 gelatin solution was prepared by heating with moderate stirring to 40°C for 20 minutes. The solution was adjusted to pH 7.0 with dilute sodium hydroxide and incubated at 37°C for 1.5 hours. A hydroalcoholic solution, similarly incubated, was then added to the gelatin solution, so that the final mixture contained 0.2% w/w gelatin and 70% w/w ethanol. The colloidal dispersion was incubated at 37°C for a further 20 minutes and then diluted 1:30 by weight, with stirring, in a hydroalcoholic solution of similar composition and at the same temperature, but containing 1% w/w glutaraldehyde. The particles were allowed to react for 2 hours and excess glutaraldehyde neutralised by addition of 3% w/v sodium metabisulfite with stirring for 10 minutes. Separation and purification of the particles was performed by ultrafiltration on an Amicon XM300 membrane (MWCO 300 kDa [Millipore Corporation]), using distilled water as the washing agent. Samples from various stages throughout the nanoparticle production process were filtered through 0.2-µm filters and analysed by size-exclusion chromatography as described above. Similar analyses were also carried out for a control water sample taken through the entire nanoparticle production process, and a B225 gelatin solution taken through the nanoparticle production process without the presence of alcohol as a desolvating agent. A dispersion of B225 gelatin nanoparticles was also incubated at 37°C for 24 hours and subjected to HPLC analysis.

Results

Addition of the non-solvent ethanol to the initial gelatin solution resulted in removal of all but the low molecular weight species, the original gelatin solution having a characteristic broad peak extending from approximately 22 to 36 minutes of elution time (Figure 1). The filtered desolvated solution contained a much lower concentration of gelatin species with retention times between 27 to 36 minutes. (Figure 1). However, these residual soluble species were not present in the final nanoparticle dispersion, as filtrates of the nanoparticle dispersion did not exhibit any significant concentrations of eluted species (Figure 1), while the ultrafiltrate washings only contained species with retention times greater than approximately 34 minutes. (Figure 2).



Figure 1: HPLC size-exclusion chromatograms for (A) dilute gelatin B225 solution, (B) residual gelatin species following desolvation, and (C) residual gelatin species in the final nanoparticle dispersion.



Figure 2: HPLC size-exclusion chromatograms for (A) first ultrafiltrate washing, (B) third ultrafiltrate washing, and (C) residual gelatin species in the final nanoparticle dispersion.



Figure 3: HPLC size-exclusion chromatograms for (A) residual gelatin species in a nanoparticle dispersion after purification and, (B) residual species in a blank control following purification.

The chromatogram of a water control taken through the nanoparticle production process was practically superimposable on that of the filtered nanoparticle dispersion (Figure 3), as was the chromatogram of a dispersion produced by taking a B225 gelatin solution through the entire nanoparticle production process without the presence of the desolvating agent alcohol (Figure 4). The HPLC chromatograms of a filtered nanoparticle dispersion immediately after production and of a filtered nanoparticle dispersion post-incubation for 24 hours at 37°C were also superimposable (Figure 5).



Figure 4: HPLC size-exclusion chromatograms for (A) residual gelatin species in a gelatin solution post-production without desolvation and, (B) residual gelatin species in a nanoparticle dispersion.



Figure 5: HPLC size-exclusion chromatograms for residual gelatin species in a nanoparticle dispersion at 0 hours incubation and at 24 hours incubation at 37°C.

When the HPLC chromatograms pre- and postultrafiltration were compared, the first ultrafiltrate of both the nanoparticle and control preparations exhibited a sharp absorption peak at high retention times (Figure 6). This peak was practically absent in the third ultrafiltrate (Figure 6) and also in the filtered nanoparticle preparation (Figures 1 and 2). Similar ultrafiltrate chromatograms were also obtained when a water control was ultrafiltered following the crosslinking process (Figure 5). Moreover, ultrafiltration of dilute gelatin solutions was shown to be effective at removing gelatin species of low to intermediate molecular weights, with medium to high molecular weight species being detected in the retentate (Figure 6).



Figure 6: HPLC size-exclusion chromatograms for eluted species in first (A) and third (B) ultrafiltrates from gelatin nanoparticle preparation, and first (C) and third (D) ultrafiltrates from a water control.



Figure 7: HPLC size-exclusion chromatograms for eluted gelatin species in (A) dilute native gelatin B225 solution, and first (B) and third (C) ultrafiltrates, and retentate (D) of an ultrafiltered dilute gelatin solution.

Discussion

The HPLC chromatograms obtained for native gelatin solutions are consistent with those observed in earlier studies (Farrugia and Groves, 1999, 2000). The addition of ethanol to these solutions, producing a colloidal gelatin dispersion, resulted in removal of all but the low molecular weight species, as indicated by the absence, in the colloid filtrate, of species with retention times between 22 to 27 minutes, these species having been present in the original gelatin solution (Figure 1). These results are consistent with those observed in earlier studies.

