Review: Anaerobic treatment of municipal sanitary landfill leachates: the problem of refractory and toxic components

D. Alkalay,* L. Guerrero, J.M. Lema, R. Mendez and R. Chamy

The wide use of municipal sanitary landfills has drawn attention to the leaching effluent generated, this may be problematic to the site’s environment, whether by infiltration or other contaminating modes. Anaerobic digestion has been shown to be one of the most efficient systems with which to treat this type of effluent. This article reviews the techniques used by different authors for leachate characterization, specifically related to refractory and toxic components and their effect on anaerobic treatability. In addition, it covers the treatment of refractory organics, organic and inorganic toxic materials and the nutrient balance for adequate system operation. The main conclusions are that there is ample availability of methods by which to identify the different components present in leachates as well as for their toxicity assessment and that nutrients are in general available in sufficient amounts. Treatability studies are presented which are shown to be of general value and can be used in a straightforward manner.

Key words: Anaerobic digestion, anaerobic toxicity, municipal sanitary landfills, refractory, sanitary landfill leachates.

The problem

There is worldwide consensus that landfilling is the most cost effective, least polluting and safest means of disposing of solid urban waste (Lema et al. 1988). Different technologies have been developed, and most of the larger cities of the world have implemented one that suits their needs.

However, there remains one important aspect to be resolved, that is, the best way to eliminate the leachates which in different volumes and for different reasons are always produced in the landfills. Several publications have dealt with this matter and a number of reviews of available technologies have been made (Cossu 1982; Parsons 1983; Robinson & Maris 1985; Andreottola et al. 1988; Lema et al. 1988; Senior & Shibani 1990; Pohland 1991; Tchobanoglous et al. 1994).

There is general agreement that the main problem to be confronted is the organic load present in the leachates, because the presence of significant amounts of inorganic pollutants is more a matter of specific situations and as such, has specific solutions (Imai et al. 1995).

The more general problem of the organic pollutants present in the leachates needs to be dealt with specifically because it becomes a new source of pollution of groundwater, surface waters, or even the immediate environment of the landfill. Several treatment alternatives for landfill leachates exist and have been investigated (Hoeks & Borst 1982; Mennerich & Albers 1986); and some of them are being applied (Piscaer & de Man 1986; Schafer et al. 1986; King & Murebee 1988; Fernández et al. 1990; Keenan et al. 1993; Alkalay et al. 1994; Wilderer 1995). However, the final solution to the problem is far from being resolved. If the cost of a certain technology is not prohibitive, then the risk of further pollution, or other diverse problems must be considered. Specifically, biological processes have proved to be the best way of eliminating the organic compounds present in the leachates, whether applied before, after, or together with chemical/physical or hydraulic procedures.

The biological alternatives are two: aerobic or anaerobic treatment. Aerobic treatment is often the easier to apply of the two but does produce large amounts of organic material as biomass. This poses a subsequent problem of disposal. Odour generation is another of its drawbacks, and the high energy consumption may become a further one, depending on the particular process chosen, and the current cost of energy. These three disadvantages do not apply to anaerobic processes.

However, before deciding to apply an anaerobic treatment, the decision has to be made whether the leachate is equally treatable aerobically or anaerobically.
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Several indicators are available in the literature to help take this decision and they will be reviewed in the section on leachate characterization.

Once it has been decided that the leachate is anaerobically treatable, there is one problem remaining, namely that there is no universal technology which is applicable to all kinds of leachate. Therefore, we feel that an overview of available procedures, be they on laboratory- or industrial-scale, could be an important contribution to the adoption of a definite solution to the problem.

There exist only a few publications on general overviews of leachate treatments together with a number of articles on specific anaerobic processes (Parsons 1983; Andreottola et al. 1988; Lema et al. 1988; Senior & Shibani 1990; Iza et al. 1992).

Why a Review?

In a previous publication (Lema et al. 1988), a review was made of the different alternatives which exist for the treatment of landfill leachates and their efficacies in a large number of practical applications. However, from the mentioned general overviews, and from our own experiences, the main problem which still has to be dealt with is the presence of refractory and toxic components in the leachates. These components are of varied origin and have complex structures, and depend on the nature of the wastes disposed of at a particular landfill and on the type of leachate management (including also the landfilling technology, the characteristics of the site, the age of the landfill, and the climate). All this militates against a single solution to the problem.

