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INTERNATIONAL BIODETERIORATION BULLETIN

BIODETERIORATION CENTRE
UNIVERSITY OF ASTON
ST. PETER'S COLLEGE,
SALTLEY, BIRMINGHAM B8 3TE.

Editor-in-Chief of Biodeterioration Centre Journals
Dr H O W Egkins

Editors
Professor T A Oxley and Christine Allsopp
Business Manager
Dr D Allsopp

The Editors are able to call upon the assistance of an Editorial Board whose members are in Britain, various countries of Europe, and the U.S.A.

NOTES FOR CONTRIBUTORS
The International Biodeterioration Bulletin is published four times per year (Spring, Summer, Autumn and Winter). Typescript contributions should be sent to the Editors, at the above address.

The Bulletin acts as a vehicle for the publication of original works, including reviews, on all aspects of biodeterioration, i.e., deterioration of materials, artefacts or facilities, of economic importance by living organisms, which include microorganisms, insects, rodents, birds, higher plants, etc. Articles on biodegradation, that is conversion of materials to less objectionable, more easily disposable, or higher value products by living organisms, are also published.

Contributions are published only in English. Each article must be accompanied by a summary in 50 - 150 words which will be translated into French, German and Spanish. Native speakers of these languages are invited to submit their summaries in their own language; in certain circumstances complete articles may be submitted in French, German or Spanish and will be translated into English for publication.

Illustrations must be very clearly drawn, normally larger than the size finally desired. The suggested final size should be clearly indicated but the Editors reserve the right to vary this in the interest of economy and clarity.

As far as possible diagrams will be reduced to single column width (80 mm) or to half page (170 mm). In any event, neither these nor half tone photographs can exceed full page (260 by 170 mm). Authors should bear in mind that it is generally more convenient for readers if legends which accompany diagrams or photographs appear with them on the same page and should proportion their illustrations accordingly. Lettering on diagrams will normally be inserted by the printer; authors are therefore asked to insert lettering or symbols in pencil on the originals or preferably, in ink on a photocopy.

All articles are submitted by the Editors to one or more independent referees for advice on their clarity, originality, and general suitability for publication, but the final decision whether or not to publish an article rests with the editors. If articles are rejected the substance of the referee's report will usually be communicated to the author and in suitable cases the Editors will be pleased to help authors to improve their papers with a view to possible publication.

Bibliographic references are indicated in the text by author names (no initials) and year only, viz: Reese and Levinson (1952); or: Darby et al., (1968) and in the bibliography in strict alphabetical order of first author's names, thus: Reese E T and Levinson H G (1952)

Comparative study of the breakdown of cellulose by microorganisms

Physiologica Plantarum 5: 354-366

or:

Darby R.T. Simmons E G and Wiley B J (1968)

A survey of fungi in a military aircraft fuel supply system

International Biodeterioration Bulletin, 39-41

References to books, conference proceedings, etc. should quote first the author(s) or editor(s), then the year of publication and title followed by the city in which it is published and the name of the publisher. As far as possible titles of journals should be given in full except for such abbreviations as 'Journ', 'Proc', 'Trans.' etc. 20 reprints will be sent free of charge to the first named author unless otherwise instructed. Any number (normally not more than 50) of additional reprints may be purchased at a reduced price in advance. An order form and price will be sent giving about one month's notice.

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BIODETERIORATION SOCIETY NEWSLETTER

Society Treasurer

Members may need to be reminded that a new treasurer was appointed at the last annual general meeting of the Society. The new treasurer is:

Dr. Graham Lloyd,
63, Thurlstone Road,
Penistone,
SHEFFIELD
S30 6EF

Subscriptions

The treasurer reminds all members that subscriptions for 1983 - 84 will be due on 1st April 1983. The rates are:

U.K. and Ireland members: £5.50
(or £4.50 if paid by Bankers' Order on 1st April)

Overseas members: £3.00
(Those unable to remit in sterling are asked to add £1 to this to cover bank charges)

Nottingham Meeting

The next meeting will be held at the University of Nottingham on Tuesday 29th March and the subject will be: "Fungal Physiology". The local organizer is:

Dr. J.F. Peberdy,
Department of Botany,
University of Nottingham,
University Park,
Nottingham. NG7 2RD

Sixth Symposium

The date of the Sixth International Biodeterioration Symposium has just been announced. It will be held from the 5th. through the 10th August 1984 at George Washington University, Washington, D.C. USA.
Specialised bibliographies are produced from the Biodeterioration Information Centre's document collection from 1965 as listed in the bibliographic journals Biodeterioration Research Titles (B.R.T.) and Waste Materials Biodeterioration (W.M.B.).

Bibliographies may be updated by use of B.R.T. and W.M.B. or purchase of new editions of existing titles. Copies of papers listed may be purchased from the Biodeterioration Information Centre.

Following are Bibliographies currently available — all currently updated

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Orders for published Specialised Bibliographies, or requests for the preparation of Specialized Bibliographies in other subjects should be addressed to:

Dr. D. Allsopp, Biodeterioration Centre, University of Aston, St. Peter's College, College Road, Birmingham B8 3TE England
ANNOUNCING
THE 1983 SHORT COURSES
AT
THE BIODETERIORATION CENTRE

We are pleased to announce our provisional programme of short courses for 1983, and for the first time, on a pre-
scheduled basis, our tutorial courses which have proved so popular with industry over the past three years.

One and Two Day Courses

VC 831 Moisture in Materials - Thursday 24 February 1983
Problems caused by moisture in a range of structures and products will be covered, with techniques for monitoring and
measurement.
COST: Including lunch and refreshments - £55.00

VC 832 Biological Testing of Materials - Wednesday 2 March 1983
Laboratory and field techniques for biological testing, using fungi, algae, insects (including termites) and rodents.
Biological standards.
COST: Including lunch and refreshments - £55.00

VC 833 Safety and Handling of Micro-Organisms - Tuesday/Wednesday 29/30 March 1983
Based on our previous and popular courses on this topic, this course is designed to familiarise laboratory staff in the
basic skills of using micro-organisms in industrial testing. No previous knowledge is required. The course is of interest to
general laboratory staff and in particular to those carrying out mould growth tests such as BS 2011 Test J. The course
includes basic manipulation, laboratory safety and basic fungal biology and recognition. It is also hoped to cover aspects
of safety legislation. Part of this course will be taught by practical laboratory exercises.
COST: Including overnight accommodation and meals - £95.00

VC 834 Biology of Buildings - Tuesday/Wednesday 12/13 April 1983
Problems of structures, rot and insect damage, mould growth, condensation-induced problems, rodent proofing, insect
infestation. Of interest to architects, designers, builders and planners as well as applied biologists.
COST: Including overnight accommodation and meals - £95.00

VC 835 Sterilisation - Tuesday 17 May 1983
A course on the methods available to obtain sterile products of many types. Use of heat, gasses, ultra-violet and gamma
irradiation.
COST: Including lunch and refreshments - £55.00

VC 836 Deterioration of Cellulose-containing Products - Thursday 26 May 1983
The course covers not only the obvious and traditional materials such as wood and wood products, boards and paper,
but also cellulose containing fillers and adhesives.
COST: Including lunch and refreshments - £55.00

VC 838 Biological Problems of Museum Specimens, Antiques and Monuments - Tuesday 12 July 1983
Held during an international UNESCO course on the biodeterioration of cultural properties. The day’s lectures and
demonstrations will be given by Centre Staff and scientists and conservationists from London and Birmingham
Museums. Fungal, insect and rodent damage will be explained and the problems associated with paper, textiles, wood
and leather will be considered. This course is of interest to antique dealers as well as Museum and associated staffs.
COST: Including lunch and refreshments - £55.00

VC 839 Microbial Toxins in Food and Feedstuffs - Wednesday/Thursday 7/8 September 1983
Following the success of last year’s one day course, it has been decided to expand the topic this year. The course will
concern itself with toxic agents of biological origin in both human and animal foodstuffs. Special emphasis will be given to
Mycotoxins. Bacterial toxins and poisonous plant fragments will also be covered.
COST: Including overnight accommodation and meals - £95.00
VC 840 Weed Control - Wednesday 5 October 1983
(This course immediately follows the Garden, Sports and Leisure Exhibition at the nearby National Exhibition Centre 2-4 October 1983).
Various aspects of weed control (physical, chemical and biological) will be considered both in agricultural and amenity situations. Of interest to agriculturalists, local authorities and building conservators.
COST: Including lunch and refreshments - £55.00

VC 841 Hydrocarbon Microbiology - Tuesday 1 November 1983
This course is designed to explain problems in the oil industry including microbially induced corrosion and biological problems in drilling.
COST: Including lunch and refreshments - £55.00

SUMMER SCHOOL - 4-13 JULY 1983
VC 837 Biodeterioration Summer School - With Special Emphasis on Museum and Cultural Property Problems
Designed primarily for researchers from developing countries and sponsored by UNEP/Unesco/ICRO, this course is also open to individuals and companies from the U.K.
COST of full residential course, including accommodation and meals - £400.00

TUTORIAL COURSES
These forms of training are very different from the usual short courses. A small number of trainees from industry receive individual attention and most of the course is laboratory based. The training programme for each is individually tailored, e.g, for trainees with no previous biological experience, or for laboratory chemists, or for laboratory workers to practice special microbiological techniques. The main theme is handling and using test micro-organisms safely in the industrial laboratory. We shall be pleased to discuss your requirements and the training needs of your staff.
We are booking now for two training periods:
VC 830A 25-28 April 1983
VC 830B 17-21 October 1983

All courses, unless otherwise stated, are held at the Biodeterioration Centre. Further details of courses and booking forms may be obtained from:
Dr D Allsopp, Course Organiser, Biodeterioration Centre, University of Aston in Birmingham, St Peter's College, College Road, Saltley, BIRMINGHAM, B8 3TE. Telephone: 021-328-5950, Telex: 336997 (Mark - Attention Biodeterioration Centre).
The Centre reserves the right to modify any part of this programme, or cancel courses if bookings are insufficient to run a course economically.
Enquiry Form

Please send full details of the following courses when available:
*Tick appropriate item(s) of interest

VC 831 Moisture
VC 832 Testing
VC 833 Safety
VC 834 Buildings
VC 835 Sterilisation
VC 836 Cellulose
VC 838 Museums
VC 839 Toxins
VC 840 Weeds
VC 841 Hydrocarbons
VC 837 Summer School

Please telephone to discuss training on tutorial courses.