Ultrafiltration appeared to be an effective method for separation and purification of the nanoparticles. The ultrafiltrate chromatograms exhibited an absorption peak sharper in intensity and eluting at higher retention times than the low molecular weight species present in either the native gelatin solution or the desolvated gelatin dispersion (Figures 1 and 2). The absence of these species eluting at 34 minutes or greater in the desolvated gelatin preparation prior to crosslinking (Figure 1), and the fact that these species were also present in a water control subjected to the crosslinking process (Figure 6) indicates that this peak is probably due to the glutaraldehyde-metabisulfite addition product formed during the neutralisation process. Moreover, the intensity of this peak decreased in successive ultrafiltrate washings, decreasing to less than 10% in peak height by the third ultrafiltrate (Figure 6). The absence of this peak the nanoparticle dispersion retained in the in ultrafiltration apparatus (Figures 1 and 2) is indicative of the effectiveness of the technique at removing this byproduct of the nanoparticle production method.

The effectiveness of the ultrafiltration process at removing gelatin species should theoretically not have been of any direct concern, since nanoparticle dispersions did not appear to contain any significant amount of residual gelatin species, and dispersed gelatin nanoparticles incubated in aqueous media did not appear to undergo any hydrolysis to release soluble gelatin that could be detected by HPLC (Figure 5). Nevertheless, ultrafiltration of dilute gelatin solutions was shown to be effective at removing gelatin species of low to intermediate molecular weights, with medium to high molecular weight species being detected in the retentate (Figure 7).

It was furthermore observed that the residual low molecular weight species present in solution following desolvation of the gelatin preparation, with retention times between 27 and 34 minutes, were not present in the final nanoparticle preparation, as filtrates of the final nanoparticle dispersion did not exhibit any significant concentrations of eluted species (Figures 1 and 2), while the ultrafiltrate washings only contained species with retention times greater than approximately 34 minutes (Figures 2 and 6). Moreover, the similarity between the chromatograms of the filtered nanoparticle dispersion and that of a water control taken through the nanoparticle production process (Figure 3) indicates that the solution gelatin species present post-desolvation were effectively absent following cross-linking and neutralization. An explanation for this observation is that the glutaraldehyde crosslinked both the desolvated and the soluble gelatin, a hypothesis supported by the fact that crosslinking of an undesolvated gelatin solution also did not have any residual detectable gelatin species (Figure 4). The residual gelatin species following desolvation thus appear to be crosslinked onto the surface of previously existing nanoparticles (nanoencapsulation), possibly establishing a gelatin 'brush border' and accounting for the dispersion stability of the nanoparticles (Mifsud, 2003).

Conclusion

We conclude that, during nanoparticle production, the ultrafiltration process is effective both at removing the addition reaction impurities and low molecular weight gelatin species. However, the latter do not appear to be present in the nanoparticle dispersion prior to purification since the crosslinking process not only crosslinks the colloidal gelatin particles but also removes residual soluble gelatin fractions from solution, probably by crosslinking to the surface of the existing nanoparticles.

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Research Article

Fine dust emissions from softstone quarrying in Malta

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Summary. The Lower Globigerina Limestone (softstone) provides stone blocks for the construction industry in Malta: primitive techniques are used to extract and convert limestone into such blocks. An analysis is presented of the work methods and practices employed by the industry, along with estimates of fine respirable dust (PM_{10}) emission from such techniques, to show that the rate of PM_{10} emission is 0.38 kg of limestone dust per building stone produced; taking into account mitigation of dust release during the wet months, it is estimated that the 67 active open pit quarries which lie in close proximity (0.2 to 2 km) to urban centres generate, annually, about 1200 t of PM_{10} dust. Considering that dust emission occurs mainly during the dry summer months, the average PM_{10} emission rate from quarries during this period is 11 500 mg m⁻² day⁻¹ which is well above international guideline values $(100 - 350 \text{ mg m}^{-2} \text{ day}^{-1})$. The main emission sources accounting for 97% of fine dust are the cutting tools (76%) used to extract the mineral from the quarry bed and the dressing tools (21%) that convert the blocks into 'fair-faced' stones suitable for use in construction. The reason why emission factors are so large is due to the fact that all dust generated is allowed to escape unchecked to atmosphere. It is concluded that in view of the magnitude of the emissions and the vicinity of sources to residential areas, the quarrying industry may be a significant factor contributing to the lowering of air quality on the islands with possible impacts on the health of the general population and, in a more serious manner, that of the quarrying community. Artificial water wetting of the quarry bed prior to extraction may provide an effective and relatively cheap mitigation measure during the dry weather when the problem of dust emission is at its worst.

Keywords: limestone, quarrying, PM_{10} , environment, dust, emission factors

Introduction

With a total land area of c. 316 km² and a population of 389 000 (in 2001) (MPA, 2001a) Malta is one of the smallest and most populated countries. Limestone quarrying on the islands has played a central role in the country's economy from earliest known times: from the magnificent 5000-year old temples at Hagar Qim and Ggantija to the more recent and numerous churches, palaces and medieval fortifications, these edifices in stone testify to the importance of the industry and its effect on the social fabric of the inhabitants. In Malta, the main construction material is Globigerina Limestone (a softstone locally known as *franka*) and it has been used for any type of building from rural sheds to housing units to schools etc. During the last 60 years or so, roofing elements made from concrete have totally replaced limestone alternatives and concrete bricks are also being employed for building walls although for this use franka blocks remain a preferred choice. The Tertiary Globigerina Limestone Formation, which outcrops in several places in Malta and also in Gozo provides a soft, yellow biomicritic limestone from which 67 quarries (Mallia et al., 2002) are currently extracting material for the construction industry.