From another point of view, there are many common characteristics between the refractory and toxic components of different leachates, which makes the findings of the various researchers in the subject of a great value (Pohland & Harper 1987). It facilitates, by means of a certain degree of generalization, a first approach to be made to solving the leachate problem at the engineering design level. This is why we feel that the best thing to do at this stage is to make a thorough and systematic review of the literature available to date. To facilitate this systematic approach, the study has to be restricted to municipal sanitary landfill leachates since industrial waste landfill leachates depend strongly on the waste disposed of, and each treatment is almost predetermined by this. However, in many cases the sanitary landfill is used not only for the disposal of urban wastes but also for industrial wastes (co-disposal). In these cases, when the latter are of limited importance in terms of strength or contaminating power, the treatment may be considered within the scope of this work. Moreover, when primary and secondary treatments are being considered, which could take care of specific components of industrial origin, the application of an anaerobic process to leachates of industrial landfills could again become part of the scope of the present review.

This review then will consider the following steps, with regard to the literature analysed: (i) treatability of leachates by anaerobic digestion. This includes their physical, chemical and, eventually, biological characterization. (ii) Identification of the different problems of treatability encountered, and the solutions given to them, especially the ones of general validity. The problems would be mainly: the presence of refractory materials; the presence of toxic components; and nutrient imbalances.

Leachate Characterization

For the purpose of characterizing a leachate in view of its further processing, it is important to state how the composition has to be considered.

First of all, it is important to know the amount and composition of suspended solids (SS) present, and the possibility of eliminating them through physical or physical/chemical processes (flocculation, sedimentation, filtration, centrifugation) (Alkalay et al. 1994).

But by far the most complicated problem to deal with, with regard to the further treatability of the leachate, is the soluble part. To characterize this soluble part it is best to consider it from two viewpoints. First, composition and concentration of components refractory to biological treatments, and secondly the nature and concentration of organic and inorganic toxic materials present.

The ways to identify the presence, quantity and composition of these kinds of materials are varied but some of them have been more successful than others. They are: (i) biological assays [residual oxygen bioassay (ROB); biological methane potential (BMP); anaerobic toxicity assessment (ATA)]; (ii) physical methods (membrane ultrafiltration, gel permeation, HPLC); (iii) chemical identification (inorganics, organics: specific, and by functional groups, etc.).

Table 1 gives a list of methods used to characterize leachates. General procedures for trace organics have been described by Afghan & Chau (1989). These methods are the same as the ones employed to characterize any type of wastewater; we will give special attention to refractory and toxic materials present, in view of their effects on anaerobic digestion.

Refractory Compounds

This is the name given to organic compounds which are recalcitrant to biological degradation. They differ from toxic substances in that their concentration does not affect the biological process. Simply, the microorganisms are not able to metabolize them or, sometimes, they
happen to be end products of biological processes (Harmsen 1983). Many authors have found that, in general, the same kinds of substances are recalcitrant to both aerobic and anaerobic treatment (Gourdon et al. 1989; Millot et al. 1987). These substances are very difficult to characterize chemically and even more so structurally, therefore they are identified by separation procedures. There are, however, possibilities for their further characterization by elemental analysis and functional group analysis (Afghan & Chau 1989). Rebhun & Manka (1971) characterized the soluble organics in secondary effluents and found that they contain no more than 50% of so-called humic substances (humic, fulvic and hymatomelanic acid). Chian & DeWalle (1977) used membrane fractionation and gel permeation techniques, and identified leachate components in the range of MW 500–10,000 as being mainly fulvic acid-like materials, and consisting principally of carboxyl and aromatic hydroxyl groups. Higher molecular weight fractions (> 10,000 MW) would be mainly humic carbohydrate-like substances. Wu et al. (1988) found that the refractory parts of the leachates they studied were mainly composed of intermediate molecular weight fractions (500–10,000) of fulvic acid-like materials.

Lema et al. (1987) and Méndez et al. (1989) in their digestibility studies of old and young landfill leachates, found that even if young landfill leachates are much more degradable, eventually the amount and nature of the refractory organics are very much the same as the ones found in medium-aged and old landfills. Ragle et al. (1995) found that overall, mass emissions per unit waste mass in place, decreased with increasing waste age for total dissolved solids and Mn, indicating that these components were leachable and independent of degradation processes. Gourdon et al. (1989) and Millot et al. (1987), found that gel permeation techniques were very useful to study the performances of biological treatments of leachates.

After this rather limited way of characterizing the refractory components, what might be valuable is to elucidate the mechanisms of recalcitrance to biological treatment in order that an alternative treatment may be selected.