NAME: ________________________________
ADDRESS: ____________________________________________
__________________________________________
__________________________________________
TELEPHONE: ________________________________________
DEGRADATION OF TRIBUTYL Tin OXIDE BY FUNGAL CULTURE FILTRATES

R. J. Orsler and G. E. Holland

Summary
The culture filtrates of Coniophora puteana, Coriolus versicolor, and Sistotrema brinkmannii have been shown to be capable of degrading the wood preservative tributyltin oxide, principally to a dibutyltin compound. The degradation products have been examined by polarography and thin-layer chromatography.

Introduction
The study of the degradation and permanence of tributyltin oxide (TnBTO) carried out by Henshaw et al (1978) indicated inter alia that a wood-destroying fungus could degrade TnBTO to di- and monobutyltin compounds during its attack on a suitable wood source. It was also observed that the white and brown rots used in this work appeared to exhibit different mechanisms of degradation.

In an attempt to investigate further this aspect of the work, culture filtrates of selected fungi were reacted with TnBTO. The technique is based on the assumption that it is the extracellular enzyme systems secreted by the fungi that are most likely to produce TnBTO degradation, although it is recognised that in treated timber other factors, eg the wood itself, may play some part in the degradation process. This approach has the advantage of allowing a rapid and repeatable assessment of the system's action on the preservative, and of not requiring acid-based solvents to recover the TnBTO and its breakdown products. Extraction with a neutral solvent is prudent since other workers (Kimmel et al 1977) have found some organotin intermediates to be acid labile.

Three fungi were used in this study, Coniophora puteana (FPRL 11E) a brown rot, Coriolus versicolor (FPRL 28A) a white rot and Sistotrema brinkmannii (FPRL B730). Although both C. puteana and C. versicolor have been isolated from decaying window joinery, they are not generally regarded as typical of the fungi found in these components. Nevertheless, they are commonly used for bioassay work in the laboratory. S. brinkmannii is a Basidiomycete which has often been found in window joinery. It has been isolated from timber treated with 1% TnBTO solution, and is clearly tolerant to this preservative (PRL unpublished data). S. brinkmannii shows cellulolytic activity but, as yet, has not been shown conclusively to be a wood destroyer.

Experimental
Culture procedure A pad of glass wool was placed in a 1 litre Roux culture flask to which was added 240 ml of medium A (King 1966). The composition of this medium is as follows:

- KH₂PO₄: 1.5 g
- MgSO₄.7H₂O: 0.5 g
- NH₄NO₃: 0.7 g
- CaCl₂: 0.1 g
- Thiamine hydrochloride: 1.0 mg
- H₂BO₃: 570 μg
- FeCl₃: 145 μg
- CoCl₂.6H₂O: 40 μg
- CuSO₄.5H₂O: 60 μg
- MnCl₂.4H₂O: 30 μg
- (NH₄)₂MoO₄.4H₂O: 20 μg
- ZnSO₄.7H₂O: 310 μg
- Water to 1 litre and pH adjusted to 5.0 - 5.5 with 4 M NaOH

(Received, September 1982)
To this medium was added 3.2 g of Scots pine sapwood un-classified sawdust, such as would be produced by a hand held cross-cut saw, as a carbon source. After shaking to mix, the glass wool was arranged so that it projected above the liquid level in places. After stoppering with a cotton wool plug, the flask was autoclaved and cooled. A 4 mm disc cut from a 2% malt agar culture of the appropriate fungus was placed on the glass wool above the liquid and the complete system incubated for at least 4 weeks at 25°C. Progress in fungal growth was observed. Some flasks had to be inoculated a second time due to lack of growth. 3 x 1 litre flasks were employed for each fungus.

After incubation, the liquid was filtered off through a No 4 Whatman paper and its pH adjusted to 5.0-5.5 by the addition of dilute NaOH. The combined filtrates for each fungus were then divided into 30 ml aliquots and stored in a freezer until required.

Reaction procedure. 2 x 30 ml aliquots of the chosen frozen filtrate were allowed to thaw and were transferred to a 100 ml conical flask. 50 μl of TnBTO solution (2 g TnBTO in 100 ml EtOH) was added to the flask and the whole kept at 37°C for one hour with constant stirring. The resulting solution was cooled to room temperature and extracted with chloroform.

Polarographic analysis. The selected chloroform solutions were evaporated to dryness and the resulting residue dissolved in 0.05% HCl in EtOH. This solution was submitted to the standard PRL polarographic analysis procedure (Anon 1980) including the preparatory clean-up stage using Amberlite CG 120 cation-exchange resin.

Thin-layer chromatographic analysis. Chloroform solutions were evaporated to near dryness and an aliquot of these concentrates spotted, as appropriate, on to TLC plates. In all investigations 20 x 20 cm plates coated with a 250 μ layer of silica gel were used. Developing solvent systems included (a) di-isopropyl ether/n-hexane 1:1 (b) di-isopropyl ether/acetic acid 99:1 (c) carbon tetrachloride/acetylene/acetic acid 20:1:1 (d) 1,4-dioxan (e) n-hexane/acetic acid 9:1. After development, compounds were detected by exposing the plate to broad spectrum UV light for about 20 minutes and then spraying with catechol violet solution (approximately 0.5 g/1 EtOH).

Both one and two dimensional systems were investigated.

Results and Discussion

Polarography. This technique has been adopted at PRL for the routine determination of the proportions of tri-, di-, and monobutyltin compounds within a given mixture. While it has the advantage of providing a relatively rapid quantitative assessment of these butyltins without prior separation, the fact that the analysis is carried out in an acid medium does not allow further details on the nature of the butyltins to be ascertained.

Immediately after the production of the culture filtrates, and before freezing, samples were reacted with TnBTO and examined by polarography to obtain an early indication of the likely extent of degradation. This was carried out both before and after the adjustment of pH with dilute NaOH.

Peaks associated with the reduction potentials of mono-, di-, and tributyltin compounds were present, although in this first assessment no attempt was made to quantify the degradation since, in some instances, an unidentified peak with a reduction potential between tri- and dibutyltin obscured the true dimensions of the peaks of interest. This intrusive peak did not appear in any subsequent polarograms; no explanation is offered for its presence.

Similar polarograms obtained by reacting TnBTO with medium A with the pH adjusted to 5.0-5.5 by addition of NaOH showed that no degradation occurred without the contribution from the fungi and that initially only TnBTO was present. Nevertheless, these early polarograms did indicate that no gross differences in degradation pattern were introduced by the adjustment of the pH of the filtrates with dilute NaOH.

Repeat experiments using culture filtrates that had been frozen produced conventional polarograms from which the degree of breakdown could be estimated. These results appear in Table 1.

Again, all fungal preparations produced degradation, the greatest being achieved by the white rot C. versicolor. All three produced only a small proportion of monobutyltin compared with the quantities of dibutyltin present. For the white rot this observation contrasts with the earlier findings of Henshaw et al.

<table>
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<tr>
<th>Culture filtrate</th>
<th>% butyltin composition (TnBTO equiv.)</th>
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<tr>
<td>Coniophora puteana</td>
<td>Tri  84  Di 13.5  Mono 2.5</td>
</tr>
<tr>
<td>Sistotrema brunikmannii</td>
<td>Tri 73  Di 24.5  Mono 2.5</td>
</tr>
<tr>
<td>Coriolus versicolor</td>
<td>Tri 66.5  Di 32  Mono 1.5</td>
</tr>
</tbody>
</table>

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(1978) in which *C. versicolor* produced predominantly monobutyltin. However, this disparity and the generally more advanced degradation apparent in the earlier experiment may be due to a difference in the running time of the two experiments; the earlier work used TnBTO-impregnated wood blocks exposed to an attacking fungus for six weeks, whereas the enzyme experiment lasted just one hour. If it is assumed, as is usual, that the degradation process is a step-wise loss of butyl groups, such that dibutyltin will be formed before monobutyltin, it follows that the earlier experiment is probably demonstrating a more advanced stage in the degradation process. Both experiments, then, would indicate that *C. versicolor* exhibits a faster rate of reaction than *C. puteana*.

Overall, the degradation observed for *S. brinkmannii* may have the more serious implications, for this fungus has been shown to be a TnBTO-tolerant early coloniser of joinery timber (Baker et al 1979). It is therefore able to exist in TnBTO-treated joinery provided the moisture content in the wood is adequate. Should this occur, its ability to degrade TnBTO could eventually provide a more amenable environment for the less TnBTO-tolerant wood-destroying fungi.

**Thin-layer chromatography.** Using tributyltin chloride, dibutyltin dichloride, and monobutyltin trichloride as standards, various eluting systems were assessed for their ability to provide chromatograms with the three butyltins well separated. The investigation was based on systems proposed by Kimmel et al (1977). Rf values appear in Table 2.

