

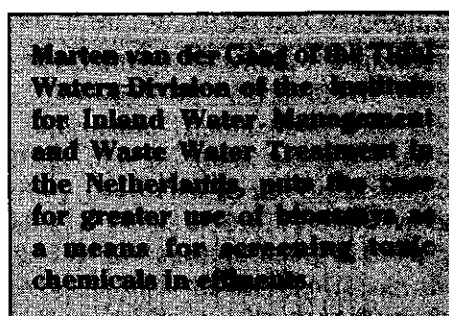
Testing time for toxic effluents

Ecotoxicological tests are proving to be a valuable means of evaluating the toxicity of effluents before starting lengthy chemical analyses. Conventional chemical screening only allows for a limited characterization of the toxic substances present in a discharge because of the resource constraints on most laboratories. This can result in some toxic compounds going undetected, causing more damage to the ecosystem than the rest of the discharged effluent.

Even when toxic compounds are identified, further assessment of the impact they might have on a receiving water is hampered by a lack of toxicity data. This often results in discharge limits being based on only part of the effluent, with no allowance made for the effects of unidentified toxics. Simple toxicity assays provide a useful tool in the initial assessment of a wastewater, and can indicate the likely source of toxicity without lengthy chemical analysis of each waste stream.

The Netherlands has used assays in toxicity reduction evaluations for almost ten years. They have also been used to control discharge permits, particularly in pesticide manufacturing. Although the high costs involved in standard assays have prevented their widespread use, limiting costs can be achieved in two ways:

- Preselecting discharges on the basis of the type of industry, variations in effluent quality, compounds expected to be found in the effluent, and their ecotoxicological profile. Pre-selection will also indicate the type of assay that should be used, and a decision strategy is now being developed.
- Adapting the protocols of ecotoxicological tests to their application in wastewater, making them simpler and more efficient.



Marten van der Grint, of the Dutch Waters Division of the Institute for Inland Water Management and Waste Water Treatment in the Netherlands, gave the case for greater use of laboratory as a means for assessing toxic chemicals in effluents.

A major reduction in the toxic burden of wastewaters can be achieved without the need for complicated schemes and regulations. A preliminary screening involving short term tests using *Daphnia* or fish can identify the most toxic effluents without having to determine their constituents. Repeating the exercise through each contributory waste stream identifies the source, and serves as an indicator of the efficacy of the wastewater treatment process involved. A more detailed chemical analysis can then be undertaken appropriate to the probable compound involved, and the treatment process improved.

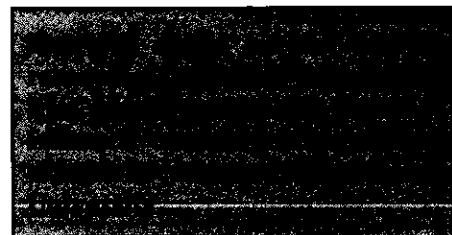
A recent example of the usefulness of this technique was demonstrated by a treatment unit for leftover pesticide chemicals. Even though concentrations were reduced to levels below detection limits, the effluent still caused deaths in fish and *Daphnia* in short term tests and inhibition of algal growth, indicating that some toxics were not being removed by the treatment process. Because a wide variety of pesticides are involved, further investigations are now underway to optimize the process.

Short term tests, unfortunately are not the answer to all effluent quality problems. Some toxics may not show their effects without longer exposure, and others with more specific modes of action may be missed completely. *Daphnia* too are not the only alternative, though fish can only be

used in registered laboratories and should only be used for preliminary testing. Luminescent bacteria offer a possibility, but as their end point, reduction of light emission, is not relevant to other species studies must first be carried out to provide a correlation with other toxicity tests. DNA-damaging compounds cannot be detected in tests for acute toxicity, so specific assays will have to be developed for them.

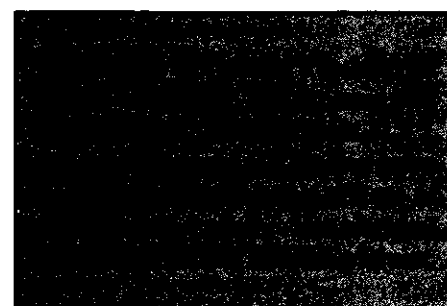
Whilst assays prove useful in determining the toxicity of an effluent, it is not practical to use them as a means of alert to accidental spills. Several biological early warning systems already exist to detect spills in rivers and near drinking water intakes, but this is often too late to prevent damage to the ecosystem. Instead it would be better to monitor the effluent leaving the wastewater treatment plant, so that effluent could be diverted to a holding pond. As this would involve substantial cost to the dischargers, these systems will have to demonstrate reliability in the coming years before their application becomes routine.