Table 2 shows the systematization work of Alexander (1973) on the different mechanisms of recalcitrance and the causes of each of them (Table 2).

**Toxic Components**

These may be either organic or inorganic. They usually have different origins (Pohland & Gould 1986) and require different treatments. Also, the researchers who have developed methods for their identification and toxicity measurement, have studied them separately. What they have in common is that toxicity is not only dependent on the nature of the material but also on its concentration and availability.

Toxicity is a measure of how a substance affects a living being; the assessment of toxicity of different substances will be through so called bioassays which study the effects of chemicals or environmental conditions, in this case, on microorganisms and more specifically on methanogens. The most classical bioassays are BMP, and ATA developed on the basis of the Hungate serum flask technique by Owen et al. (1979). Alkalay et al. (1994), used a modified Hungate technique, adapted by Soto et al. (1993), which was used not only for toxicity determinations but also for leachate biodegradability and even for the assessment of methanogenic activity of sludge. Another method is the Microtox® test, developed by the Microbics Corporation, which provides the instrumentation and consumables, and is based on the bioluminescence of reactivated freeze-dried *Photobacterium phosphoreum*.
Inorganic Compounds. These are anions or cations of salts, or specific elements, such as: (i) light metals (Al, K, Na, Mg, etc.); (ii) heavy metals (As, Ba, Be, Ca, Co, Cd, Cr, Cu, Fe, Hg, Mo, Ni, Mn, Se, Sb, Pb, W, V, Zn, etc.); (iii) anions (Cl⁻, NO₃⁻, NO₂⁻, SO₄²⁻, PO₄³⁻, S²⁻, etc.); (iv) NH₃. Ammonia is one of the most common toxins present in anaerobic digestion and many studies have been carried out on it. However, in landfill leachates it rarely reaches the level of toxicity, due to a low protein content, not exceeding 700 mg/l, referred to as NH₃ nitrogen; leachate ammonia content is usually measured by classical methods (colorimetric or specific electrode) and it is compared to the universally accepted toxicity level of 3000 ppm. This figure must only be taken as a first approach, particularly with respect to ammonia, because many examples have been found of microbial acclimation to concentrations of double this figure. In any case, there is proof that up to 10,000 mg/l ammonia is not bactericidal but only bacteriostatic and that activity is restored 7–10 days after the high concentrations are reduced to < 3000 mg/l (Farina et al. 1988; Speece & Parkin 1991).

The anions mentioned in the list are rarely present in toxic concentrations and are readily determined by chemical methods. The light metals are always present but never in toxic concentrations, and their characterization is carried out by classical methods also; mainly atomic absorption spectrophotometry. In the case of heavy metals, even minute amounts can be highly toxic. Identification is straightforward, and is most often done by atomic absorption spectrophotometry. Another important point is that they tend to be ubiquitous and, consequently, increase in concentration in the case of inadequate final disposal (e.g. in recycle systems).

In general metals can act as: essential microelements for enzymatic action; inhibitors of sulphide toxicity; binding agents of essential nutrients (such as phosphates); inhibitors and toxicants of the microbial biomass; biomass stimulants, such as bacterial aggregation promoters. In this section we will analyse their toxic effects and the mechanisms of toxicity.

Oleszkiewics & Sharma (1990) concluded that heavy metals are, in general, non-specific, reversible, non-competitive inhibitors and that some of them could even have stimulatory effects up to a certain concentration above which they may cause gradual inhibition, or even an abrupt failure.

The mechanisms of inhibition proposed by these authors included: substitution of metallic enzyme cofactors; combining with the outstanding sulphydryl group (SH); inactivation of the mercapto group in coenzyme M of methanogens; and tight binding to acid groups in the side chains of the polypeptide chain (salt linkages may be broken and the proteins precipitated). Analysis of toxicity
levels for anaerobic bacteria led them to the conclusion that measurement of the toxicant’s total concentration is not meaningful enough because there is no equilibrium between the bacterial components and the environment. The effect in any case would be mainly bacteriostatic and not bactericidal, and would, therefore, be reversible.

The other issue about which all authors agree is that metal inhibition is by soluble metals. Thus, precipitation is one of the best ways to cope with the problem. Experiments on metal toxicity assessment in landfills are diverse (Bull et al. 1983; Wu et al. 1988; Kennedy et al. 1988; Chang 1989; Thirumurthi 1990; Keenan et al. 1991). Some agree that the normally encountered concentrations are below the minimum required to affect the anaerobes (Cameron & Koch 1980a; Bull et al. 1983), and others state that some of these heavy metals are responsible for inhibition of methanogenesis (Harries et al. 1990).