The guarries are situated mainly in the central and eastern areas of Malta (Figure 1) and occupy a total land area of 1.2 km² which represents almost 0.4% of the national land territory. The open-pit quarries are located in sites most of which lie within about 0.2 to 2 km from residential centres. Such a preponderance of quarrying activity occurring practically in the midst of urban development is probably unique to Malta. Nevertheless, any impacts which this industry has on the quality of the environment, especially the atmosphere, have not been hitherto evaluated. To our knowledge, this is the first attempt at quantifying emissions to air from softstone quarrying of fine respirable limestone dust, i.e. that component having nominal aerodynamic diameter < 10 μm (PM₁₀): such material is probably the most problematic waste arising from the industry. The need for industry to adopt measures for reducing the dust impact, which appears likely to have potential for affecting the health of both quarry workers and general population, is also discussed.

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Figure 1: Location of softstone and hardstone quarries in Malta and Gozo (from Mallia et al, 2002).

Work methods at softstone quarries and associated dust emissions

Limestone blocks are extracted from the quarry bed and 'dressed' (given three fair faces) using rotary steel cutting tools. No attempt is made at controlling dust released. Judging by visible observation, these operations are the ones that generate most dust. Not only is a substantial quantity of limestone turned into a fine powder through the grinding processes involved in both operations, but the material so produced is ejected into the air, both as the cutting machine moves along the cut lines of the quarry face and as limestone blocks pass through the dressing machine. The dressed stones are loaded onto trucks for use offsite: this loading operation entails some dust emission although more dust is generated from loading, by mechanical shovel, of limestone wastes, fine cuttings $(xa\hbar x)$ and other stone debris that is removed from the quarry either for use off-site (as backfill) or for disposal to landfill. Finally, as material is conveyed away from the quarry in trucks, dust is again raised from the action of wheels on the unconsolidated materials constituting the surface of these dirt roads.

Limestone extraction from softstone quarries is performed using circular saws (Figure 2a), operating at 1500 revolutions per minute, that make horizontal cuts followed by other saws that make vertical cuts into the bedrock (Figure 2b), resulting in the formation of blocks of material having a thickness of either 23 or 15 cm, but the same length (56 cm) and height (26 cm). The blocks require finishing (or 'dressing') and this is performed using a machine (Figure 3) with three mutually perpendicular grinders to remove any edges or imperfections from three contiguous faces parallel to the long axis thus forming 'fair faced' building stones. The blocks issuing from the dressing machine are generally loaded directly onto trucks by conveyor and are transported away for use as construction material in truckloads of about 300 23 cm-blocks or 400 15 cmblocks. Stockpiling of blocks occurs to a very limited

extent involving about three to four thousand blocks that are kept in an area of the quarry away from active stone extraction. The cutting/grinding machinery is electrically driven, powered either from the mains or using diesel generators. The production of stones generates a significant quantity of fine limestone powder from the cutting and dressing processes and the rudimentary machinery employed is not equipped to control dust. The heavier fraction of dust collects next to the cutting and dressing machines and a small part of this material, referred to locally as "xahx", is used in making mortar, although a significant fraction is discarded as a solid waste product. The finer fraction remains airborne and may be dispersed from the quarry pit by wind action and convective flow. In the dry months during stone extraction and dressing, the visibility in the pit is so low that the workers can barely be seen. It has also been noticed that when the quarry bed and the extracted stones are humid from rain, there is barely any visible dust since the damp cuttings clump together and drop to the ground practically without formation of airborne fines. It is clear that the simple expedient of water wetting of the bed rock prior to extraction of limestone would afford one method of eliminating the fine dust problem but the industry hasn't felt the need to respond to the problem, possibly because it is not regarded as being significant or as potential for affecting occupational having environmental health.





Figure 2. Typical cutting machines as used in softstone quarrying: (a) machine used to make horizontal cuts through bedrock and (b) machine used for vertical cuts.



Figure 3. Typical dressing machine as used in sofstone quarries.

An experiment was conducted to measure directly the concentration in air of particulate matter with aerodynamic diameter nominally less than 10 μ m (PM₁₀) generated by cutting limestone blocks using a typical tool as employed locally for the purpose. This was in order to obtain an order-of-magnitude estimate of the emission factor for PM₁₀ particles associated with the limestone block cutting operation.

The tools employed for cutting blocks off the quarry face and those involved in the dressing operation are very similar and this suggests that dusts generated from both might possess similar size distributions. This hypothesis was tested by collecting dust generated from both cutting and dressing operations in local quarries and analyzing the particle size distributions in each. Moreover, the particle size distribution of deposited dust collecting on unpaved access roads in quarries was also analysed.