Cells cut chromium concentrations



Chromium wastewaters are an unpleasant by-product of many industrial processes, with its hexavalent form Cr^{6+} toxic to most aquatic organisms. Conventional methods to remove chromium include chemical reduction, ion exchange and adsorption, but these involve high energy costs or large amounts of chemicals. With bacteria increasingly being used to remove toxics, two researchers in Hiroshima University's fermentation technology

Taipei's tributaries hold heavy pollution load



The Keelung River in northern Taiwan is a major tributary of the Tansui River and runs through Taipei City and much of Taipei County. The river receives a heavy pollution load from industrial and mining wastewaters upstream of Taipei City and municipal sewage, landfill leachates and urban storm runoff downstream. Recognizing the problems, the Taiwanese

department began looking for a bacterial way to reduce Cr^{6+} to its less harmful Cr^{3+} ion.

Ohtake and Hardoyo began by isolating a strain of Cr^{6+} -reducing bacteria from activated sludge samples taken from a municipal treatment plant. What they obtained was a short, gram-negative, motile rod, which they identified as *Enterobacter cloacae*. Although resistant to Cr^{6+} under aerobic and anaerobic conditions, Cr^{6+} could only be reduced anaerobically. Reduction is thought to take place on the cell surface, as the reduced chromium was mainly found in the external medium in the form of insoluble chromium hydroxides.

Rates of reduction appear to be dependent on the number of bacterial cells and the amount of Cr^{6+} added to the culture. As the concentration of Cr^{6+} increases the reduction rate decreases, and the time required for complete reduction goes up. Concentrations as high as 520 ppm Cr^{6+} can be removed in 11 hours at

temperatures between 1050°C and over a pH range of 6.5-8.5. Batch-fed cultures showed high performance in detoxifying Cr^{6+} , as they have the advantage of keeping the concentration of Cr^{6+} below the toxic level and can maintain an adequate population under Cr^{6+} stress.

For practical application, two types of bioreactor were tested: dialysis bag and anion-exchange membrane reactors. In the dialysis bag, *E. cloacae* cells were put in a semi-permeable membrane bag and submerged into a Cr^{6+} -containing solution. The hexavalent ions diffuse into the culture and are reduced to the trivalent form which readily precipitates as an insoluble hydroxide inside the bag. About 90% of the total chromium can be removed in this way, but performance depends on the size of surface area of the membrane and the cell density in the bag.

Anion exchange also showed itself to be effective in removing chromium from wastewaters. The membrane allowed chromate ions CrO_4^{2-} to pass

through while preventing Cr^{3+} from diffusing back. Potassium chloride was used as the counter anion to the chromate, and no electric potential needed to be applied between the chambers. Nearly 94% of Cr^{6+} could be removed from the waste solution within 50 hours.

Increasing the surface area of the membrane would again improve performance of the system. Results so far seem to show the potential of *E. cloacae* in removing Cr^{6+} from wastewaters. Its advantages over other microbial methods lie in that removal occurs under mild conditions; it doesn't need chemical additives or aeration; anaerobic reduction minimizes excess sludge production in aqueous systems; no toxic by-products are formed; and that the reaction is reproducible and reusable. Chromium hydroxides are stable and not taken up by living organisms. Although only a laboratory study at present, its results seem to show promise for a full-scale development.

government set up a series of water quality management meetings and in 1984 decided to embark on a plan to intercept and treat wastewaters and then discharge effluent to the ocean. Studies on the impact this would have on the river environment showed that there would still be a substantial benthic (sediment) oxygen demand. Dredging would be necessary to meet proposed water quality standards for the river. Although trace organic compounds were present in the sediments, the major pollutants were found to be heavy metals, mainly iron, copper, manganese, lead and zinc.

Samples of the sediments were taken on six occasions between November 1988 and July 1990 covering both the wet and dry seasons. Most metals were found to be in greatest concentration 40 km upstream, where several coal mines are located. Maximum concentrations occurred during the dry season due to low flowrates. Compared to established background concentrations for metals in river waters, results of Fe 8249 $\mu\text{g/l}$; Mn 1240 $\mu\text{g/l}$;

Zn 110 $\mu\text{g/l}$; Cu 240 $\mu\text{g/l}$; Pb 270 $\mu\text{g/l}$ and Cd 104 $\mu\text{g/l}$; for the Keelung River show that heavy metals are a serious problem, and that dumping dredged sediments will require careful control.

Apart from the high concentrations found at the 40 km sampling site, on average most metal pollution was found in the downstream reaches of the river. Much of this may be due to the Min-Sheng wastewater treatment plant in Taipei City, which was found to contain high concentrations of metals in its sludge, particularly copper. A further 40 point sources were identified, however, along the length of the river as a result of the sampling. More work is to be undertaken to identify possible non-point sources.

Full proceedings of the conference on Hazard Assessment and Control of Environmental Contaminants in Water from which these articles are taken will appear in *Water Science and Technology* Vol. 25 No. 10 later this year.