In the first group, Bull et al. (1983), in batch experiments performed with landfill leachates, proved no effect whatsoever in response to the heavy metals present. They compared H₂S pretreated batches (to precipitate and remove heavy metals) with directly digested ones. From the second group, Harries et al. (1990) found that Zn in the normally encountered concentrations (64–134 mg/l) is inhibitory, whereas Fe at 1000 mg/l, Pb at 10 mg/l and Cu at 5 mg/l were harmless. They proved the issue by removing the heavy metals by precipitation with H₂S and filtration. What most probably happens is that enough S²⁻ ion is present in many leachates in an amount sufficient to precipitate the heavy metals to a degree that makes the residual soluble concentration harmless. The proof of it is that most of the heavy metals are found in the solid parts of the treated leachates (Cameron & Koch 1980a).

Table 3 shows the normally encountered concentration ranges of metals in leachates, and the concentrations accepted for their disposal.

Organic Compounds. Many authors have investigated and characterized the presence of potentially dangerous organic compounds in liquid wastes. Some of those studied are wastes related to either industrial or municipal landfill leachates (Cameron & Koch 1980b; Harmsen 1983; Reinhard et al. 1984; Albaiges et al. 1986; La Regina et al. 1986; Venkataramani et al. 1986; Murray & Beck 1989; O’Connor & Young 1989; O’Connor et al. 1989, 1990; Watson-Craik & Senior 1989; Dienemann et al. 1990; Reinhart et al. 1991) and the general problems of toxicity of organic chemicals to methanogens (Wilson et al. 1986; Field & Lettinga 1987; Blum & Speece 1991). Table 4 shows a list of the priority toxicants examined and the methods used by the different authors to evaluate their effects.

With regards to the general problem of toxicity to methanogens, it is very important to state the correlation that exists with other toxicity measurements. This was studied by Blum & Speece (1991) who assayed and analysed between 50 and 100 chemicals with respect to three groups of bacteria: aerobic heterotrophs, Nitrosomonas and methanogens, and correlated their culture inhibition by 50% (IC-50) to the effect on fathead minnow and on the Microtox™ assay. They found excellent correlation between aerobic heterotrophs and methanogens,

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**Table 3. Metals in leachates.**

<table>
<thead>
<tr>
<th>Metal</th>
<th>Concentration (mg/l)</th>
<th>Limits accepted (mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Chile*</td>
</tr>
<tr>
<td>aluminium</td>
<td>1.5–2.7</td>
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</tr>
<tr>
<td>antimony</td>
<td>0.05–0.5</td>
<td></td>
</tr>
<tr>
<td>arsenic</td>
<td>0.009–0.05</td>
<td>0.05</td>
</tr>
<tr>
<td>barium</td>
<td>0.16–0.23</td>
<td>20.0</td>
</tr>
<tr>
<td>beryllium</td>
<td>0.005–0.05</td>
<td></td>
</tr>
<tr>
<td>boron</td>
<td>5.1–8.9</td>
<td></td>
</tr>
<tr>
<td>cadmium</td>
<td>0.002–0.007</td>
<td>0.3</td>
</tr>
<tr>
<td>calcium</td>
<td>1500–1900</td>
<td></td>
</tr>
<tr>
<td>chromium</td>
<td>0.10–0.28</td>
<td>0.05</td>
</tr>
<tr>
<td>cobalt</td>
<td>0.01–1.78</td>
<td></td>
</tr>
<tr>
<td>copper</td>
<td>0.01–0.060</td>
<td>3.0</td>
</tr>
<tr>
<td>iron</td>
<td>770–1090</td>
<td></td>
</tr>
<tr>
<td>lead</td>
<td>0.002–0.33</td>
<td>0.05</td>
</tr>
<tr>
<td>magnesium</td>
<td>223–284</td>
<td></td>
</tr>
<tr>
<td>manganese</td>
<td>47.5–68.1</td>
<td>0.1</td>
</tr>
<tr>
<td>mercury</td>
<td>0.1</td>
<td></td>
</tr>
<tr>
<td>molybdenum</td>
<td>0.25–0.75</td>
<td>0.1</td>
</tr>
<tr>
<td>nickel</td>
<td>370–470</td>
<td></td>
</tr>
<tr>
<td>selenium</td>
<td>0.1–1.0</td>
<td></td>
</tr>
<tr>
<td>sodium</td>
<td>750–1010</td>
<td></td>
</tr>
<tr>
<td>tin</td>
<td>0.03–0.3</td>
<td></td>
</tr>
<tr>
<td>vanadium</td>
<td>0.16–0.54</td>
<td></td>
</tr>
<tr>
<td>zinc</td>
<td>57–80</td>
<td></td>
</tr>
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</table>