It was unfortunate that the only non-acidic solvent system failed to provide adequate movement of the standard components. The rest did prove suitable, although some were extremely time consuming. It was concluded at this stage that for routine assessment of the tri-, di-, and monobutyltin constituents, a single development with one of the faster running eluants, e.g. n-hexane/acetic acid 9:1, would be the most effective.

The exercise was repeated using the chloroform extract of the solution produced by challenging TnBTO with the *S. brinkmannii* culture filtrate. In all cases only tri-, di- and monobutyltin spots were revealed, suggesting that no acid-tolerant intermediates were formed during degradation.

An alternative non-acidic eluate, 1,4-dioxan, was tried, both with standards and with chloroform extracts from all three culture filtrates after TnBTO reaction. The results are presented in Table 3.

As is often the case with single solvent systems, the 1,4-dioxan produced a degree of streaking on the developed TLC plates. For the standard mixture both di- and monobutyltin components produced streaks rather than discrete spots. The chloroform extracts all produced a similar pattern on the plate in which the only component that precisely matched the standards was the leading spot at Rf 0.58 (tributyltin). The streak at Rf 0.25-0.27, and the spot which basically remained at the origin, were close in value to the dibutyltin and monobutyltin standards respectively. However the spot at Rf 0.34, almost mid-way between the...
tributyltin and dibutyltinspots, appeared only in the chloroform extracts. Kimmel et al (1977) in their studies on the metabolism of organotin compounds found that the butyltins occupying this position on developed chromatograms were hydroxybutyl dibutyltin compounds which under acidic conditions, formed dibutyltin derivatives. Similarly, in the present work, the spot at Rf 0.34 may be indicative of an intermediate in the degradation process, but so far no identification of the associated compound has been attempted.

Conclusions

Filtrates prepared from cultures of Coniophora puteana, Coriolus versicolor, and Sistotrema brinkmannii are capable of degrading TnBTO, principally to a dibutyltin compound. A thin-layer chromatographic examination of the degradation products so formed has suggested that intermediates may be formed during the debutylation process. Although the work confirms, to some extent, the earlier observations by Henshaw et al (1978), further work is needed to establish the full mechanism of degradation and thus the limits to the performance of TnBTO in the service environment.

Table 3

<table>
<thead>
<tr>
<th>Culture filtrate</th>
<th>Butyltin derivatives (Rf values)</th>
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<tr>
<td></td>
<td>Tri</td>
</tr>
<tr>
<td></td>
<td>Di</td>
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<td>Mono</td>
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References

Anon (1980)
Polarographic determination of butyltin compounds in timber samples and in preservative solutions.


The permanence of tributyltin oxide in timber.

Bio-organotin chemistry. Metabolism of organotin compounds in microsomal mono-oxygenase systems and in mammals.
Journal of Agriculture and Food Chemistry 25 (1) 1-9.

The extracellular enzymes of Coniophora cerebella.
Biochemical Journal 100 (3): 784-792.
THE MECHANISM OF BLACKENING OF TILE SURFACES

T K Dan1, V P Sreedharan2, M Patel3 and F K Rohatgi4

Summary

General observations on blackening of roofing tiles and building bricks in various parts of India have been reported. Questionnaires sent to the various tile and brick manufacturers of Kerala confirmed that blackening of tiles is a problem for the industry which requires solution. The green coloured species which develop on tiles in the initial period of growth have been identified to be algae (Oscillatoria, Eudorina, Microcystis, and Chlamydomonas) and one moss (Bryophyta). These species turn black as a result of drying in the sun, presumably due to natural decay. In addition to aesthetic degradation, the growth of the contaminating organisms and their subsequent blackening, can affect the mechanical and physical properties of tiles and bricks. Some suggestions for preventing the growth of contaminating species and subsequent blackening of tiles and bricks are made, and results of some experiments along these lines are reported.

Introduction

The surfaces of ceramic materials play a unique and important role in the determination of the properties of the finished product. They are the first line of defence against external attack by chemical, mechanical or biological forces.

Although many studies have been conducted in the past to analyse and interpret the degradation at ceramic surfaces, these have been mainly confined to controlled laboratory experiments and with more or less pure materials. It has been observed that clay roofing tiles and building bricks blacken on weathering, especially in hot and humid climates. A questionnaire sent to tile and brick manufacturers in Kerala (Patel, Dan and Rohatgi 1980) indicated that this is a serious problem deserving attention and requiring an economic solution. There have been some studies on the effects of weathering on the strength of tiles and bricks in Europe (Butterworth, 1934, 1936, 1946; Llewellyn, 1964) but no scientific study of the process of blackening has been reported.

This paper deals with the blackening of tiles and bricks due to growth of microorganisms in hot and humid weather. It describes the process of growth and decay of these species and explores economic methods to prevent blackening.

General Observations

Tiles and bricks manufactured in Kerala from clay soils, using firewood as a fuel, blacken after only a few months when used in a hot and humid climate although blackening is much slower when they are...
used in a hot dry climate in other parts of India. Tiles made from alluvial soils, fired using coal as fuel and used in a tropical climate like that of Kerala, blacken much less than tiles made from clay soils.

Figure 1 shows a typical pattern of blackening on a tile roof in Trivandrum. It can be seen that tiles in the shade of the overhang blacken less than those in open positions, which are exposed to excessive rain and sunshine. While the blackening of tiles is not uniform and is frequently patchy, tiles placed in a sloping position near the ridge blacken less than tiles close to the horizontal position. If new tiles are placed near to already blackened tiles, the new tiles blacken faster.

These observations indicate that the factors which affect blackening are the type of soil and fuel used during manufacture; the surface properties of the tiles; the residence period of water on the surface of the tiles and the extent of exposure to rain and sunshine.

Tiles made in Kerala use two different clays, one highly plastic, the other non-plastic, which are mixed and fired at 850 - 900°C. Sometimes the mixing is not complete. If too much plastic clay is used the particle size is low and the number of capillary moisture films increases. On drying there may be warping and distortion and during firing plastic clays have a higher shrinkage rate leading to linear cracks (Figure 2b).

In other parts of India the clay is good enough to make bricks without blending. These clays are fired at a higher temperature (1000 - 1050°C) and the tiles do not blacken. This suggests that blackening is related to surface cracks or pores. This is also supported by the observation that pore free vitrified ceramics such as glazed tiles and stoneware pipes do not blacken even after years of exposure in Kerala.

The residence time of water is also important as tiles in near vertical positions do not blacken appreciably. Tiles under trees where droppings accumulate tend to blacken more readily, presumably because these accumulations act as nutrients.

The colour of roofing tiles varies from buff to dark red (Krishna Pillai, Thomas and Patel, to be published; Mukundan et al., 1980) depending upon the iron content in the clay, the firing temperature and the extent of soaking. The growth of microorganisms colours the tiles green initially but sun drying turns them grey and finally black. These colour changes take one to two years to complete depending on the extent of exposure to rain and sun.

The colour change can be simulated by putting green tiles overnight in an electric oven at 105°C. The tiles turn black, similar to the conversion on tiles exposed to sunlight for appreciable periods.
Figure 2a  Optical microscopic view on surface of fresh tile Bar represents 100μ

Figure 2b  Optical microscopic view on surface of fresh tile Bar represents 100μ

Figure 2c  SEM picture of fresh tile surface Bar represents 10μ
The Mechanism of Blackening of Tile Surfaces  T.K. Dan, V.P. Streeharan, M. Patel and F.K. Rohatgi

Microbiological study

Comparative studies were conducted on recently manufactured and blackened tiles. Figure 2 shows the surface of a fresh tile and Figure 3 and 4 show the surface of green and black coloured tiles respectively.

Scrapings from three tiles (fresh, green and black coloured) were collected, diluted with sterile water and identified under the microscope (Figure 5).

The scrapings from fresh red tiles showed small particles without limiting layers. The particles were not aggregated in clumps and some looked red. Presumably these were particles of clay.

Scrapings from green coloured tiles were found to contain the blue-green algae (Cyanophyceae) Oscillatoria and Microcystis and also the green algae (Chlorophyceae) Eudorina, Chlamydomonas and Ulothrix (Figure 5b). Occasionally the moss Funaria was also seen (Figure 5d).

The scrapings from black tiles showed small particles with a greenish colour, with limiting layer and shape and aggregated into clumps. The large clumps seldom showed filamentous algae (Figure 5c).

Scrapings from each of the above three samples were put into separate petri dishes and overlayed with a sterilised medium consisting of 2% agar plus 2% fresh tile powder in water. After cooling the dishes were incubated at a room temperature of 30 C where ample sunlight was available for 15 days.

In the first set, where scrapings from fresh tiles were added, no algal growth was seen. In the second and third sets, taken from green and black tiles respectively, algal growth produced green patches. Slides were prepared from the second and third cultures and showed most of the algae identified earlier in the scrapings.

In an attempt to simulate the spread of algal growth, black and green tiles were kept in touch with fresh tiles. As a control fresh tiles were kept in touch with fresh tiles. The tiles were kept in moist conditions at room temperature of 30 C. After 45 days algal growth appeared on the tiles in contact with black and green tiles but it took 150 days for algal growth to appear on the control.

Prevention of blackening

It can be concluded from the experiments that the presence of cracks and pores in the surface of tiles, as well as the environment, is responsible for blackening. The number of pores on the surface can be minimized by increasing the firing temperature and time, more uniform firing, better surface finishing, possibly by salt glazing or by decreasing the amount of non-clay materials in tiles.