Materials and methods

(a) Experimental determination of nominal PM_{10} emission from softstone cutting

The cutting tool consisted of two electrically-powered rotary blades, each of width 4 mm and diameter about 30 cm, which cut into the stone block from opposite ends as the block moves on a steel surface. The blades of this cutting tool are of similar shape but smaller in width than those employed for limestone block manufacture. The tool is, however, actually used for cutting stone blocks to size on site during construction. The cutting tool had no provision for collecting dust. The tool was placed centrally in a window-less chamber* of dimensions 1.9 m x 2.7 m x 5.3 m having limestone walls and a concrete ceiling and provided with a wide steel plate door for access. An electric fan was placed at ground level pointing upwards in order to provide turbulence of the inside air without causing visible disturbance of deposited dust.

A Lecker low volume air sampler (Model LVS3) containing a 47 mm diameter glass fibre filter (Whatman) was placed in the chamber about 2.5 m from the cutting tool and the collecting head was placed at a height of 1

m: the experiment was repeated six times, in three of which the sampler was placed at the front of the chamber and in the other three at the back to correct for uneven distribution of airborne dust. The filter paper was equilibrated in a constant humidity glove box and weighed inside the box to the nearest 0.1 mg and it was then inserted in a clip-seal polythene sachet pending use in the low volume sampler.

The limestone used for the experiment was a dry block (moisture content = 1.2 %) extracted from a limestone quarry in Qrendi. Each experimental run consisted of cutting a segment of stone with cross section 17 cm x 3 cm, an operation which generated 20.4 cm³ pulverized limestone. After each cut, the airborne fine dust produced inside the chamber was sampled using the low volume air sampler for a measured period of approximately 15 minutes: the rate of air sampling was 2.3 m³ h⁻¹ and during the sampling period, the concentration of suspended fines in the chamber decreased from a maximum value to nearly zero. Prior to each run, the 'background' airborne dust was measured by passing air through the sampler for 15 minutes and the mass of dust so collected was deducted from that obtained in the subsequent experimental run. Each loaded filter paper was replaced in the polythene sachet and taken back to the constant humidity box for re-equilibration and weighing.

(b) Determination of size distribution and moisture content of dust from quarries

A size distribution analysis was carried out on dust generated in three quarries, two of which are located in Qrendi (quarry nos. 15 and 55) and the other at Siggiewi (known as "extension to quarry no. 15"). Samples were collected from both cutting and dressing machines while working on stones that were wet from previous heavy rainfall. No visible dust was emitted in the cutting and grinding processes and it was thus concluded that most of the fine dust had collected with the coarser material as a result of water damping. The moisture content of dust was measured by drying at 110°C to constant mass. About 30 g of dried dust was analyzed granulometrically using brass laboratory test sieves (Endecotts Ltd.) for the larger sizes and an LS Coulter Counter (Model LS100Q) for the size fraction smaller than 45 µm. The Coulter Counter provided direct values for the dust fractions \emptyset < $10\mu m$ and $10\mu m < \emptyset < 45\mu m$ (Ø is the particle diameter), whereas the mechanical sieves allowed measurement of the total fraction $\emptyset < 45 \ \mu m$ as well as four larger-sized fractions, namely, $45\mu m < \emptyset < 63 \mu m$, $63\mu m < \emptyset < 125$ μ m, 125 μ m < Ø < 500 μ m and 500 μ m < Ø. It is noted that data on particle size distribution obtained with the sieves and Coulter Counter do not refer to aerodynamic particle sizes and cannot be directly compared with data on airborne dusts obtained using size-selective air samplers.

Using the same techniques, dust collected from the surface of unpaved quarry access roads was also

^{*} Actually, the chamber was a small garage cleared and converted for the purpose.

analysed: the dust was sampled from the tracks defined by truck tyre markings in these roads.

Results and discussion

(a) Nominal PM_{10} emissions from cutting of softstone

Table 1 shows the results obtained in the sampling of PM₁₀ dust generated by cutting softstone using the tool as described in the experimental section. During each sampling period, the visibly-dusty atmosphere in the chamber cleared completely before the period had elapsed and this was confirmed by the value of airborne dust measured in the background runs (filter numbers 1, 3, 5, 7, 9 and 11): these were typically between 1 and 2% of the values for dust generated during the cutting operation. It is most likely that airborne dust collecting in the chamber settles out through sedimentation, particle aggregation and collision with walls and ceiling of the chamber. The last column in Table 1 refers to the 'nominal' concentration of PM10 dust generated as a result of the cutting operation. The calculation assumes that the airborne particles remained at some fixed mean nominal value throughout the measuring period which was between the maximum value obtaining immediately after the cutting process and the nearly-zero value after approximately 15 minutes of air sampling. This nominal concentration is likely to be an underestimate of the true (maximum) value, but it suffices for the purposes of this paper, which is intended primarily to provide an 'orderof-magnitude' estimate of the environmental impact from dust generated by softstone quarrying.

