

Mercury pollution from irrigation with treated sewage water (TSW)

A. E. Pillay, B. Yaghi, J. R. Williams and S. Al-Kindy

ABSTRACT

The lack of potable water in arid countries leads to the use of treated sewage water (TSW) for crop growth. Mercury accumulation (up to 500 ng/g) in agricultural soil originating from daily irrigation with TSW was found at two sites fed separately from a hospital sewage plant and an industrial plant. A control site irrigated with potable water ([Hg] < 0.01 ng/ml) had much reduced levels in soil (< 12 ng/g). Cold-vapour analysis of TSW revealed that Hg concentrations fluctuated widely, and were between 10-100 times higher than those of potable water. The TSW data originated from a total of 46 samples (1L each), from both plants, collected over a 6-month period. The Hg levels varied from 0.1 to 1.0 ng/ml, which suggested that the possible source of the accumulation could be found in continuous irrigation with comparatively higher Hg levels. Remedial measures could be approached from the perspective of curbing this inconsistency to produce more consistent Hg concentrations below 0.5 ng/ml. It was found that the electrical conductivity of TSW is a useful indicator to rapidly monitor fluctuations in treatment. A novel development in the study was the potential capacity of the plastic TSW discharge-pipes to behave as crude 'chromatographic' columns for possible Hg adsorption. If this property of the pipes is developed further it could have a considerable mitigating effect on the Hg levels. Possible recommendations for remediation to limit the Hg levels and promote sustainable development are discussed.

Key words | mercury, hospital effluent, industrial waste, sustainable development, treated sewage water

INTRODUCTION

Treated sewage water (TSW) is used largely for irrigation in many desert regions. The Sultanate of Oman is located in the southeastern corner of the Arabian Peninsula (Lat. 16° 38'–26° 52'N; Long. 51° 52'–59° 50'E). It is a developing country in an arid region, and therefore, water is vital for all forms of its development (Victor 2003, Victor & Al-Ujaily 1999). The demand for good quality water is rapidly increasing, and most areas rely heavily on TSW for irrigation. Total mercury in TSW in excess of 0.5 ng/ml could significantly increase alkylation of the element in soil and water bodies (Bodaly *et al.* 1998) and subsequently threaten all forms of sustainable development. Sewage

effluent itself could contain mercury levels in excess of 10 µg/ml (Zaki & Esmale 1997). This is a few orders of magnitude more than the mercury content of natural waters. Therefore, the treated water emanating from the effluent could contain a significantly high concentration of mercury, which could pose an ecological hazard, leading to contamination of plants, aquatic resources and bioaccumulation in the food chain (De 1990; Favretto *et al.* 1997). Although elemental mercury is relatively innocuous and non-toxic, it can be converted to organomercurials, which are particularly toxic and are retained in the cells of plants and living organisms. Bodaly *et al.* (1998) have reported that

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treated sewage water discharged into rivers and similar water bodies could result in an appreciable increase in the build up of alkyl mercury. Further reports by Tanaka (1977) and Goldstone *et al.* (1990) have dwelt on the natural alkylation of total mercury in waste water and water bodies. Therefore, depletion of total mercury in TSW is of considerable ecological significance, and will undoubtedly contribute towards a more sustainable environment.

An independent soil study conducted by the Petroleum and Chemical Engineering Department at the Sultan Qaboos University (Private Communication (Yaghi) 2004) revealed that there was mercury accumulation in agricultural soil irrigated on a daily basis with TSW. The objective of this investigation, therefore, was to determine why continuous irrigation with TSW led to the build-up of total Hg in soil. For this purpose we investigated two sites, irrigated independently from a university/hospital sewage plant and an industrial plant (processing sewage and industrial waste). TSW levels were closely monitored to establish if the possible source of accumulation arose from irrigation with comparatively higher Hg levels. Data were compared with those from a control site irrigated with potable water. Suggestions for the development of possible remedial measures are discussed.