However, although there may be several ways to close the pores, only a few may be economical. In the wood fired kilns which are used for firing tiles in Kerala salt glazing will not create any problems (Singer, S. and...
Figure 5a  Fresh tile. Bar represents 100μ.

Figure 5b  Green tile. Bar represents 100μ.

Figure 5c  Black tile. Bar represents 100μ.

Figure 5d  *Bryophyta* from green brick scrapings. Bar represents 100μ.

Figure 5  Photomicrographs of scrapings from the surface of fresh tile, green tile, black tile and green brick.
Singer, F.S., 1968). It has been observed that glazed pipes made in Kerala from the same clay that is used for tiles do not blacken even after long outdoor exposure.

In simulation experiments in the laboratory glazed tiles and pipes were kept in moist conditions at a room temperature of 30°C. We found that apply 3-5% salt (in a clay suspension) on the surface of the tiles before firing, or even blending it during the mixing of clays, will give a glazed surface which prevents the blackening of tiles.

The process of applying glaze is inexpensive and does not require any special apparatus or skilled labour so that it can easily be adopted in rural and cottage industries. Care should be taken to avoid adding excess salt, otherwise the lining of the furnace may be affected. Other salt glazing defects, like bloating and crazing, may arise. It has been calculated that the price might increase by 10 paise per tile (25 paise = 2p) due to salt glazing. The glazing will, on the other hand, increase the durability and aesthetic appearance of the tiles.

Blackening can also be prevented by chemical spraying or painting onto the surface of the tiles. The chemicals used need to be non-toxic, readily available and inexpensive. We conducted inhibition studies on plant pots made from the tile clays using mineral oil, crystal violet, a mixture of tetramethylthiuram disulphide (TMTD) and zinc oxide, mercuric chloride and trichloroacetic acid. A control pot was also kept without applying any chemicals to its surface. The pots were watered every day. Growth was seen on the control pot within 15 days of the start of the experiment and on the crystal violet treated pot within 30 days. Mineral oil smeared pots had a fungal growth but no algal growth. No growth was seen on the pots smeared with trichloroacetic acid even after 120 days. Further trials showed that no growth occurs on tiles treated with 5% and 10% trichloroacetic acid, even after six months exposure.

Acknowledgements
The authors acknowledge with thanks the help rendered by Mr S.G.K. Pillai in Optical Microphotography and by Mr. Peter Koshy in Scanning Electron Microscopy. Thanks are also due to all members of the Glass and Ceramics Section of the laboratory for their kind cooperation in this work.

References
Butterworth, B. (1934)
Butterworth, B. (1936)
Trans. Brit. Ceram. Soc. 35: 105
Butterworth, B. (1946)
Krishna Pillai, P., Thomas, D. and Patel, M.
Evaluation of seven Kerala clays.
Trans. Ind. Ceram. Soc. (to be published)
Llewellyn, H.N. and Butterworth, B. (1964)
Evaluation and utilization of three Kerala clays for structural industry
Indian Ceramics 22 (11)
Internal report on results of questionnaire sent to the tile manufacturers of Kerala.
Industrial Ceramics
MICROORGANISMS PRESENT IN DETERIORATED MATERIALS OF THE "PALAZZO DELLA RAGIONE" IN MILAN

C. Sorlini¹, L. Allievi¹, M. Sacchi¹ and A. Ferrari

Summary

Viable counts of different groups of microorganisms were determined in superficial samples taken from inside and outside walls of a 13th century building (Palazzo della Ragione) in Milan. Samples were taken in March and December 1979 and in May, July, and November 1980. The numbers of all organisms were high in Spring 1979 but decreased in subsequent samplings, possibly due in part to a light cleaning treatment having been applied, and the windows closed, after the first sampling. Both autotrophic and heterotrophic organisms were present, the former including thiobacilli. No autotrophic nitrifying bacteria were observed.

Introduction

The hypothesis that the bacterial microflora of building materials contributes to their biodeterioration has been put forward for a long time. Various investigations (Pochon et al., 1960; Krumbeln and Pochon, 1964; Paleni and Curri, 1972; Thiebaud and Lajudie, 1963) have, in particular, shown the connection between high numbers of microorganisms of the genus Thiobacillus and highly degraded areas. These findings support the hypothesis that such bacteria, transforming calcium carbonate into calcium sulphate, could be important in deterioration, even if definite proof of their role is not yet available (Ferrari et al., 1979; Barcellona et al., 1975). Even though the various sulphur compounds necessary for the growth of these bacteria may not be originally present in building materials, in plasters or frescos, they can nevertheless arrive in various ways: conveyed from the ground in water by capillarity, deposited from the air with dust and soot, either as hydrogen sulphide or sulphur dioxide (which is transformed into sulphite in a damp and alkaline environment), or originating from the decomposition of the excrement of pigeons or other animals (Pochon and Jaton, 1968; Paleni and Curri, 1974).

The degrading activity of fungi on materials, however, has been widely investigated and proved (Paleni and Curri, 1970; Gargani, 1968). Such microorganisms, piercing into the material with their hyphae, also contribute to its deterioration by mechanical activity.

Because of either the biological activity of bacteria, fungi and other organisms, or merely chemical causes, or both; many monuments and buildings of historical and artistic value are suffering from considerable degradation, accelerated by atmospheric pollution and age. However, microbiological knowledge of this subject is still poor.

Among the deteriorated buildings of artistic value there is the Palazzo della Ragione in Milan, dating back to the XII century. The work reported in this article is part of a larger project aimed at studying biodeterioration in this building, already known as a place where biodeterioration is evident. The hypothesis is advanced that the bacterial microflora of the Palazzo della Ragione are the cause of biodeterioration.

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paper has been carried out to study the different microorganisms present in spoiled plasters and frescos of this palace in different periods of the year and to examine the effectiveness of a biocide intended for the elimination of this microflora as part of a sanitation treatment.

Methods

Samples The material for test was taken at eye level from the inside walls, and from the outside wall beside the entrance to the Palazzo della Ragione in Milan. Indicating the inside walls by A, B, C, D, the sampling zones, as numbered in Fig. 1 were:

1. Material of the second part of a frescoed baluster which appeared remarkably deteriorated: colours fading, blackening, and the presence of a grey-green patina.
2. Material from blackened and corroded bricks.
3. A layer of mortar, blackened and showing more intense spots, corrosion and extreme friability here and there.
4. Plaster of doughy consistency, presumably frescoed.
5. Splinters taken from the peeling “coat-of-arms” fresco.
6. (Outside wall of the building), doughy whitish material looking like a bulge in the wall.

Sampling Each sample was taken under sterile conditions from various points of the most spoilt areas, scraping off surface material to a depth of 1 - 3 mm. The depth depended on the conditions and kind of the materials, being more superficial for frescos and bricks, deeper from mortar which was extremely friable. Sampling was performed in March and December 1979 and in May, July and November 1980.

Microbiological analysis The following organisms were evaluated at 28°C either in liquid or agar media, inoculated with dilutions of the samples. In the liquid media, the most probable number (MPN) of viable microorganisms were determined using the McGrady statistical table.

a. Heterotrophic bacteria: Plate Count Agar. For anaerobic bacteria the “Gas-Pak” system, BBL was used.

b. Fungi: Malt Extract Agar with addition of 100 µg/ml of oxytetracycline.

c. *Thiobacillus thioparus*: Hydrogen sulphide liquid medium (pH 7) (Pochon and Tardieux, 1962). Sulphates were detected as above.

d. *Nitrosomonas*: Ammonium sulphate liquid medium (Pochon and Tardieux, 1962). Nitrite and/or nitrate were detected using diphenylamine-H₂SO₄ reagent.

Sanitation treatment A sanitation treatment was attempted on the mortar zone of wall C. A solution of Desogen (Desogen Geigy, an aqueous solution of a (p-tolyl)-dodecyl-trimethylammonium-oxymethyl-sulphate and isopropyl alcohol. Ciba-Geigy s.p.a., Origgio, VA) was used. After a preliminary trial at a lower concentration, which was unsuccessful, an aqueous solution (3% v/v) was sprayed on to the surface to give a dose of 2.5 mg Desogen per cm². This test was carried out between February 5th and July 1st. 1981.

Results

Microbiological analysis

The results obtained, reported in Figures 2 to 5, can be summarized as follows:

In the samples of spring 1979, heterotrophic organisms were present in considerable number, showing a clear predominance in number over fungi. The numbers are similar to those referred to by other
The numbers and types of organisms found in samples taken from the sprayed and untreated areas are shown in Table 1. It will be seen that the treatment lowered the numbers of microorganisms to values which are considered "not deteriorative" by the Italian committee (biological section) which studies the standardization of research methods on deterioration of artistic works and of treatment methods (NORMAL - B) (CNR, ICR, 1982). This effect lasted for up to about two months but had ceased to be effective after five months.

Conclusions

The results obtained show that in Spring 1979 heterotrophic and autotrophic organisms were present in a number high enough to be considered to be responsible for deterioration, although subsequent analyses showed a general decrease in numbers with only limited seasonal differences ascribable to variations in temperature. These data suggest that biodeterioration occurs slowly. The further decrease was probably accelerated in some degree by the fact that, after the first sampling, the palace underwent a light cleaning treatment; the floor was cleared of dust and debris and washed thoroughly with water and sawdust, so that the room air was no longer dusty. In addition, cobwebs were removed from the walls and the windows were closed so that rain water, polluted air and the numerous pigeons which formerly took refuge inside the building could no longer enter. This treatment, however, could not have affected the outside site, number 6. It is noteworthy that, during 1980, a decrease was observed in the atmospheric pollution rate in Milan (Mandruzzato, 1980; Cavallaro, et al. 1980).