* For infiltration.
and between each of them and fathead minnows; and fair
to good correlations between Microtox data and each
of the three groups of bacteria and fathead minnows
(Figure 2). The accuracy of correlation to predict toxicity
would be about one order of magnitude, which is very
reasonable when it comes to using published data for
engineering design purposes. It also may be used as an
approach to estimate toxicity to higher organisms or
other types of bacteria in the aquatic environment.

Field & Lettinga (1987) studied the toxicity of
hydrolysable tannin, specifically gallotanic acid polymer,
and the two monomeric derivatives, gallic acid and
pyrogallol. These appear in leachates or wastewaters
where significant amounts of tannins may be present.
This is the case in sources of contamination rich in fruit
or vegetable wastes (apples, bananas, grapes, coffee, ca-
cao, sorghum, beans and bark). They found that the
gallotanic acid polymer was much more toxic than its
monomers, probably due to the ‘tanning’ effect on pro-
teins of the methanogenic bacteria.

They used for this purpose serum flask batch digestion
fed with volatile fatty acids. They found that gallic
acid and pyrogallol in concentrations of 4000 mg/l were
inhibitory to methanogenesis, whereas at 2000 mg/l or
less they were readily metabolized after a certain time.
At less than 2000 mg/l the effect was stimulatory to

Table 4. Priority toxicants in landfill leachates.

<table>
<thead>
<tr>
<th>Contaminant</th>
<th>Concentration ≤ mg/l</th>
<th>Method</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>0.61</td>
<td>Microcosm serum bottles</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>1.93</td>
<td>Modified Hungate bioassay</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>3.8</td>
<td>Soil packed bed bioreactor</td>
<td>3</td>
</tr>
<tr>
<td>Toluene</td>
<td>0.55</td>
<td>Microcosm serum bottles</td>
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</tr>
<tr>
<td></td>
<td>16.2</td>
<td>Modified Hungate bioassay</td>
<td>2</td>
</tr>
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<td></td>
<td>41</td>
<td>Soil packed bed bioreactor</td>
<td>3</td>
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<tr>
<td>Phenol</td>
<td>12.5</td>
<td>Soil packed bed bioreactor</td>
<td>3</td>
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<tr>
<td></td>
<td>188</td>
<td>Refuse packed columns</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>BMP &amp; ATA bioassays</td>
<td>5</td>
</tr>
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<td>Ethylbenzene</td>
<td>0.27</td>
<td>Microcosm serum bottles</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>2.2</td>
<td>Soil packed bed bioreactor</td>
<td>3</td>
</tr>
<tr>
<td>Dichloroethane</td>
<td>0.18</td>
<td>Modified Hungate bioassay</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>34</td>
<td>Soil packed bed bioreactor</td>
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<td>Trichloroethane</td>
<td>0.49</td>
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<td>0.15</td>
<td>Microcosm serum bottles</td>
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<td>7.70</td>
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<td>Xylene</td>
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<td>200</td>
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<td>5</td>
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<td>Dimethylphthalate</td>
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<td>BMP &amp; ATA bioassays</td>
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<tr>
<td>Diethylphthalate</td>
<td>200</td>
<td>BMP &amp; ATA bioassays</td>
<td>6</td>
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<tr>
<td>Dibutylphthalate</td>
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<td>BMP &amp; ATA bioassays</td>
<td>6</td>
</tr>
<tr>
<td>Diethylhexylphthalate</td>
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<td>BMP &amp; ATA bioassays</td>
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<tr>
<td>Gallotanic acid</td>
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<tr>
<td>Pyrogallol</td>
<td>1000</td>
<td>Serum flask batch digestion</td>
<td>4</td>
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<tr>
<td>Gallic acid</td>
<td>4000</td>
<td>Serum flask batch digestion</td>
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<tr>
<td>Methylisobutylketone</td>
<td>2.00</td>
<td>Modified Hungate bioassay</td>
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</table>

* References: (1) Wilson et al. (1986); (2) Venkataramani et al. (1986); (3) Dieneman et al. (1990); (4) Field & Lettinga (1987); (5) O'Connor & Young (1989); (6) O’Connor et al. (1989).
methane production. In contrast, the gallotannic acid was inhibitory at any concentration, reaching values of 50% inhibition at 1000 mg/l and total inhibition at 2000 mg/l.