MATERIALS AND METHODS

Sample collection and treatment

Treated sewage water samples were collected from two treatment plants, one near the hospital on the campus of Sultan Qaboos University (SQU), and the other based off-campus in an industrial area about 5 km away. The 'hospital' plant processed only sewage effluent; whilst the industrial plant processed both sewage effluent, from the residential area near by, and industrial waste, which included waste from several paint factories in the vicinity. Roughly 6000 m³ of waste were daily pumped into both treatment plants, and subjected to standard treatment (Manahan, 2000). The effluent and other waste were subsequently segregated into water and sludge phases. Several tons of the sludge proceeded to the drying beds; whilst the water was clarified and disinfected by addition of

chlorinated compounds. A schematic of the industrial plant appears in Figure 1, which is similar to the plant at the hospital (Salih & Pillay 2004). The hospital itself is based in the University complex, which includes student and staff residences, three restaurants and a section that houses maintenance and technical staff. With regard to sample collection, a total of 46 TSW samples (1L each) were collected from 'drip' discharge-tubes (discharge-pipes or 'drip-tubes') near the hospital plant, and from an open reservoir at the industrial plant. Sampling was conducted over a period of 6 months at appropriate intervals. Prior to analysis each sample was measured for conductivity and pH, and subsequently preserved with 2 ml HNO₃ and stored at 4°C.

The mercury analyzer

TSW samples of 100 µl were analyzed by the cold vapour atomic absorption technique using a Nippon SP-3D analyzer (Osaka, Japan). The detection wavelength was 253.7 nm, and the instrument had a detection limit of 0.1 ng/ml. Calibration curves were constructed by diluting a 10 mg/l mercury stock solution, prepared in 0.02% nitric acid solution containing 0.001% L-cysteine (Sigma Aldrich, Frankfurt, Germany). Linearity consistent with R² values in the vicinity of 0.9986 was attained. The principle of the technique is well known and involves decomposition of the sample by heating to 850°C in the presence of additives of alumina, sodium carbonate and calcium hydroxide to neutralize acidic gases produced during the vaporization process. Minimal background levels were maintained, and blank samples were measured under the same conditions as the TSW samples.

Accuracy and repeatability

To establish that our methodology worked successfully, a study of the analytical repeatability was conducted by subjecting some of the collected samples to replicate measurements. These data appear in Table 1a. The relative standard deviation for three replicate measurements on samples from both plants was less than 7% in each case. The accuracy was subsequently investigated by analyzing a