A preliminary sanitation treatment with Desogen caused a decrease, maintained for two months, in the number of microorganisms to a level which was considered to be no longer deteriorative.

The presence of heterotrophic microorganisms on the biodeteriorated materials could represent an example of an ecological sequence. It may be supposed that the inorganic materials would first be utilised by autotrophic thiobacilli for growth; subsequently the organic material so produced, together with air-polluting particles and pigeon excrement, would constitute the growth substrate for heterotrophic microorganisms. All the microorganisms which have been found would thus contribute in different ways, to the deterioration of the palace walls and frescos.

Sanitation Treatment

Desogen, a colourless, water-soluble, non-volatile, biocide was chosen for test because of its low toxicity to man and high effectiveness against both bacteria and fungi.

The numbers and types of organisms found in samples taken from the sprayed and untreated areas are shown in Table 1. It will be seen that the treatment lowered the numbers of microorganisms to values which are...
Microorganisms Present in Deteriorated Materials on the "Palazzo Della Ragione" in Milan  C. Sorlini, L. Allievi, M. Sacchi and A. Ferrari

Figure 2  Trend of the viable counts of aerobic Bacteria from March '79 to November '80.

Figure 3  Trend of the viable counts of Fungi from March '79 to November '80.

Figure 4  Trend of the viable counts of *Thiobacillus thioxidans* from March '79 to November '80.

Figure 5  Trend of the viable counts of *Thiobacillus thioparus* from March '79 to November '80.
<table>
<thead>
<tr>
<th>Time From the Treatment (days)</th>
<th>Aerobic bacteria</th>
<th>Anaerob. bacteria</th>
<th>Aerobic spore-for. bacteria</th>
<th>Anaerob. sp.-f. bacteria</th>
<th>Fungi</th>
<th>Aerobic bacteria</th>
<th>Anaerob. bacteria</th>
<th>Aerobic spore-f. bacteria</th>
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<th>Fungi</th>
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</table>

Table 1: Sanitation treatment on the mortar wall with desogen (2.5 mg/cm²)

(n. of cells/g dry weight)
Microorganisms Present in Deteriorated Materials on the “Palazzo Della Ragione” in Milan

C. Sorlini, L. Allievi, M. Sacchi and A. Ferrari

L’evoluzione della concentrazione di SO₂ in Milani: interventi attuali e prospettive per una ulteriore riduzione del tasso di inquinamento.
1° Convegno “Il disinnquinamento in Italia. Acqua, aria, suolo, rumore” (Riva del Garda, Italy)

Consiglio Nazionale delle Ricerche; Istituto Centrale del Restauro (1982)
Identificazione culturale della microflora eterotrofa ed autotrofa (in press)

Utilizzazione dell’anidride solforosa da parte un ceppo di batteri solfosidant in relazione all’alterazione dei materiali calcari.
3rd. International Congress on the Deterioration and Preservation of Stones (Venice)

Funder, S. (1968)

Gargani, G. (1968)
Fungus contamination of Florence art-masterpieces before and after the 1966 disaster.
Biodeterioration of Materials, 1. (eds. A.H. Walters and J.J. Elphick)

Krumbein, W.B. and Pochon, J. (1964)
Ecologie bacterienne des pierres alterees des monuments

Mandruzzato, U. (1979)
L’inquinamento atmosferico a Milano nella stagione invernale 1978-1979
Acqua Aria 6: 503-507.

Mandruzzato, U. (1980)
L’inquinamento atmosferico di Milano nel periodo invernale 1978-1980
Acqua Aria 6: 757-761.

L’inquinamento atmosferico di Milano nella stagione invernale 1980-1981
Acqua Aria 6: 693-698.

L’ambiente ecologico e le opere d’arte (I lipidi nei prodotti della degradazione)

Paleni, A. and Curri, S. (1972)
Biological aggression of works of art in Venice.
Biodeterioration of Materials, 2 (eds A.H. Walters and J.J. Elphick)

Disfacimento dei materiali e delle opere d’arte. Cause remote ed attuali, prevenzione e pulitura.
Atti Congresso “Petrolio e Ambiente (Roma-EUR)

Pochon, J. and Jaton, C. (1968)
Facteurs biologiques de l’alteration des pierres.
Biodeterioration of Materials, 1. (eds, A.H. Walters and J.J. Elphick)

Pochon, J. and Tardieux, P. (1962)
Techniques d’analyse en microbiologie du sol.
St. Mandé. Ed. de la Tourelle.

Degradation des temples d’Angkor et processus biologiques.

Thiebaud, M. and Lajudie, J. (1965)
Associations bacteriennes et altérations biologiques des monuments en pierre calcaire.
THE EFFECT OF VIBRIO ANGUILLARUM ON THE ANAEROBIC CORROSION OF MILD STEEL BY DESULFOVIBRIO VULGARIS

C.C. Gaylarde¹ and J.M. Johnston¹

Summary

The rate at which the sulphate-reducing bacterium Desulfovibrio vulgaris promoted the corrosion of mild steel was increased by the addition of Vibrio anguillarum despite the fact that the latter had no corrosive effects in pure culture. Estimations of the numbers of free viable Desulfovibrio were shown to be unreliable indicators of the aggressiveness of the environment.

Introduction

Desulfovibrio is an anaerobic, dissimilatory sulphate-reducing bacterium which is able to induce the corrosion of ferrous metals in anoxic environments. This can have considerable economic impact (Postgate, 1979). Quantitative or semi-quantitative tests for the presence of sulphate-reducing bacteria may be used to assess the aggressive nature of the surroundings towards steel structures (Mara and Williams, 1977). There are some doubts about the applicability of such tests (Postgate, 1970) and alternative methods, such as the measurement of redox potential (Starkey and Wight, 1945; Booth and Tiller, 1968b) have been recommended. Both types of measurement, however, fail to consider the possible influence of microorganisms other than sulphate-reducers on corrosion rates. This study was undertaken in order to ascertain what corrosive changes, if any, are produced in steel coupons when they are incubated with Desulfovibrio and other bacteria from the same ecological niche.

Materials and Methods

Metal Mild steel, grade EN2 (carbon content less than 0.2%) was used. Coupons of dimensions 40 x 15 x 1mm were cut from the sheet metal and used in the experiments without further preparation apart from cleaning and degreasing.

Organisms and Medium The medium used throughout was Postgate's medium B (Postgate 1979). The pH at the time of inoculation was 7.4.

Desulfovibrio vulgaris was isolated from River Thames' sediment by repeated subculture in medium B and the same medium solidified with agar. Once isolated, the organisms were maintained in tubes containing deep API sulphate agar (Difco) and in medium B. They were identified as Desulfovibrio genus by their sulphate reducing activity, morphology and absorption spectra (indicating the presence of cytochrome C3 and desulfoviridin). The species was identified by carbon source and electron donor and acceptor utilisation tests (Postgate and Campbell 1966). Vibrio anguillarum was isolated from River Medway sediment, after initial growth in medium B, by aerobic subculture on nutrient agar. Morphological, cultural and biochemical criteria were employed for identification (Shewan and Veron 1974).

Growth conditions Batch culture experiments were carried out using 2 litres of medium B in tightly stoppered bottles with side flasks containing alkaline

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The Effect of *Vibrio anguillarum* on the Anaerobic Corrosion of Mild Steel by *Desulfovibrio vulgaris*  C.C. Gaylard and J.M. Johnston

pyrogallol. Weighed metal coupons were placed into the vessels after sterilisation by immersion in alcohol and flaming. Media were inoculated as follows:

1. *D. vulgaris*. Final concentration $1.15 \times 10^3$ cells cm$^{-2}$. 2. *V. anguillarum*. Final concentration $4.4 \times 10^6$ cell cm$^{-2}$. 3. *D. vulgaris* plus *V. anguillarum* at the above concentrations. A large inoculum of *V. anguillarum* was used, since it had previously been noted that these organisms survive less well than *Desulfovibrio* under these conditions. 4. *No inoculum*. Duplicate cultures were incubated at room temperature (approximately 22°C) for 61 days.

**Determination of corrosion rates and bacterial concentrations.** At two weekly intervals duplicate metal coupons were removed from the cultures, cleaned ultrasonically in 4% sodium citrate and weighed. Corrosion was expressed as weight lost. The metal surfaces were examined, after weighing, under the scanning electron microscope (Hitachi 450). Contemporaneously with the removal of coupons, samples of medium were collected and used for enumeration of viable bacterial cells by the poured plate method, using API sulphate agar and nutrient agar. The pH of the medium was also determined.

**Results**

Within one week of inoculation, all cultures containing *D. vulgaris* assumed a black colouration, indicating growth of the bacteria. A black sulphide-containing deposit covered the metal specimens removed from these cultures. At two weeks the deposit was readily removed and the metal so revealed showed signs of corrosion to the naked eye. This macroscopic evidence of corrosion was confirmed by scanning electron microscopy (Fig. 1) and by weight loss measurements (Table 1). Both techniques indicated that metal strips incubated in mixed cultures were being corroded more rapidly than those in the presence of *D. vulgaris* only.

Viable counts showed that *D. vulgaris* was multiplying in both pure and mixed cultures, but that *V. anguillarum*, whilst growing slightly at first in pure cultures, was not surviving well in media containing *Desulfovibrio* (Fig. 2). On day 61 the vibrio count in the mixed cultures was $10^7$ that obtaining for pure vibrio. *D. vulgaris* also showed slightly depressed growth in mixed cultures.