With respect to the identification of organic toxic components in landfill leachates there are only a small number of publications but they are nevertheless very interesting because of their scope. Specific studies were made by Young (1984), O'Connor & Young (1989), O'Connor et al. (1989) and O'Connor et al. (1990). They worked on phthalic acid esters, substituted phenols and other aromatic compounds. Phenolic and phthalic compounds appear naturally in the leachates of urban waste landfills. Phenol is the basic structural unit for a variety of synthetic organic compounds in common use, and a transformation product of pesticide dissimilation, while diesters of phthalic acids are used widely as plasticizers in polyvinyl chloride plastics. These studies were conducted with the pollutants as the only added carbon source (in the concentration range 20–200 mg/l) by performing the BMP and ATA tests and checking mineralization. Venkataramani et al. (1986) investigated the toxicity of an industrial type leachate using a modified Hungate bioassay. They found that most of the so-called toxins, were short-chain (MW < 500) volatile fatty acids and alcohols generated by the activity of acid formers in the landfill site. Wilson et al. (1986) made microcosm studies in serum bottles on actively methanogenic aquifer material and studied the effects of alkylbenzenes and halogenated aliphatic hydrocarbons (see Table 3).

### Anaerobic Treatment of Leachates

As stated earlier, this review focuses on the anaerobic treatment of leachates and the way refractory and toxic materials can be dealt with.

First of all, the anaerobic treatability of these leachates must be determined. In this respect a very interesting first approach proposed is the 'Decision model for the leachate treatment train selection' of Forgie (1988) which, on the basis of the biological oxygen demand/chemical oxygen demand (BOD/COD) ratio, the BOD/N-NH₄ ratio, and the metal content, recommends: (i) anaerobic or aerobic treatments alone; (ii) either of them, followed by physical–chemical treatment (PCT); (iii) a combination of anaerobic–aerobic treatment, followed or not by PCT; (iv) in some cases, when high metal contents may cause inhibition or other problems, their elimination or abatement by a chemical pretreatment may be advisable.

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**Figure 2.** Comparison and correlation of toxicities among species. From Speece et al. (1991).
What follows is an analysis of the different approaches that the researchers in the field have made to solve the problems of treatability that arise with respect to municipal landfill leachates.

Treatment of refractory organics
These components of leachates, as their name suggests, are either difficult or impossible to eliminate by anaerobic digestion; the general opinion of researchers is quite consistent on the cause and the procedure to follow.

Gourdon et al. (1989) detected that the recalcitrant components found after aerobic or anaerobic treatments were the same, despite the fact that there might be up to 50% more degradation by aerobic treatment than by anaerobic treatment. All this occurred in their reactors, even after adding phosphorus and beef extract, which showed that this effect was not due to a lack of essential nutrients. The effect of inhibitory substances was also rejected since added fatty acids were readily biodegraded.

This situation might become important when it is intended to further polish the treated leachate by a physicochemical process. Millot et al. (1987), in their aerated lagoon study, found that a concentration–flocculation post-treatment reduced the remaining total organic carbon (TOC) from 34% at the exit of the lagoon to 0.5%. They also found that the biologically treated effluent consisted mainly of substances with MW above 5000.

Thirumurthi et al. (1986) found that what they called humic acid constituted 52% of the total volatile solids (TVS) of the effluent of anaerobically treated leachates and 56–62% of the composition of aerobically treated leachates. This was the case after about 99% of the BOD and 97% of the COD had been removed in the anaerobic or combined anaerobic–aerobic treatment. It has to be noted that even these high performances in BOD and COD removal, from strong leachates (BOD = 17400, COD = 22300) still means that a significant amount of organic material may remain in the effluent (COD approx. 700 mg/l, in this last case). In the solely aerobic lagoons, they found a BOD removal of 98% but a COD removal of only 79% which indicated the presence of an important amount of refractory organic compounds. Furthermore, the removal of humic acid in the aerated lagoons was 37.5%, whereas in settling lagoons without mechanical aeration an increase of 3.5% was found. With respect to the anaerobic process, performed in a fixed film reactor, the removal was 9.1%. This confirmed, with respect to the results of aerated lagoons, what Gourdon et al. (1989) had stated earlier about higher aerobic capability. Finally, the combined process, anaerobic (continuous fixed film reactor, CFFR) + aerated lagoon gave a 48.3% removal of humic acid, showing it to be the best alternative encountered.