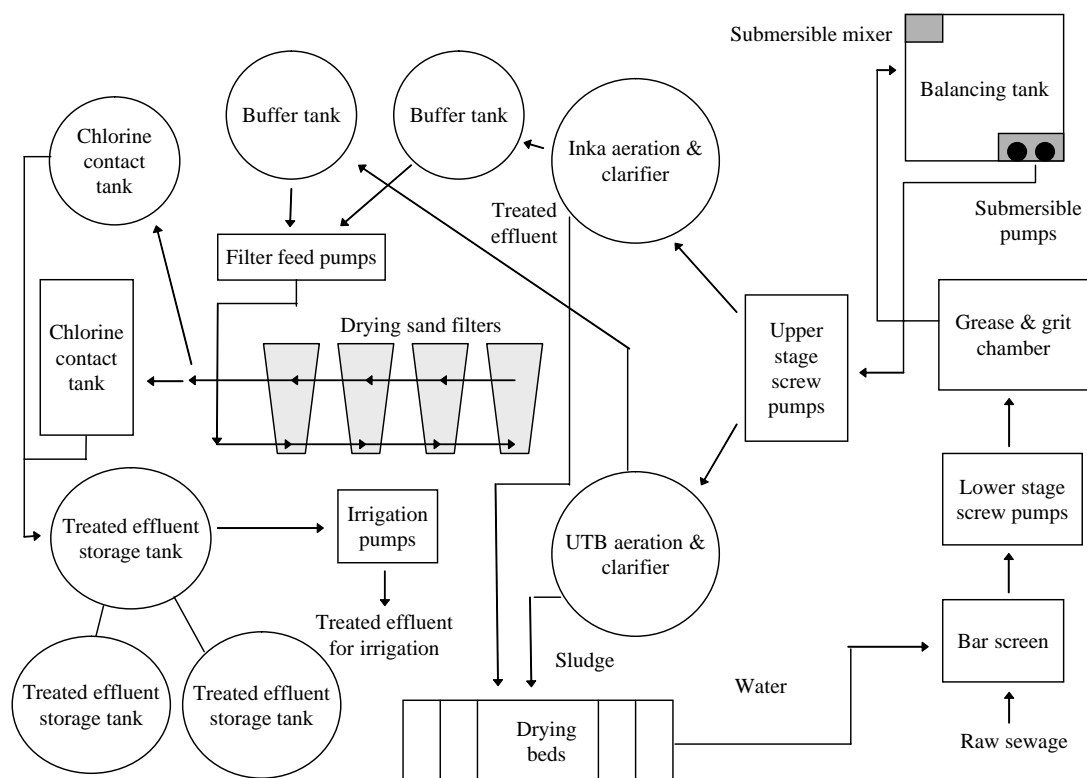


Figure 1 | A schematic diagram of the industrial treatment plant processing domestic sewage and paint waste.

Table 1a | Mercury levels (ng/ml) from replicate analyses of TSW samples

Sample	Hg concentration hospital plant	Industrial plant
1	0.33	0.52
2	0.30	0.56
3	0.33	0.59
Mean	0.32	0.56
Standard deviation	0.017	0.035
RSD (%)	5.3	6.3

Table 1b | Mercury levels (ng/ml) from investigation of a water standard

SRM 1641d certified reference standard	Experimental value	Relative error (%)
1.590	1.587	<0.2

certified water standard (SRM 1641d), which produced a relative error of <0.2% (Table 1b). These results indicated that the operational performance of the system was satisfactory, and that the analytical technique functioned effectively.

RESULTS AND DISCUSSION

Mercury pollution in soil

As previously stated, an independent study (Private Communication (Yaghi) 2004) showed that there was mercury build-up in agricultural soil. Accumulation of mercury in soil creates two immediate environmental problems: (i) it assimilates in plants; and (ii) it reaches the water table and overhead streams through gradual infiltration and agricultural run-off (De 1990), respectively. The soil at a control site irrigated with potable water ($[Hg] < 0.1$ ng/ml) produced Hg concentrations in the region of 12 ng/g. The hospital site, irrigated with TSW, produced levels in soil close to

500 ng/g. The industrial site, also fed with TSW, showed increasing Hg levels in soil: about 30 ng/g for areas irrigated for 1 year; and about 100 ng/g for areas irrigated for more than 5 years. The acceptable mean value (De 1990) for Hg in soil is approximately 50 ng/g, which indicates that the accumulation at the sites of interest is significant. All sites contained groves of date palms. Each palm tree consumes roughly 250 L of water per day; hence appreciable amounts of Hg are expected to be deposited in the soil if levels in TSW are elevated in comparison with potable water. Continuous irrigation at such levels could lead to a tremendous build-up of Hg in the soil, and optimum depletion of Hg in TSW was therefore, necessary.

Mercury levels in TSW

The mechanism involving natural alkylation of total mercury in sediments *via* waterborne mercury is not well understood (Manahan 2000). Such processes could have a particularly chronic impact in desert areas where there is a shortage of high quality water, and for this reason minimizing the conversion of total mercury in TSW to such alkylated products in arid regions deserves priority. The toxicity and reactivity of mercury depends on its oxidation state (Perez-Bendito & Rubio 1999). The different species of mercury can be empirically classified into Hg^0 , inorganic mercuric compounds (Hg^{2+}X , where $\text{X} = \text{Cl}, \text{OH}, \text{SO}_4$, etc.) and organic compounds (RHg^+ and R_2Hg where $\text{R} = \text{methyl, ethyl, phenyl, etc.}$). Methyl mercury compounds are roughly between 10–100 times more toxic to biota than inorganic mercury species. Organomercurials are soluble in fats, lipids and brain tissue. The covalent Hg-C bond is not easily broken and the alkyl mercury is retained in human and animal cells for considerably long periods. The ominous ability of RHg^+ to infiltrate the placental barrier of all organisms and enter foetal tissues is one of the greatest dangers (Perez-Bendito & Rubio 1999).