In spite of the lower numbers of *D. vulgaris*, weight losses were higher in mixed than in pure cultures (Table 1). *V. anguillarum* alone caused negligible weight losses, significantly lower, at 61 days, than control values. ($p < 0.01$). Corrosion differences were not associated with changes in pH, which varied little between control and other cultures. The most acid conditions occurred during growth of pure cultures of either organism, the lowest pH measured being 5.9. At that time, the mean pH in the control flasks was 6.0.

**Discussion**

Cultures containing *D. vulgaris* and *V. anguillarum* together produced the highest corrosion rates in the metal coupons even though the numbers of suspended sulphate reducers were lower than in pure *D. vulgaris* cultures. A number of hypotheses may be postulated to explain this phenomenon.

Since *V. anguillarum* is not corrosive, its effect on metal dissolution must be a potentiation of that induced by *D. vulgaris*. The action of the latter organism on metal is itself poorly understood. Costello (1974) considered that all the corrosive effects of sulphate-reducing bacteria could be explained by the hydrogen sulphide produced during growth. It seems unlikely that this is so, however, since metal separated from growing cells by dialysis tubing (which allows free passage of dissolved gases) does not corrode at rates above control values (Gaylard and Johnston 1980).

**Table 1**

Weight losses of mild steel coupons incubated in medium B with *D. vulgaris* and/or *V. anguillarum*

Mean weight loss (mg/cm$^2$/day) ±S.D.

<table>
<thead>
<tr>
<th>Incubation Time (Days)</th>
<th><em>D. vulgaris</em></th>
<th><em>D. vulgaris</em> and <em>V. anguillarum</em></th>
<th><em>V. anguillarum</em></th>
<th>Control</th>
</tr>
</thead>
<tbody>
<tr>
<td>14</td>
<td>0.56 ± 0.06</td>
<td>0.61 ± 0.07</td>
<td>0.06 ± 0.02</td>
<td>0.01 ± 0.01</td>
</tr>
<tr>
<td>28</td>
<td>0.42 ± 0.00</td>
<td>0.51 ± 0.01</td>
<td>0.06 ± 0.01</td>
<td>0.06 ± 0.04</td>
</tr>
<tr>
<td>42</td>
<td>0.36 ± 0.04</td>
<td>0.33 ± 0.27</td>
<td>0.04 ± 0.00</td>
<td>0.07 ± 0.05</td>
</tr>
<tr>
<td>56</td>
<td>0.30 ± 0.06</td>
<td>0.34 ± 0.12</td>
<td>0.09 ± 0.12</td>
<td>0.05 ± 0.04</td>
</tr>
<tr>
<td>61</td>
<td>0.31 ± 0.11</td>
<td>0.36 ± 0.05</td>
<td>0.03 ± 0.00</td>
<td>0.06 ± 0.02</td>
</tr>
</tbody>
</table>
An alternative explanation implicates the *D. vulgaris* enzyme hydrogenase, which might remove the polarising layer of hydrogen from the metal surface, thus allowing metal dissolution (Booth and Tiller 1968a). This enzyme occurs in both periplasmic and membrane-bound forms (Barton et al. 1970; Bell et al. 1974). Thus an increase in the number of bacterial cells in contact with the metal would, presumably, incur a rise in hydrogen removal and a corresponding increase in corrosion rate. The effect which *V. anguillarum* exerts upon corrosion could, therefore, be a reflection of the ability of this bacterial species to facilitate the adsorption of *D. vulgaris* to the metal. In our experiments, coupons removed from mixed cultures were covered with a more closely adherent film than those from pure *Desulfovibrio* cultures and this might indicate such an increase in adsorbed sulphate-reducing cells. Increased adsorption of *Desulfovibrio* might also explain, in part, the lower concentrations of suspended and free-swimming forms in the mixed cultures. The sulphide-containing films have themselves been implicated in the corrosion mechanism. Iron subjects can be corrosive (Booth, Elford and Wakerley 1968), but it has been suggested that strongly adherent deposits protect the metal against further attack and reduce final weight losses (Booth and Tiller 1960; Iverson 1971). Our observations do not confirm the latter view, as the surface film produced in mixed cultures was considerably more strongly bound to the metal than was that formed in the presence of *D. vulgaris* alone.

A second possible interaction between *D. vulgaris* and *V. anguillarum* is the potentiation of some metabolic activity. We have as yet no evidence for any such interaction, although a qualitative assessment of blackening in the cultures in these experiments indicated more rapid sulphate reduction in flasks containing both bacterial genera. Under these experimental conditions, sulphate reduction would be coupled to hydrogenase activity (Wood 1978), so that increased corrosion rates might be mediated in this way. It seems, however, unlikely that the increased energy production would not lead to increased numbers of *D. vulgaris*.

The most probable explanation of the observed effects is the postulated increase in the adsorption of *D. vulgaris* to the metal surface. It has already been shown that bacterial adsorption is important in metal corrosion (Gaylarde and Johnston 1980; Obwkewe et al. 1981) and further experiments on this aspect of the phenomenon are planned. The implications of these results for *Desulfovibrio* testing procedures are extremely important. The data show a relationship between the logarithm of the concentration of free *D. vulgaris* and metal weight loss in pure cultures (correlation coefficient 0.95, \( p > 0.001 \)), but when all cultures containing sulphate-reducers are considered, this relationship disappears (correlation coefficient 0.27, \( p < 0.1 \)). These results demonstrate conclusively that the relative concentrations of unattached sulphate-reducing bacteria in two different samples do not necessarily indicate the relative aggressiveness of the two sampling sites. Work is now in progress to determine methods which will give a true reflection of corrosive potential.

References


Figure 1:

Scanning electron micrographs of mild steel surfaces after incubation for 14 days in Postgate's Medium B with or without bacteria. Magnification X1200.

The photographs demonstrate the most severe form of attack seen at this stage. Since this is never uniform, the true extent of metal dissolution may be inferred from Table 1.

(a) Control (no inoculum)
(b) *V. anguillarum*
(c) *D. vulgaris*
(d) *D. vulgaris* + *V. anguillarum*
Viable cell concentrations over 61 days in batch cultures of Postgate's medium B inoculated with pure or mixed cultures of \textit{D. vulgaris} and \textit{V. anguillarum}. 

Figure 2:
The Effect of *Librio Angilharum* on the Anaerobic Corrosion of Mild Steel by *Desulfovibrio Vulgaris*  
C.C. Gaylard and J.M. Johnston

Surface changes in mild steel coupons from the action of corrosion-causing bacteria.  
Applied and Environmental Microbiology, 41: 766-774.

Postgate, J.R. (1979)  
The Sulphate-reducing Bacteria.  

Classification of Desulfovibrio species, the non-sporulating sulphate reducing bacteria.  
Bacteriological Reviews, 30 (4): 731-738.


Starkey, R.L. and Wight, K.M. (1945)  
Anaerobic Corrosion of Iron in Soil.  

Wood, P.M. (1978)  
A chemiosmotic model for sulphate respiration.  
FOULING OF FILTERS FOR NORTH SEA OILFIELD INJECTION WATER

R G J Edyvean¹ and J A Pearson²

Summary

The fouling and blockage by plankton and detritus of 200 μm mesh seawater filter elements is described for samples taken between August 1981 and May 1982 at a site in the Norwegian sector of the Central North Sea oilfields. Copepod material, especially the waxes and oils produced from crushed copepods, was found to be the main cause of blockage of the filters, but dinoflagellates play a major role in consolidating the blockage by providing a skeletal framework.

Introduction

Many North Sea Oil Fields require pressure maintenance to keep oil flowing to the surface (Crouch and Mitchell, 1981). Most fields have an extensive pocket of water on which the oil floats, and it is into this area that water is injected to maintain the flow of oil to the production platforms. Sea water is generally injected at the edges of the reservoir and moves through the pores of the rock to the producing wells at the centre, pushing oil ahead of it. The injected seawater has to be free of any material likely to plug the pores in the rock and must, therefore, be filtered and treated chemically before use. Considerable problems have arisen in the initial filtration of the large amounts of seawater needed for the injection system (Finch, 1979) especially during plankton blooms, where often the system has to be shut down.

Although studies of plankton have been made around oil platforms in the North Sea, these are mostly internal reports by oil companies and little has been published on the effect of plankton and plankton blooms on seawater filtration. Plankton, especially copepods, produce large amounts of oils and waxes as food storage products which can cause considerable blockage when the copepods are crushed in a filter. The work described in this paper forms a baseline in a programme designed to develop a more efficient filter system, carried out by Swinney Engineering Limited for a major oil company. The filter tests were carried out on an oil production platform in the Norwegian sector of the North Sea (Fig. 1). Test filters were assessed through the seasonal changes in plankton abundance in order to determine the nature of the species involved and the mechanisms by which the plankton and other material are entrapped in, and block the filter mesh.

Materials and Methods

200 μm (nominal) stainless steel wire weave filter mesh was used to form a baseline against which to compare other filter materials and to elucidate the mechanism and the organisms causing blockage. Wire weave mesh was chosen as it is in widespread use in the North Sea and the 200 μm mesh was found to give optimal retention of plankton and detritus. Fig. 2a shows the form of the weave. Sea water was taken from a depth

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² Swinney Engineering Limited, Morpeth, Northumberland, U.K.

(Received July 1982)
of 20 m, filtered through a coarse (9 mm) screen, chemically treated, and then filtered through the filter elements under test in Swinney Mark II filter units (Swinney Engineering Limited, Morpeth), prior to fine filtration in sand bed filters. An essential feature of the filter system is that the filter elements are regularly backwashed. Samples were run for periods up to 24 hrs, or until they blocked, on the following dates, 24th/26th August, 1981, 27th September/2nd October, 1981, 17th/20th November, 1981, 22nd/27th January, 1982, and 11th/13th May, 1982. Filter elements were removed from the filter system, stored in formalin and brought back to Newcastle.