Filter Number	Volume of air sampled (m ³)	Mass of PM ₁₀ dust (mg)	Nominal corrected PM ₁₀ concentration (mg m ⁻³)
1	0.67	0.2	-
2	0.72	31.4	43.6
3	0.67	0.3	-
4	0.68	32.8	48.2
5	0.64	0.1	-
6	0.7	34.2	48.9
7	0.58	0.4	-
8	0.63	32.3	51.3
9	0.64	0.4	-
10	0.67	33.1	49.4
11	0.65	0.8	-
12	0.65	31.1	47.8

Table 1. Results obtained from six consecutive limestone cutting experiments together with the measurements of background airborne dust.

The data obtained when the sampler was in the front part of the chamber (filter numbers 1 to 6; nominal PM_{10} concentration = 46.6 ± 2.9 mg m⁻³) and those obtained from the back area (filter numbers 7 to 12; nominal PM_{10}

concentration = $48.6 \pm 2.0 \text{ mg m}^{-3}$) show that airborne dust in the chamber was reasonably uniformly dispersed throughout. Preliminary runs involving larger cut volumes of limestone produced nominal dust concentrations that did not increase proportionately with the mass cut, showing that significant particle aggregation and rapid settling was occurring at higher dust concentrations.

From Table 1, the mean nominal PM_{10} concentration is 47.6 \pm 2.5 mg m⁻³. The total mass of PM_{10} dust generated in the chamber for every cut is (47.6 mg m⁻³)(28 m³) = 1333 mg; taking the density of Globigerina limestone (Camilleri, 1991) as 1900 kg m⁻³, the mass of limestone ground away per cut is (2.04 x 10⁻⁵ m³)(1900 kg m⁻³) = 0.039 kg and this yields a nominal PM_{10} emission rate for cutting limestone equal to 34.2 kg / Mg pulverized rock.

(b) Size distribution of dust from quarries

Table 2 lists data from the three quarries as it pertains to the cutting and dressing machine in each quarry. For quarries 1 and 2, the data for the dressing machine is the average from two separate samples collected on different dates. In all cases (except where indicated), the limestone was humid with moisture content varying from 8.9 to 23% and with a mean value of 15%. Dry stone from quarry 2, with moisture content 0.74%, on dressing produced dust with composition as shown in parenthesis.

The data show that both cutting and dressing machines generate an appreciable quantity (mean value 18%) of respirable dust (of diameter < 10 μ m) which precipitates out of the air immediately or soon after it forms: this is true not only for wet conditions, when little or no dust emissions are visible to the eye during the grinding operations, but also when the stones are dry: it appears that a considerable fraction of fine dust particles are scavenged out of the air by the larger particles, presumably by impaction, and this factor helps to lessen the dust impact from the machines.

Statistical analysis (Friedman's test) showed that the size distribution of deposited dust generated from tools in use in the three different quarries were not significantly different (respective *p*-values for dust from cutting and dressing tools in the three quarries = 0.203 and 0.565; for the null hypothesis, p > 0.05) and also that particle distributions of deposited dust from the cutting and dressing machines were statistically indistinguishable (for the fractions of dust with diameter, in μ m, < 1.5 and 1.5 – 10, the respective *p*-values = 0.717 and 0.307; similar results were obtained for larger dust sizes; for the null hypothesis p > 0.05). The data therefore suggests that the dust emitted from cutting and dressing tools has similar size distribution and the nominal emission factor for PM_{10} dust for both types of tool was taken as identical: this is not unreasonable given that the rotary blades employed in each tool are very similar. Moreover, the emission factor was assumed to be the same as that obtained from the cutting tool employed in the experiment described in (a) and again this assumption is reasonable in view of the similarity of cutting tools involved.

Dust from the access roads (Table 3) also had a statistically indistinguishable size distribution from that of dust deposited near the working tools. It is interesting

to note that the fine dust content of unpaved roads within quarries is not significantly higher than that found next to the cutting and dressing machines and this suggests that surface material on these roads is constantly being replenished from the quarry face through wind transport.

		% fraction by mass of dust						
Particle Diameter (Ø) (um)	Quarry 1		Quarry 2		Quarry 3			
Tarticle Dianceer (0) (µm)	Cutting	Dressing	Cutting	Cutting	Dressing	Cutting		
Ø > 500	4.6	4.8	6.4	2.6 (14.6)	1.8	4.1		
125<Ø<500	10.8	11.2	11.7	10.7 (20.5)	10.8	17.5		
63 < Ø < 125	47.9	42.6	37.3	45.0 (26.5)	34.2	27.1		
45 < Ø < 63	15.3	14.1	18.3	17.4 (15.3)	20.6	17.0		
$10 < \emptyset < 45$	8.1	10.0	9.7	8.3 (8.9)	11.2	11.2		
Ø < 10	13.2	18.3	16.7	16.1 (14.6)	21.3	22.9		
Ø > 500	4.6	4.8	6.4	2.6 (14.6)	1.8	4.1		

Table 2. Size distribution of deposited humid dust (mean moisture content 15%) from limestone cutting and dressing machines in three quarries in Malta. For quarry 2, the data in parenthesis refers to dust generated from dry stones (moisture content 0.74%).