The experimentally determined mercury levels from the two plants appear in Figure 2. The data in Figure 2 are arranged in ascending order for purposes of comparison and clarity. It is evident from this figure that fluctuations and certain trends exist in the data between the two plants. A brief inspection of the results shows that roughly 44% of the hospital samples, and 50% of the industrial samples,

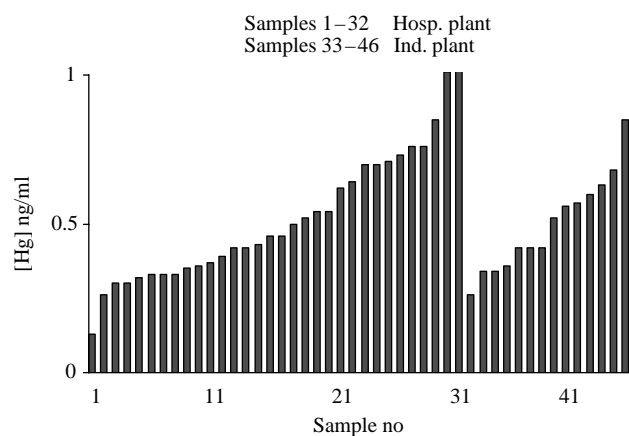


Figure 2 | A comparison of mercury levels from the two plants. Samples are arranged in ascending order for purposes of comparison and clarity. The gridline at 0.5 ng/ml denotes the 'ideal' mercury level in TSW.

have levels in excess of 0.5 ng/ml. This particular trend was expected and could arise from the effect of the combined domestic sewage and paint waste that entered the industrial plant. A brief literature survey denoted that hospital sewage yields lower mercury concentrations than industrial waste. The use of mercuric drugs in clinical treatment is an ongoing practice, and ultimately the mercury ends up as waste or sewage. Rutherford *et al.* (2003) surveyed 17 hospitals in Nova Scotia, Canada, and found that levels of mercury up to 0.3 ng/ml can exist in hospital wastewaters. Another study by Sarangapani (2000) revealed that it is possible to get mercury levels much higher than this, in the 1–5 $\mu\text{g}/\text{ml}$ range. In our case there was no exact knowledge of the extent of mercury usage at the SQU Hospital, but it was assumed that such usage was on a par with general clinical practice. On the other hand, much of the industrial waste was paint-waste, and the concentration of mercury in paints (Hefflin *et al.* 1993) can reach as high as 1500 mg/L. To prevent human exposure to mercury in paint, effective removal can reduce this value to between 1–10 ng/ml. The contemporary literature contains several reports on the elevated levels of mercury in paints. For example, Hefflin *et al.* (1993) discuss the relatively high concentration of mercury in paints, and outline the toxic nature of such paints in tests conducted on human subjects. A further report by Beusterien *et al.* (1991) alludes to mercury vapour exuding from such paint, and states that the air subject to this exposure could contain levels up to 1.5 $\mu\text{g}/\text{m}^3$. In general, appreciable concentrations of mercury from paint

end up in the waste water, and treatment plants removing such mercury therefore, have a considerable task in improving the water quality.

Development of remedial measures

We focused on three factors that could possibly reduce Hg in TSW: (a) use of electrical conductivities for monitoring and rectifying fluctuations in the treatment process; (b) development of 'chromatographic' discharge-pipes for mercury adsorption; and (c) rotation with potable water. Each of these is discussed in detail below.

(a) The use of electrical conductivities to monitor fluctuations in treatment

Several factors govern the processes implemented at treatment plants. Inconsistencies in these processes could create fluctuations in the data. Returning to [Figure 2](#), it is interesting to note that levels can show a pronounced increase up to and above 1.0 ng/ml. The reason for this could be attributed to some deficiency in the treatment process. It is common knowledge that public sewage treatment plants involve a primary treatment of waste water, followed by a secondary treatment ([Manahan 2000](#)). The flow diagram in [Figure 1](#) denotes that the treatment passes through several complex stages, prior to releasing the effluent for irrigation. Each of these stages presents its own problems with regard to water quality, but generally about 90% of the mercury is depleted if each stage is maintained and is working well. Common technical problems ([Manahan 2000](#)) arise with the grease and grit chambers or the filter feed pumps ([Figure 1](#)), and the fluctuation in levels could be due to glitches in these areas of the plants. Grit removal is important to prevent its accumulation in other parts of the treatment system. This reduces clogging of pipes which tends to fragment flocculent particles and produce minute colloids that could escape through the system, thus increasing the level of dissolved ions, which is measured by the electrical conductivity. These colloidal particles contain mercury (and other metals), and may pass through the filter feed pumps, leading to higher levels of total mercury in TSW. It was possible to indirectly and rapidly determine if inconsistencies in