Figure 1  Oil Fields in the North Sea. N = Norwegian Sector, F = Forties, W = West Sole.

Figure 2  A. S.E.M. of 200 μm wire weave filter. B. Light Micrograph of surface of blocked filter. C. L.M. of scrapings from filter surface showing large numbers of dinoflagellates. D. S. E.M. of Ceratium longipes. Scale bars A = 200 μm B = 2 mm C = 100 μm D = 50 μm.
The filter mesh was initially examined under a low power microscope. Scrapings were then taken from the mesh, suspended in alcohol and examined under a light microscope to identify the organisms present. Small samples, (5mm x 5mm) were cut from the mesh of the filter and prepared for the Scanning Electron microscope by fixation in sodium cacodylate buffered 0.25% gluteraldehyde solution, dehydrated in acetone and critical point dried. The prepared specimens were gold coated and examined in a JEOL JSM-51 S.E.M. Both inflow and outflow surfaces of the mesh were examined.

**Results**

During the test period, general plankton blooms occurred between late August/early October, 1981, and during May, 1982 when copepods were in very high numbers. The other prominent organisms, dinoflagellates, were present in large numbers between August and November, 1981, but in very low numbers between January and May, 1982.

Initial examination of the filter mesh showed large numbers of copepods and copepod pieces on the inflow surface of all the samples (Fig. 2b), the predominant copepod being *Calanus helgolandicus*. Closer examination showed blockage of the mesh to a greater or lesser degree by a brown amorphous material and a large number of dinoflagellates in all but the May 1982 sample. Other plankton similar in size to copepods were found in small numbers, for example gastropod molluses, ostracods, isopods and a number of tintinnids.

After removal of loosely attached copepods, scrapings were taken to identify the organisms present. Dinoflagellates were the prominent organisms found, embedded in a brown amorphous material (Fig. 2c), except in scrapings from the May 1982 run. The prominent dinoflagellate was *Ceratium longipes* (Fig. 2d).

Species of dinoflagellates found from each test are given in Table 1.

Diatoms were only occasionally encountered in the August and September, 1981 samples, but were more...
noticeable in the samples from November, 1981, January and May, 1982 when Prawia sultana and Rhizosolenia spp. were the dominant species. Corethion criophilum was a common diatom in the November, 1981 samples and centric diatoms were common in January, 1982. In comparison to copepods and dinoflagellates, diatoms contributed little to the blockage of these filters.

Figures 3 and 4 show scanning electron micrographs of the inflow and outflow surfaces of the filter mesh for four of the sample dates. The samples taken from the filter runs at the end of August and the end of September 1981 were very similar and of these only the August samples are shown. Figure 3a shows the inflow surface of a filter from the August 1981 run. Material is wrapped around the wires of the mesh and has been dragged into the mesh gaps. There is blockage of a hole by a copepod and dinoflagellates are bridging the gaps between the wires. The outflow surface of the filter is shown in Figure 4a. There are large numbers of dinoflagellates and part of a copepod protruding through the mesh in the centre of the picture. Figure 3b shows the inflow surface of a November 1981 test filter. There is less material covering the mesh, though the filter was still blocked with lipids, strand-like material and copepod debris. Figure 4b shows the outflow surface with dinoflagellates embedded in amorphous material. The inflow surface of a filter run in January 1982 is shown in Figure 3c. Blockage is much less than in the previous runs with dinoflagellates embedded in mucilage which coats the wires, but little crushed copepod material to cause blockage. The outflow surface (Fig. 4c) is quite clear, with only occasional blockage of some pores. The filter run in May 1982 was remarkable for the lack of dinoflagellates, giving rise to a much less consolidated blockage as can be seen in both inflow and outflow surfaces (Fig. 3 and 4d) even though there was a considerable copepod bloom.

Blockage is mostly by copepods plugging the holes in the mesh, and there is far less strand-like and amorphous material trapped between the wires. However, Figure 3d does show that the strand-like material originates from copepods.

The combined effect of dinoflagellates, notably
Ceratium longipes, mucilage and strand-like copepod material, causing blockage of the filters is shown in Figure 5. The dinoflagellates are caught in large numbers in the pores and on the outflow surface of the filter (Fig. 5a). Mucilage accumulates more on the inflow surface, and here traps dinoflagellates and detritus (Fig. 5b). The dinoflagellates act as a framework, and along with copepod material, mucilage and detritus (Fig. 5c), gradually completely block the filter pores (Fig. 5d).

Discussion

The composition and abundance of plankton from any locality in temperate waters varies according to season and depth, and also from year to year (Newell & Newell, 1973; Round, 1975; Dodge & Hart-Jones, 1977). In British waters there is usually a spring and autumn bloom. The spring bloom of phytoplankton occurs about March to April and is shortly followed by an increase in zooplankton. After a fall in numbers, plankton abundance remains at a fairly high level during the summer. In the autumn, mixing of surface and deeper waters enabled a further bloom to occur and this is followed by low levels of plankton over winter.

Finch (1977) reporting on Forties field conditions shows the main concentration of zooplankton to be in May and occasionally April - August with a smaller bloom in October and November.

Phytoplankton maxima were reported in March and April followed by a decline. This seasonal variation in plankton abundance can be seen in Figs. 3 and 4 with high numbers of copepods in August, September and May lower in November and lowest in January. Dinoflagellates are in very large numbers in August, September and November, lower in January and almost completely absent in May (Table 1). Finch (1977) found Ceratium tripos, C. furca and C. fusus in large numbers in the Forties field, while off Blyth on N.E. coast of Britain Dinophysis norvegica and C. lineatum were found to be most abundant in bloom conditions (Dodge & Hart-Jones, 1977). Previous work at Newcastle has found C. longipes to be

Figure 5
A. Dinoflagellates trapped on outflow of filter. B. Dinoflagellates (Di) entrapped in mucilage (M) (inflow surface). C. Strands of copepod material (S) Dinoflagellates (Di) and mucilage (M) wrapped around the wires of a filter mesh (inflow surface). D. Blockage of filter (outflow surface) by mucilage (m) built up on strands of copepod material (S) and Dinoflagellates (Di). Bar = 100 μm.
Table 1. Dinoflagellate species found trapped on 200 μm mesh filters.

<table>
<thead>
<tr>
<th>SPECIES</th>
<th>DATE</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>24-26.8.81</td>
</tr>
<tr>
<td>Ceratium longipes</td>
<td>++++</td>
</tr>
<tr>
<td>C. fusus</td>
<td>+++</td>
</tr>
<tr>
<td>C. furca</td>
<td>++</td>
</tr>
<tr>
<td>Dinophysis acuta</td>
<td>++</td>
</tr>
<tr>
<td>Peridium spp.</td>
<td>+</td>
</tr>
</tbody>
</table>

++++ = abundant, +++ = very common, ++ = common, + = occasional, - = not detected

abundant in the West Sole field (F.G. Hardy, Pers. Comm.). These differences may be explained by the different bodies of water found in the North Sea, though differences in Dinoflagellate composition can be quite localised (Dodge & Hart-Jones, 1977).

Most plankton species either produce a sticky mucous coating for protection or eventual settlement, or store various waxes, oils and esters as food reserves. When crushed against a filter a large amount of sticky slime can soon be produced entrapping other organisms and blocking the filter.

Blockage of the filters appears to be caused by whole copepods strand-like material derived from copepods and a sticky mass of “mashed” copepods, mucilage and other detritus (silt, etc.) supported on a framework of dinoflagellates (Fig. 5a). Ceratium longipes has three strong horns enabling it to cover a large area, while C. fusus is long and thin, and both provide a skeletal framework for the deposition of the copepod remains and other material. The importance of dinoflagellates in providing a framework for blockage can be seen by comparing the two bloom periods (a and d in Figure 3 and 4). The wire weave of the filter mesh provides a good support for the mucilage/detritus accumulations entrapping dinoflagellates etc. which provide an anchorage for subsequent blockage (Fig. 5c & d). The movement of the wires of the mesh under the seawater pressure enhances the entrapment and crushing of copepods, releasing their storage products. Finch (1979) suggests that lipids and wax esters occurring in copepods may block pores in the oil-bearing rock and is pessimistic about any fine filter system removing these lipids, thus a system which does minimal damage to the copepods will have considerable advantages.

Conclusions

The characteristics of the wire weave mesh enable it to be easily blocked by planktonic material especially in bloom conditions. The inherent movement of the mesh when in service and the undulating nature of the weave are major factors in the blockage by plankton and associated material. Copepods, when damaged, provide a large amount of the blocking material; the degree of blockage, however, is much enhanced by the presence of dinoflagellates which provide a framework for entrapment of other material. The details of the shape and size of the plankton, and the mechanism by which the plankton block the filters, has enabled new filter elements to be designed. Instead of a wire weave “cloth”, filter elements have been designed using closely spaced straight wires with a flat surface, enabling a very smooth filter surface to be achieved. This system avoids the movement associated with a woven wire mesh and the inherent strength of the wires used provides a more durable filter element. One such design, using a 100 micron filter gap is performing with high efficiency in trials underway for the last twelve months (Curzon et al., 1982) and had run through the spring bloom 1982 at the design differential without stopping for manual cleaning and with a great reduction in damage to copepods, a major source of the blockage material.