Quarry	Dust % fraction (in µm)					
Quarry	Ø< 10	10 < Ø <45	45<Ø<63	63< Ø <125	125<Ø<500	Ø > 500
1	11.0	3.8	5.2	13.1	15.8	51.0
2	21.8	11.1	19.8	31.8	11.0	4.4
3	13.2	10.9	18.3	35.6	16.2	5.7

Table 3. Size distribution of (wet) deposited dust (moisture content 7 - 23%) from unpaved access roads in quarries

Modelling fine dust emissions from quarrying

There is a dearth of available data on the properties of local materials and methods to allow accurate prediction of dust emissions from each of the operations involved in the sofstone industry. Besides new data presented in this paper, published information on comparable systems from other countries has also been used in order to obtain an estimate of total fine dust (PM_{10}) emission from softstone quarrying. Calculations were based on a virtual typical quarry where the open pit has a footprint of 20 000 m² and a depth of 75 m and then this data was used to estimate total emissions as applicable to the softstone quarrying industry as a whole.

(a) Fine dust emission from limestone cutting and dressing of stones

In this model, it was assumed that all limestone blocks measure 56 by 26 by 23 cm. It was further assumed that the 12 mm rotary blade forms a cut in the limestone bed that is 1.3 cm thick: this value is supported by actual measurements in a quarry which gave values in the range 1.25 and 1.35 cm (n = 5). When the blade makes a cut

parallel to the opposite faces, with dimensions 56 by 26 cm (faces A_1 and A_2) of incipient blocks in the quarry bed, it grinds away from the bedrock and pulverizes a cuboid of limestone of volume VA equal to [(0.013 m)(0.56 m)(0.26 m)] or 1.89 x 10⁻³ m³; similarly, a cut parallel to opposite faces B1, B2 of dimensions 56 by 23 cm, would remove a volume $V_{\rm B}$ equal to 1.67 x 10⁻³ m³, while a third cut parallel to the remaining set of faces, C₁, C2, of dimensions 23 by 26 cm, would remove volume $V_{\rm C}$ equal to 7.77 x 10⁻⁴ m³. To detach a single block from the quarry bed will thus theoretically require the removal of a total volume $V_t = 2(V_A+V_B+V_C)$ which amounts to 0.00876 m³ of pulverized rock. However, limestone blocks are not removed singly from the quarry bed but in groups involving several stones: indeed, for the purposes of this analysis it is convenient to regard stone extraction as involving theoretical removal of a three-dimensional array of stones where a series of cuts will cause each block to form simultaneously with six other nearest neighbours: thus, any single cut in the quarry face will make possible the release of two adjacent blocks of limestone. Therefore, the volume of rock cuttings formed per block produced is equal to $\frac{1}{2}$ V_t or 0.00438 m³. To this volume, an additional element of limestone of volume V_s equal to $4(0.0065)^2(0.56 + 0.013)$ also actually requires removal during the grinding process representing four cuboids along the edges of each extracted block. The total volume of rock cut per block extracted is therefore 0.00448 m³. This model ignores the situation at the boundaries of the quarry but the error is small since only a very small proportion of blocks constitute the boundary layer for a typical quarry.

The mass of rock cut and converted into total dust is equal to 8.5 kg. Since each block has a mass of 64 kg, the mass of limestone dust generated per block is equivalent to 13.3 % by mass of extracted rock and the rate of total dust released during stone cutting is 133 kg total dust/Mg limestone blocks produced.

A typical stone dressing machine grinds away 0.64 cm from one of the larger faces of the block (measuring 56 cm by 26 cm) and 0.15 cm from the two contiguous faces with dimensions 56 cm by 22 cm: the volume of pulverized rock is therefore 1.3 x 10^{-3} m³ which is equivalent to 2.5 kg limestone dust generated per block or 39 kg total dust/Mg limestone blocks produced. Assuming that the amount of PM₁₀ dust generated for both cutting and dressing operations is 34.2 kg/ Mg pulverized limestone, we calculate an *emission factor*, $E_{c+d, n}$, being the amount of PM₁₀ dust generated in the production of *n* fair-faced limestone blocks, as follows:

$$\mathbf{E}_{c+d,n} = (0.29 + 0.085)n = 0.38n \tag{1}$$

(b) Fine dust emission from limestone waste removal

Limestone wastage associated with *franka* quarrying is claimed to vary from almost 50% of production (Mallia et al., 2002) to about 20% and wastage depends on the presence of such features as bedding joints, fractures and so on in each quarry: using the lower, more conservative value, it follows that in producing *n* stones, (64 n/80)(20) kg = 16n kg limestone waste is formed. Transferring this waste, with front-end loader, from a pile onto a truck constitutes a batch drop operation for which the PM₁₀ dust emission factor is given by the following empirical equation (USEPA, 1995):

$$E_{wr}$$
 (in kg Mg⁻¹) = [k (0.0016)(U/2.2)^{1.3}/(M/2)^{1.4}] (2)

where k is 0.35 for particle sizes < 10 μ m, U is the wind speed and M is the moisture content. Taking the moisture content as 0.7% typical of the dry months when the problem of dust emission is greatest, and substituting for M in eq 2 using a value for 'typical' wind speed (Chetcuti et al., 1992) of 10 m sec⁻¹ gives a value for the *emission factor for waste removal*, E_{wr}, equal to 0.017 kg Mg⁻¹. Thus the dust released from removal by haulage of limestone waste involved in the formation of *n* stones, E_{wr,n} is given by:

$$E_{wr, n} = (16n)(0.017/1000) = 2.7 \times 10^{-4} n \text{ kg}$$
 (3)

Since this emission factor is already much smaller than $E_{c+d,n}$, it was decided to ignore the ostensibly even smaller dust emission associated with loading of limestone blocks onto trucks, an operation which is carried out without actual 'dropping' of the material

(which would damage the stones through fracturing and chipping).