treatment existed, by carefully monitoring fluctuations in the conductivities of the discharged TSW. For TSW with Hg levels <0.5 ng/ml the average conductivity was in the region of 500 $\mu\text{S}/\text{cm}$. But when the levels rose to about 1 ng/ml, conductivities exceeded 1000 $\mu\text{S}/\text{cm}$. Although there was no definite relationship between the mercury content and conductivity, this is a useful indicator to monitor possible irregularities in the process, and is a suggested procedure for a quick and reliable check on the efficiency of a plant. Plant operators could monitor electrical conductivities on a daily (or even hourly) basis to determine if some form of minor maintenance may be needed to maintain consistent levels.

(b) Development of 'chromatographic' discharge-pipes for Hg adsorption

As previously stated, drip-tubes were used at the hospital plant and an open reservoir at the industrial site. We found that the drip-tubes could be responsible for a reduction in Hg levels by about 30%. This observation prompted speculation that the drip-tube itself could possibly adsorb the mercury. Other authors ([Reeve 1999](#)) have found that mercuric ions can react with polythene, and possibly adhere to it. The drip-tube could play the same role. It generally runs for several metres, and can be described as a type of hard durable plastic pipe, which could become soft and malleable (and 'sticky') during high ambient temperatures and serve as a crude 'chromatographic' column with an affinity for heavy metals. To verify our observations, a series of independent tests was conducted on a similar crude, hard plastic pipe at an alternative site in the hospital complex, and it was discovered that in general, mercury levels were affected by about 30–40%, by the passage of TSW through the pipe. Therefore, a possible remedial measure, for reducing the mercury levels in TSW, is to produce drip-tubes with more stringent 'chromatographic' ability. A suggested development in this direction is presented in [Figure 3](#), which proposes the use of a replaceable 'fish-net' polythene sleeve within the drip-tube for enhanced adsorption of Hg ions. If such pipes could be developed with greater 'chromatographic' potential for separation of mercury (and other heavy metals) from TSW it will be highly beneficial, and mitigate the impact on the environment.