All these studies tend to confirm what Boyle & Ham (1974) had already found, that there exists a certain amount of organic material in landfill leachates which is not degradable, either aerobically or anaerobically. However, if we look at this from the pollution control point of view, which is the main reason for the treatment of leachates, we see that the presence of refractory substances is generally of minor importance. This is because they are not biodegradable or toxic (to the microorganisms present in the leachate). Their contaminating impact is, in most cases, either zero or, exceptionally, there may be a specific effect towards plants, animals or humans. In the latter case, these compounds would have to undergo specific treatment. An example of this might be the remaining colour of a wastewater after undergoing full treatment. Most probably, this effluent would have to be subjected to a final polishing.

Treatment of toxic components
As mentioned above, the toxic components of leachates can be organic or inorganic. The organic toxicants can be further divided into natural and synthetic, depending on their origin. This subdivision is relevant in industrial waste landfills where a specific pollutant may be in a high concentration with respect to the other organic compounds. The solution in this case could eventually lie in a treatment prior to the dumping of the waste or, even more drastically, a change in the industrial process or the substitution of the materials causing the pollution. This is not the situation in municipal wastes landfills so that the synthetic and natural compounds present may be considered together. The inorganic toxic components, mainly ammonia and heavy metals, need clearly different treatments; they will be discussed separately.

Organic toxic materials. The anaerobic process can be divided into two phases (acidogenic and methanogenic) for which two different groups of microorganisms are responsible. These will be affected differently by the toxic chemicals present (Wu et al. 1988).

Many authors have investigated and characterized the presence of potentially dangerous organic compounds in landfill leachates but few have studied the effects of these toxins on the digestion process (Field & Lettinga 1987; Diememann et al. 1990). Studies by Young (1984) on phthalic acid esters, substituted phenols and other aromatic compounds showed that their decomposition depended on concentration, residence time and the nature of the particular substituent group(s). The acclimation of the cultures took variable times (days to weeks), depending on the substance and, in general, the studies showed that the molecules were susceptible to anaerobic degradation.

As mentioned earlier, the techniques mostly used to assess toxicity are the BMP and ATA. But what interests us at this stage of our analysis is which toxicity studies
were performed, not only on leachates but on processes where these leachates were treated. Watson-Craik & Senior (1989) studied phenol co-disposal with leachate recycle. They worked with refuse packed columns, at phenol concentrations of 200 mg/l and found that the compound was reduced to concentrations below regulatory limits at 0.202 mg/cm³. Above 400 mg/l, they found a lower mean dissimilation but phenol was nonetheless degraded.

Dienemann et al. (1990) also found that phenol was readily degraded and found nothing above 1.5 mg/l after treatment in soil packed-bed bioreactors. However, their influent contained only 12.5 mg/l phenol. Their study was aimed at investigating the viability of renovation of leachate from a high priority ‘Superfund’ site. They developed a process which can be operated in situ and proved that it was capable of removing more than 80% COD of the priority pollutants (see Table 4) and 90% of the TOC present. It consisted of two serial anaerobic–aerobic packed bioreactors, followed by a reverse osmosis (RO) post-treatment. However, the anaerobic reactor (first step) alone removed more than 95% of the toluene, dichloroethane, ethylbenzene, methylene chloride and phenol, 80% of the benzene and 70% of the bis (2-chloroethyl) ether. The latter were further reduced totally in the case of benzene and by 90% in the case of the chloroethyl ether by the combined system and RO post-treatment. No other organic pollutants were detected at the exit of the anaerobic step. They also detected no toxicity to methanogenesis when diluted below 10% strength but reactor failure was observed with 20% leachate strength. The analysis and follow up of toxic abatement were undertaken on the so-called priority pollutants which are presented in the database developed by Ghassemi et al. (1983) under an EPA contract. They found that these components were biologically degraded but were subjected to different lag times, which emphasized the need of an acclimation period for the methanogenic microorganisms. Finally, it has to be mentioned here that even if there are very few studies on the behaviour of toxic organics in landfill leachates, there exists an abundant literature on methanogenic fermentation studies of specific organic compounds. This can be seen readily in the references list of the work of Field & Lettinga (1987) and constitutes a very valuable background for further studies.