(c) Fine dust emission from transport of stones by truck over unpaved road

Trucks travelling along unpaved temporary 'roads' through a quarry represent another source of fine dust emission. When a vehicle travels an unpaved road, the force of the wheels on the road surface is expected to pulverize the unconsolidated surface material by grinding: particles are also lifted and dropped from the rolling wheels and the road surface is exposed to strong air currents in turbulent shear with the surface. The atmospheric turbulence left behind the vehicle continues to act on the surface after the vehicle has passed. The quantity of dust emitted depends on the volume of traffic, the fraction of silt (here defined as particles $< 63 \ \mu m$ diameter) in the road surface materials and the humidity of the road surface materials. The following empirical equation was used to estimate Er, kt, the quantity of PM10 dust emitted per vehicle km travelled (USEPA, 1998)

$$E_{r,kt} \text{ (in kg/vehicle km travelled)} = [0.2819 \text{ k} (\text{s/12})^{\text{a}} (\text{W/3})^{\text{b}}]/(\text{M/0.2})^{\text{c}}$$
(4)

where s is the surface material silt content (%), W is the mean vehicle weight (t), M is the surface material moisture content (%) and k, a, b and c are constants which for PM_{10} emissions have respective values 2.6, 0.8, 0.4 and 0.3.

From Table 3, the silt content ($\emptyset < 63 \ \mu m$) for access roads is seen to vary between 20 and 51%, with a mean of 38%. Thus, the following values were used in eq (4): s = 38%; M = 0.7% (dry conditions); W = 30 t, being the average weight of a loaded truck (40 t) and that of an empty truck (20 t). Substituting in the given equation yields a value for E_{r.kt} of 3.2 kg/vehicle km travelled. The distance travelled by trucks on their way in and out of the virtual quarry can be estimated from its physical size. Allowing for tortuosity, the travel distance is about 400 m per trip inside the quarry. To transport stones or waste rock away from the quarry, a truck needs to enter empty and leave full and hence to travel 800 m per load of product. If one truck carries 300 stones, then for nstones, the travel distance on unpaved road is 0.0027n km and the corresponding PM_{10} emission is given by

$$E_{r,n}$$
 (in kg) = $E_{r,kt}$ (0.0027 + 0.0008) $n = 0.011n$ (5)

In eq. 5, the emission factor also includes the contribution (second term in the brackets) made by trucking away to landfill the limestone waste arisings associated with the production of n stones based on a wastage rate of 20% of production as used earlier.

(d) National emissions and implications

Table 4 summarizes the estimated PM_{10} emissions from the various sources as they pertain to the virtual quarry. It is evident that stone cutting and dressing produce over 97% of the fine dusts, of which 76% is contributed by the cutting process; dust raised during transportation of stone over unpaved road contributes 2.8% and the handling of solid wastes accounts for an almost insignificant fraction of total emissions. For a typical production rate, n, of 900 stones per day, the total PM₁₀ dust released from the virtual quarry is 351 kg. Since the surface area of the quarry is 20 000 m², the rate of emission is 17550 mg m⁻² day⁻¹. For a 30-day month with 22 working days, the time-weighted monthly average is 12870 mg m⁻² day⁻¹) proposed as being likely not to provoke complaints at peak periods (Vallack and Shillito, 1998). Comparable guideline criteria (Williams, 1986; QUARG, 1996) from the USA and Australia range from 133 to 350 mg m⁻² day⁻¹.

Process	PM ₁₀ dust emitted in production of <i>n</i> stones (kg)
Stone cutting and dressing	0.38 <i>n</i>
Limestone waste removal (batch drop operation)	0.00027 <i>n</i>
Stone transport over unpaved road	0.011 <i>n</i>

Table 4 Estimated emissions of fine (PM10) limestone dust from operations involved in softstone quarrying in virtual quarry