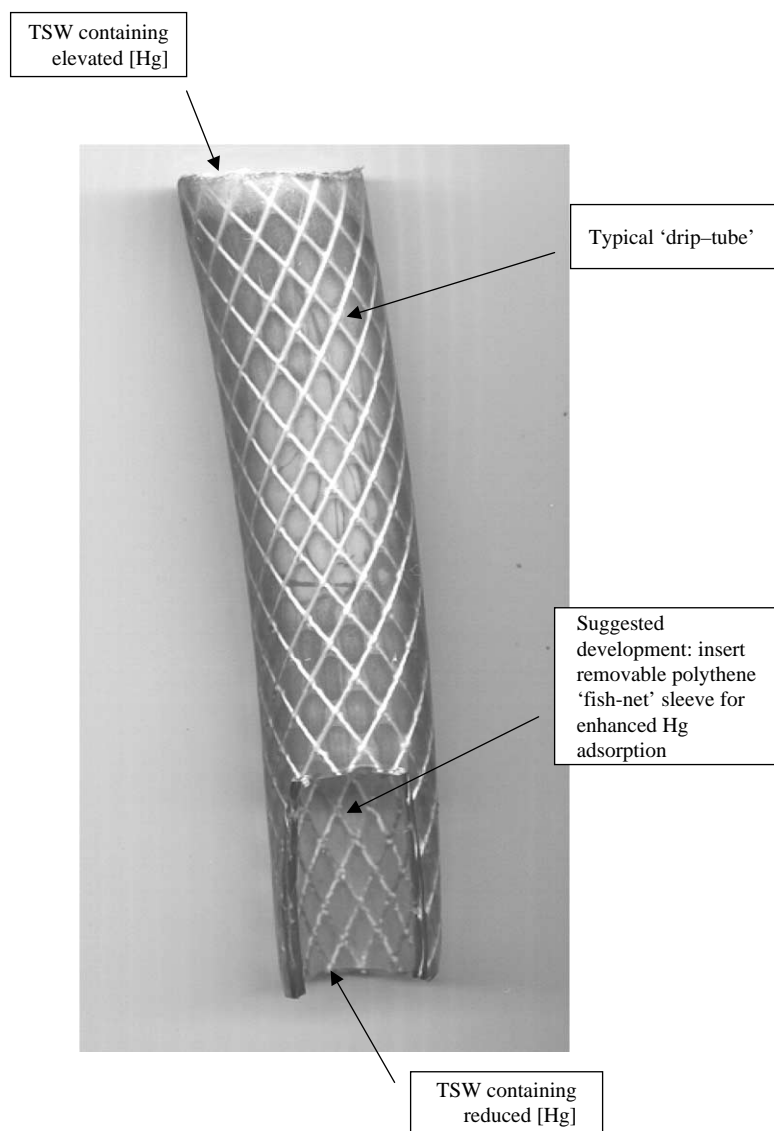


Figure 3 | A suggested remedial measure by using a replaceable 'fish-net' polythene sleeve inside 'drip-tubes' for enhanced adsorption of mercury.

Implementation of this proposed development is a subject for future study.

(c) Rotation with potable water

Mercury enters the environment from various sources (De 1990; Manahan 2000) These include discarded laboratory chemicals, batteries, broken thermometers, lawn fungicides, amalgam tooth fillings and pharmaceutical products. In our environment of interest these sources of mercury cause minimal pollution and can be safely ruled out. The use of

TSW is, therefore, the most likely source of Hg pollution, and rotation with potable water must be considered to create a safer environment. We found that the Hg levels in potable water were generally <0.1 ng/ml, but minor fluctuations produced slightly higher concentrations (Private Communication (Yaghi) 2004), which is highly acceptable. Therefore, rotating with potable water could be a good alternative to reduce the accumulation of Hg in soil. In arid countries potable water is a precious commodity and has to be used sparingly. However, the threat of polluting the soil with Hg from TSW, and indirectly contaminating

viable water supplies, makes the idea of rotation an attractive one. Our suggestion, therefore, is to use potable water in place of TSW at least twice weekly.

Sustainable development / potential environmental impact

Environmental sustainability essentially seeks to improve human welfare by protecting resources used for human needs (Shearman 1990; Robinson 1993). Our study, therefore, could make a useful contribution to ongoing sustainable development in the region because mercury from TSW (at levels >0.5 ng/ml) could ultimately contaminate water supplies. As stated above, TSW is used largely to supplement irrigation water, and this water, like rainwater (Al Taie *et al.* 1999), percolates the water table (Reichenbaugh 1977), and could pollute overhead streams and underground aquatic resources. Hence, the general impact on the environment is a cause for concern, and research programmes (Victor & Al-Ujaily 1999) have recently been launched to study this effect. Essentially, the overall potential impact on the environment is twofold. Firstly, the effect on public health, livestock and crops must be seriously considered; and secondly the effect on wildlife such as rare birds and animals is of interest (Victor & Al-Ujaily 1999).

A recent case study on date palm leaves (taken from the vicinity of the TSW irrigation area) showed that in some cases they contained elevated levels of mercury (Private Communication (Williams) 2005). These leaves are crushed and used as an additive in livestock feed. The translocation of mercury to humans *via* the food chain is, therefore, a real problem, and the role played by mercury-contaminated TSW is of genuine concern. Therefore, pollution from irrigation with mercury-contaminated TSW is emerging as a serious problem. This can be curbed by searching for solutions to deplete mercury to levels below 0.5 ng/ml in TSW.

CONCLUSIONS

Two interesting features emerged from this study: (i) the use of electrical conductivities to monitor the fluctuations in treatment; and (ii) the effect of the discharge-tubes on the

mercury levels. The former was attributed to possible irregularities in the plant processes; and the latter to the behaviour of the discharge-tubes as potential 'chromatographic' columns. Levels of mercury below 0.5 ng/ml can be attained if our suggested remedial procedures could be developed and implemented. If such levels can be consistently achieved the general environmental impact will be mitigated, and sustainable development in the region will be promoted.