Comparison of the results with other published work (Finch, 1977, Dodge and Hart-Jones, 1977), also emphasises the differences in plankton species found in different areas of the North Sea. These differences are especially noticeable in major blooms of dinoflagellates, thus different areas may have differing filtration requirements.

Acknowledgements

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References

Sterilization requirements in offshore oil production
In: Marine Fouling of Offshore Structures Conference.

Ecofisk enhanced oil recovery operations, 1979/81
Paper presented at Offshore Northern Seas Conference, Stavanger, 1982
Offshore Engineer, October 1982: 86.

Dodge, J.D. and Hart-Jones, B. (1977)
The vertical and seasonal distribution of Dinoflagellates in
the North Sea
Botanica Marina 20: 307-311

Finch, E.M. (1979)
The biological implications for the filtration of North sea
injection water.
Paper presented at the Offshore Europe Conference,
1979 Aberdeen, Scotland, September 1979
London, Society of Petroleum Engineers, Publication number OE - 79 SPE 8166.5

The Forties field sea-water injection system.
Journ. Petroleum Technology, 30: 877-884

Marine Plankton
London, Hutchinson.

Round, F. (1973)
London, Edward Arnold.
HANDBOOK OF WASTEWATER TREATMENT PROCESSES


This book, the 19th in a series on Pollution Engineering and Technology, sets out to be an overview to provide a general understanding of specific wastewater treatment processes; it is the commercial version of a manual published by the Environmental Protection Agency (EPA), USA.

The preface is essential reading, as is the list of abbreviations, if the information in the 118 two-page “capsule summaries” or fact-sheets is to be appreciated to the full. The reader is encouraged by the editors to consult the appropriate published material, listed in the 263 references (all but a handful of which originate in the USA). Well over a third of the references are from the EPA, composed of literature reviews, contract reports, manuals, etc. The reader is not expected to be able to design plant for his requirements from the data provided on the fact-sheets; rather, they provide only summaries and highlights, indicating the applicability of a given process to the user’s needs. The next step would be to consult the specific literature listed on the fact-sheet which should provide the means of carrying out the design.

Costs and energy data are also given, but with the warning that they are intended primarily for comparative analysis. The cost elements are described in an appendix, together with the means of converting construction costs to capital costs and also for indexing costs.

The whole spectrum of treatment processes - physical, chemical, biological and micro-biological - are set out in one volume of about 250 pages (printed page about 18 x 24 cm) and are grouped by process, as well as being indexed alphabetically. The last dozen or so fact-sheets are directed to “on-site” systems for single, or a small number of dwellings.

Information under a uniform set of headings, given in the same order for each fact sheet, together with ample cross-references, are further advantages of this handbook. Besides a description and modifications of the process, the reader is given indications of such matters as its application, limitations, equipment required, performance, design criteria and environmental impact. The second page of each fact-sheet is devoted to a flow diagram, notes on energy, and costs, usually in graphic form.

Condensing such a vast amount of material into such a small volume necessarily means sacrificing detail, sometimes to the point of frustration or even obscurity. Also, important topics are given only as much space as for less important ones, but in some cases, e.g. the activated sludge process, this shortcoming is overcome by devoting more (six in this case) fact-sheets to various aspects of the process.

The idea works surprisingly well, however. The reviewer dipped into a dozen topics well known to him and an equal number of which he was ignorant and found the fact-sheets, on the whole, to be very informative and useful. Of course, some difficulties were encountered due either to language or lack of definition. For example, the rate of returned sludge, said to determine the concentration of mixed liquor suspended solids, was not defined; it is probably a percentage but it could be volume/h. Neither was the important associated parameter, sludge retention time (SRT) or mean cell residence time, defined. SRT is the key to the operation of the activated sludge process and is often calculated from an incorrect formula; but these points are no doubt made clear in the three references cited.

Apart from trifling errors and puzzles - such as the definition of pH as hydrogen ion concentration, TDH (total discharge height?) not defined, NH3 written where NO3 was meant, guessing (successfully) what “wire to water efficiency” was - there are a few more serious points to take up.

It is suggested that pure oxygen can be used for nitrification, without the warning that alkali will probably be needed to counteract the acidity produced. Next, a list of chemicals said to inhibit “nitrification reactions” is given; the chemicals listed are not specific inhibitors of nitrification but will also inhibit heterotrophs to the same degree. However, since the nitrifiers grow at much lower specific rates than the heterotrophs, a given degree of inhibition will reduce the growth rate of nitrifiers to a point at which they will be washed out of the system while still retaining the heterotrophs. A last point concerning nitrification is that the sludge retention times given for achieving oxidation of ammonia are higher than found necessary in UK practice.

This leads on to a problem facing designers outside the USA in using this book. One important difference is the BOD of sewage in various countries; for example, it is about twice as high in the UK as in USA. This, in turn, leads to changes in some of the “design criteria”, e.g. to obtain a given effluent BOD, the sludge retention time needed will be much the same in the two countries, but the concentration of mixed
However, this Handbook is to be recommended because it contains a wealth of detail of virtually the whole range of method for collecting treatment and disposal of waste waters and their derived sludges set out in a clear and logical way.

H.A. Painter

DECOMPOSER BASIDIOMYCETES, THEIR BIOLOGY AND ECOLOGY

Edited by J.C.Frankland, J.N.Hedger and M.J.Swift
British Mycological Society Symposium No.4. (ISBN 0 521 24634 2) xv + 355. Cambridge University Press. £37.50

This is the edited proceedings of a Symposium of the British Mycological Society held at Queen Mary College, London, in March 1979. As the dust jacket says "This is the first symposium to focus on them" (i.e. the decomposer Basidiomycetes) and the editors and organisers of the symposium are to be congratulated on the wide range of contributions from taxonomy, spore dispersal, polysaccharide and lignin breakdown, to the role of basidiomycetes in composts and forest ecosystems.

In between are contributions on the decay of standing trees, fence posts, commercial timbers and activity in water and forest litter. However I was left with the feeling that this was primarily a good academic symposium, hence the virtual absence of mention of the many interesting problems of the interaction of Basidiomycetes with treated timbers, a matter of considerable commercial significance. Also, I am left wondering what Basidiomycetes decompose in cultivated soils. Does 'decomposer' only refer to wood and the like?

H.O.W. Eggnis

MICROBIAL AND VIRAL PESTICIDES


This book does not concern biodeterioration because it deals with biological control of living pests, not biological effects on materials. It describes one important alternative to the use of poisons - chemical pesticides - to control animal and plant pests of field and forest, and vectors of human disease. In comparison, this alternative is remarkably safe for man, with virtually no adverse environmental impact.

However, the book treats the subject with responsibility, as indeed do its protagonists, ensuring as far as humanly possible that the apparent safety is real. Research and use of microbial and viral pest control has grown exponentially over three decades.

The volume is divided into seven unequal parts. The first part comprises a conceptual review chapter by the editor, briefly discussing the agents and technologies described in detail in the book and some that are not. The next four parts cover, in order, the four main types of agent involved.

Part II, substantially the longest, covers bacterial pesticides in six chapters. Chapters 2, 3 and 5 discuss considerations and application of bacteria and their toxins as insecticides in agriculture and forestry with considerable overlap. Chapter 6 covers the potential of bacteria against vectors. Interpolated as chapter 4 is an excellent account, long overdue, of the distribution of Bacillus thuringiensis in nature. Chapter 7 introduces a new realm of activity, the use of bacteria and other pathogens in China.

Part III, the second longest, elaborates viral pesticides in eight chapters. Two describe the use of viruses in agriculture and forests. Two delve into basic principles involving the ecology of the use of pathogens, and the epizootiology and persistence of a sawfly virus in forests. Mass production in vivo, the only method as yet commercially feasible, and the possibilities of production in cell cultures occupy two chapters. Another is a specialist and very interesting account of the proposals of manipulation of pasture to allow virus to subdue moth pests of grassland. The last discusses the identification of baculoviruses.

Part IV covers the fungi rather briefly in two chapters. One does poor justice to the potential of fungal insecticides, but the second is an excellent account of mycotoxins and fungal metabolites as potential insecticides, drawn from all fungi not just insect pathogens.

Part V, entitled "Biocontrol by Protozoa Pathogens" has one chapter on this subject, which is in proportion to the limited potential of protozoa. The other is a specialized account of control of filariasis vectors that deals more with fungi and other agents than with protozoa.

Part VI is a short chapter on microbial herbicides, principally pathogenic fungi, a method still in its infancy. In due course it should be a useful complement to other forms of microbial control, but as with microbial insecticides depends on finding amenable host-pathogen relationships.

Part VII, a single chapter on the registration requirements for microbial pesticides, is the best chapter in the book. It is written by a former head of...
the appropriate department in the Environmental Protection Agency, USA. He recognises the differences in safety test requirements between microbials and chemicals. His rationalization has produced a relatively inexpensive package in place of a system that was becoming out of hand and threatening to cost out commercial interest in microbials.

The book is based, in part at least, on an international symposium held in New Zealand. As such, it lacks coherent planning as a whole, resulting in patchy coverage. It is not, as Karl Maramorosch claims in the Foreword, “the first attempt to publish in a single volume in an analytical fashion some of the principal developments ....”. It had a long gestation period and contains few references beyond 1978, even in the Editor’s introduction chapter, although most chapters have many references. At 285 Swiss Francs (ca. £96) for only 720 pages, it is overpriced. However, some chapters are very good and five cover unique topics rarely reviewed. About two thirds of the contributors are acknowledged leaders in their respective fields. Not a text book, but essentially a reference book for researchers and those seeking advanced knowledge, it is a useful addition to libraries that can afford it, aiding microbiologists, virologists, entomologists and pest controllers alike.

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