Since only dust associated with waste removal and wind whipping on the access road is dependent on the size and geometry of the quarry pit and wind conditions, and since these sources are both minor contributors, it is seen that the term $E_{c+d,n}$ in eq. 1 can be used to yield a good estimate of total fine dust emission from the quarrying industry as a whole based solely on stone extraction information. The total annual current production of softstone in Malta (Mallia et al., 2002) is 400 000 m³: since only 87.4% of rock is potentially convertible into blocks (to allow for volume removed in the cutting process and assuming only blocks of volume 0.0335 m³ are manufactured), this would generate a total number of blocks equal to $(0.874)(400\ 000)/(0.0335) = 10.4 \ \text{x}\ 10^6$ The PM₁₀ dust emission during the cutting stones. process is $(10.4 \times 10^{6})(0.29)/(10^{3}) = 3016$ t. Assuming 25% of production is discarded as waste (which is low according to Mallia et al (2002) but probably more realistic than the value 50% quoted in the reference), then the dust released in dressing is [(0.75)(10.4 x $10^{6}(0.085)/(10^{3}) = 663$ t. Hence, ignoring the minor emission sources, we estimate that national softstone production could generate 3679 t a⁻¹ of PM₁₀ dust. However, since production of dusts is largely suppressed during the wet months, namely, September through April for which the mean daily rainfall is > 0.4 mm (Chetcuti et al, 1992), we can applying a wet-month correction factor of (12-8)/12 = 0.33 to the national emission rate to yield a yearly 'rain-mitigated' total emission of 1214 t a⁻¹. Since the total land taken by quarries (Mallia et al., 2002) is 1.2 km², and considering only the four dry months during which emissions are significant, the daily average

emission rate^{*} during this period is 11 500 mg m⁻² day⁻¹ which is well above international guideline values (100 – 350 mg m⁻² day⁻¹). Even if taken over the whole year, the daily average emission rate (3679 mg m⁻² day⁻¹) remains unacceptably high.

Considering the number and geographical location of the quarry works, and the fact that the emissions are released in large open pits at sub-ground level, it is likely that airborne waste from this industry is affecting significantly the general air quality in Malta, particularly during the dry period. Routine air monitoring in Malta is a relatively recent activity and data for PM₁₀ (collected by Malta Environment and Planning Authority using the beta attenuation technique) is particularly patchy; published information (Vella et al., 2002; Stacey and Bush, 2002) reveals that the 24-h EU standard limit value (50 μ g m⁻³) has frequently been exceeded with peak values >200 µg m⁻³; also, exceedance occurs at most of the measurement sites including urban, rural and coastal locations. The data as currently available are not sufficient to allow evaluation of any spatial or temporal trends in ambiental PM₁₀ as may be associated with quarry emissions.

Sea-salt and transboundary (especially Saharan) dust are expected to be important natural contributors to the airborne particles and probably the most problematic anthropogenic source is vehicle traffic since car ownership is high, with more than 250 000 vehicles on the roads in 2000 (MPA, 2001b). However, from our results it appears that softstone quarrying is another significant anthropogenic source of dust albeit providing a less toxic particulate pollutant than that from motor traffic. The contribution from quarrying has increased six-fold during the last 20 years as a result of increased "franka" production (Mallia et al., 2002). Limestone dust derives also from the Coralline Limestone (hardstone) industry where production output is actually larger by a factor of 1.8: it is likely however that dust emissions from this industry are lower in view of the different methods of extraction and processing.

The airborne dust contribution from softstone quarrying may be the most easily controllable component of PM_{10} in local air. As mentioned earlier, when the quarry bed and the extracted stones are humid from rain, there is no formation of visible dust during works in the quarry. Clearly, artificial water wetting as a dust suppression technique during the dry months would appear to constitute a technically sound solution, not entailing excessive cost, but providing significant environmental benefits. There may be factors which have to be considered if such a control measure is applied, e.g. increased handling difficulties of heavier (wet) blocks. A technical analysis of alternative dust suppression techniques is beyond the scope of this paper, but the need to control dusty emissions from quarrying appears to be indisputable.

Conclusions

^{*} One month taken to have 22 working days.

The softstone quarrying industry in Malta utilizes rather primitive techniques to extract and process limestone blocks that are used extensively in the construction industry as a main building material. The most problematic waste from quarrying is airborne dust since no control measures are in place. On the basis of a simple mathematical model, it is shown that the rates of total dust released during stone cutting and dressing are, respectively, 133 and 39 kg/Mg limestone blocks produced. It is also shown, experimentally, that the nominal PM10 dust generated during the cutting of limestone is 34.2 kg/Mg pulverized rock and that dust generated during both cutting and dressing operations has a practically identical size distribution. From this, it can be shown that, to produce *n* stone blocks, the quantity, in kg, of PM_{10} dust emitted is 0.38*n* and that this quantity is significantly greater than that released during transport of blocks by truck over unpaved road in the quarry (0.011n), and that involved in loading limestone waste on trucks for removal from the quarry (0.00027n). On the basis of this model, and using published limestone extraction information, it is estimated that the industry generates about 1200 t of PM₁₀ dust per year. Since there are over 60 quarries situated within or very close to urbanized areas on Malta and Gozo, the air quality on the islands is likely to be significantly and negatively affected by these emissions, especially during the dry summer period. Insufficient information on air quality is available currently to establish any trends in PM₁₀ levels as might confirm effects from quarry emissions. Airborne dust from quarries is visibly reduced to negligible quantities when the quarry bed and extracted limestone blocks are wet by rainfall suggesting artificial water wetting as an effective mitigation technique during dry weather. It is therefore concluded that work practices that include this or some other appropriate dust abatement measure would lead to a general improvement in local air quality through elimination of a major proximate source of airborne fine dust.

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