REFERENCES

- Al Taie, H., Pickersgill, J. & Al Taie, N. 1999 *Oman: A Comprehensive Guide to the Sultanate of Oman*. Al Roya Publishers, Muscat, Oman.
- Beusterien, K. M., Etzel, R. A., Agocs, M. M., Egeland, G. M., Socie, E. M., Rouse, M. A. & Mortensen, B. K. 1991 Indoor air mercury concentrations following application of interior latex paint. *Archives of Environmental Contamination and Toxicology* **21**, 62–64.
- Bodaly, R. A., Rudd, J. W. & Flett, R. J. 1998 Effect of urban sewage treatment on total and methyl mercury concentrations in effluents. *Biogeochemistry* **40**, 279–291.
- De, A. K. 1990 *Environmental Chemistry*. Wiley Eastern Ltd., Delhi, India.
- Favretto, L., Campisi, B., Reisenhofer, E. & Adami, G. 1997 Sewage pollution. *Anal. Chim. Acta* **344**, 251–256.
- Goldstone, M. E., Atkinson, C., Kirk, P. W. & Kester, J. N. 1990 The behaviour of heavy metals during waste water treatment. *Science of the Total Environment* **95**, 271–294.
- Hefflin, J. B., Etzel, R. A., Agocs, M. M., Stratton, J. W., Ikawa, G. K., Barsan, M. E., Schutte, G. R., Paschal, D. C. & Kozman, A. R. 1993 Mercury exposure from exterior latex paint. *Applied Occupational and Environmental Hygiene* **8**, 866–870.
- Manahan, S. 2000 *Environmental Chemistry*. Lewis Publishers, Florida, USA.
- Perez-Bendito, D. & Rubio, S. 1999 *Environmental Analytical Chemistry*. Elsevier Publishers, Amsterdam, Netherlands.
- Private Communication (Yaghi) 2004 Department of Petroleum and Chemical Engineering, Sultan Qaboos University.
- Private Communication (Williams) 2005 Department of Chemistry, Sultan Qaboos University, Oman.
- Reeve, R. N. 1999 *Environmental Analysis*. John Wiley & Sons, Chichester, UK.
- Reichenbaugh, R. C. 1977 *Effects on Ground-Water Quality from Irrigating Pasture with Sewage Effluent near Lakeland, Florida*. Water Resour. Div., Geol. Surv., Tallahassee, FL, USA, Report No. PB-268290.
- Robinson, J. G. 1993 The limits to caring: sustainable living and the loss to biodiversity. *Conservation Biology* **7**, 20–28.
- Rutherford, L. A., Rankin, L. & Bernier, M. R. 2003 *Mercury Use, Release and Reduction Initiatives at Nova Scotia Hospitals*,

- Surveillance Report EPS (Environment Canada), EPS-5-AR-03-01.
- Salih, F. & Pillay, A. E. 2004 Be in sewage sludge: a baseline study. *Instrumentation, Science and Technology* **32**, 433–444.
- Sarangapani, S. 2000 *Process of Removing Mercury from Industrial and Clinical Waste Water*, US Patent, Application. No. US 99-431650 19991101.
- Shearman, R. 1990 The meaning and ethics of sustainability. *Environmental Management* **14**, 1–8.
- Tanaka, K. 1977 Photochemical alkylation of inorganic mercury in sewage treatment plant waste waters. *Kanagawa-ken Kogai Senta Nenpo* **10**, 198–201.
- Victor, R. 2003 Biodiversity conservation and sustainability development: a case study of Oman's national biodiversity strategy and action plan. In *Conserving Biodiversity in Arid Regions* (ed. J. Lemons, R. Victor & D. Schaffer), pp. 461–80. Kluwer Publishers, Dordrecht, Netherlands.
- Victor, R. & Al-Ujaily, S. R. 1999 *Water Quality and Management Strategies of Mountain Reservoirs in Arid Northern Oman*. Technomic Publishing Co., Lancaster, U.K.
- Zaki, M. T. M. & Esmail, M. A. 1997 Determination of total mercury in soils, waste water and sewage effluents. *Analytical Letters* **30**, 1579–1590.

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