Inorganic toxic materials: heavy metals. As mentioned above, heavy metal toxicity is not a crucial issue in the anaerobic digestion of landfill leachates, either because the process takes care of the problem naturally, by precipitating them as sulphides, or because they are in concentrations which are too low to be harmful. If, however, heavy metals are found in the raw leachate in relatively high concentrations, or the sulphate content is too low to produce enough sulphide, a lime or other alkaline pre-treatment may be advisable. This can be beneficial in two ways: by lowering the soluble heavy metals content, and by diminishing the overall solids of the system and, consequently, facilitating the use of anaerobic filters and other cloggable processes (Keenan et al. 1991).

A few authors have specifically studied the effects of soluble heavy metals on the digestion of leachate. Wu et al. (1988) found an iron removal up to 99% (from 185 mg/l in the influent) and a zinc removal up to 98% (from 40 mg/l in the influent) in their studies with two-stage anaerobic filters. They reported that the removal was due to the combined effects of chemical precipitation, coagulation and adsorption onto the biofilm. Similar results were found by Thirumurthi (1990), in a fixed-film reactor, with removals of around 90% of Fe and Zn. Chiang (1989) also studied the effect of iron in the digestion process (anaerobic filter, AF) and found no toxic effect with concentrations of up to 570 mg/l, and removals of over 90%. The same > 90% removal was encountered by Kennedy et al. (1988) in studies with upflow blanket filter (UBF) and DSF reactors. However, it has to be said that the anaerobic digestion of landfill leachate is a biological process which is not designed for heavy metal removal even if indirectly it contributes to it by transferring them from the soluble to the solid phase. This means that the final disposal of the solid produced may be a delicate issue since these metals could re-enter liquid streams by solubilization.

Nutrient Balance
Fortunately, the anaerobic processing of landfill leachates rarely suffers from nutrient imbalance. This is a general characteristic of anaerobic processes because of the little growth of biomass when compared with the aerobic process. Nevertheless, there is no guarantee of an adequate C:N:P ratio, and the proof of it is that most researchers either check it or provide enough information to allow its calculation (Boyle & Ham 1974; Pohland 1980; Cameron & Koch 1980a; Bull et al. 1983; Murebee & Funes 1986; Thirumurthi et al. 1986; Lema et al. 1987; Chang 1989; Thirumurthi 1990). In this respect Thirumurthi (1990), found the optimal COD/P ratio to be between 15000:1 and 34300:1. Below 15,000 no effect of phosphate concentration whatsoever was found which means that except in the very strong leachates the phosphorus content will be sufficient (Table 5).

Conclusions
The main conclusions of this review can be stated as follows:
there is ample availability of methods to identify the components of landfill leachates, be they toxic or recalcitrant components. Most of the methods are classical methods developed for the identification of the specific substances, adapted to the particular characteristics of landfill leachates;

(2) toxicity assessments are also the classical methods available and there are enough of them to ensure adequate identifications;

(3) recalcitrants are essentially the same in any landfill and are duly identifiable. They are of secondary importance pollutionwise and when their treatment is advisable, the mechanisms of recalcitrance become important, and information in this direction is presented;

(4) many treatability studies of leachates are presented and most of them are of general value and can be used in a straightforward manner;

(5) nutrients are in general available in sufficient amounts for anaerobic treatments.

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References


Table 5. Nutrient balance in leachates.

<table>
<thead>
<tr>
<th>C:N:P</th>
<th>COD/P mg/l</th>
<th>N-NH₃</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>New 100:0.9:0.016</td>
<td>17,800</td>
<td>42</td>
<td>Henry et al. (1987)</td>
</tr>
<tr>
<td>Mature 100:1.5:0.023</td>
<td>12,500</td>
<td>10</td>
<td>Henry et al. (1987)</td>
</tr>
<tr>
<td>Old 100:2.8:0.008</td>
<td>34,100</td>
<td>72</td>
<td>Chang (1989)</td>
</tr>
<tr>
<td>Mature 100:5.5:0.007</td>
<td>47,500</td>
<td>345</td>
<td>Thirumurthi (1990)</td>
</tr>
<tr>
<td>Mature 100:12.7:0.13</td>
<td>760</td>
<td>2800</td>
<td>Lema et al. (1987)</td>
</tr>
</tbody>
</table>
Anaerobic treatment of landfill leachates


La Regina, J., Bozzelli, J.W., Harkov, R. & Gianits, S. 1986 Volatile organic compounds at hazardous waste sites and a sanitary landfill in New Jersey. Environmental Progress 5, 18–27.


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