

# Flocculants for Wastewater Life Cycle Optimization

*Bill Sahlie<sup>1</sup>, Rob Petch<sup>1</sup> and David Hunkeler<sup>2</sup>*

<sup>1</sup> Fontis New Zealand Ltd., Hamilton, New Zealand

<sup>2</sup> AQUA+TECH Specialties, La Plaine, Geneva, Switzerland

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## ABSTRACT

The use of flocculants and coagulants in the treatment of municipal waste water was examined using Life Cycle Assessment and Environmental Life Cycle Costing as tools. For a typical wastewater treatment plant with 10-50,000 person-equivalents of capacity, the main environmental impacts and costs are both linked to the transport of the dewatered sludge from the plant as well as its incineration, in examples where thermal drying to pellets is relevant. In comparing flocculants, the resource depletion potential and eutrophication potential are the environmental impact most sensitive, both influenced by the overall sludge dryness.

## KEYWORDS

Coagulant, dewatering, flocculant, life cycle assessment, life cycle costing, sludge, wastewater.

## 1 INTRODUCTION

Wastewater, by its very nature, is an environmental burden. Contaminants therein can have severe detrimental effects on aquatic life, the ability to use water resources for various purposes and the aesthetic value of the natural environment. Furthermore, discharging municipal and industrial wastewater to the environment untreated would impose an unacceptable environmental cost and would exceed, in all but remote areas, the carrying capacity of the environment. Regional and local authorities, therefore, set limits on the quality of wastewater that can be discharged to the environment and thus mandate the level of treatment required.

Constructing and operating wastewater treatment plants is an expensive endeavor. Given this, a mandate to treat our wastewater to an acceptable standard effectively implies that we accept the economic or dollar cost of wastewater treatment in order to reduce the environmental cost of not treating. The manner and the extent to which we treat our wastewater can be viewed as finding an acceptable balance between the environmental cost and the economic cost of dealing with our wastewater.

Wastewater treatment processes serve the purpose of purifying aqueous emissions (household and industrial) to an acceptable standard so that it can be reused or safely discharged back into the environment. However, wastewater treatment processes also create additional environmental costs in other ways. For example, wastewater treatment can be an energy intensive process and, therefore, the environmental cost of energy generation and consumption must be considered. Various gases such as carbon dioxide (CO<sub>2</sub>) and methane (CH<sub>4</sub>) are emitted directly to the atmosphere at various stages of wastewater treatment and are part of the carbon footprint of the operation.

There are a range of chemicals that are used in wastewater treatment processes so the environmental cost of their production, including resource depletion, should be considered when assessing the overall environmental cost of wastewater treatment. Also the contaminants present in the wastewater are subjected to various biological, physical and chemical processes in order to remove them from the water. This results in a concentrated solid waste that must also be disposed of. In some cases this solid waste is beneficially reused, though often in New Zealand the final solid waste product from

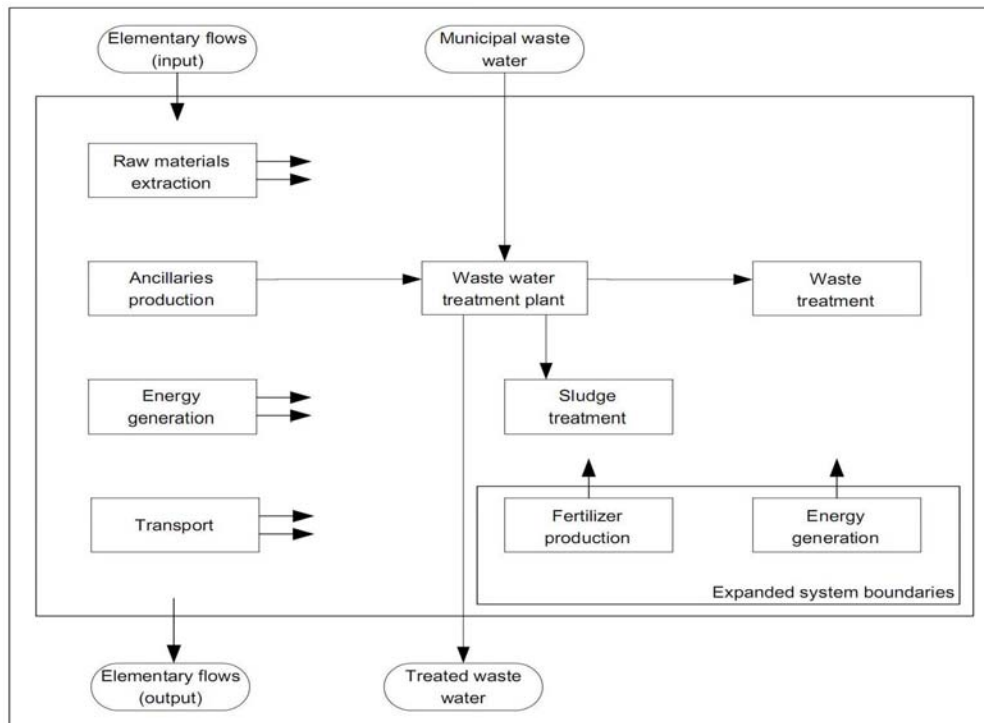
wastewater treatment is disposed of to landfill imposing a significant additional environmental cost in the form of transport and use of landfill capacity.

A simple model of evaluating the net environmental impact of wastewater treatment by assessing the net improvement in the water quality discharged from the facility as compared to that arriving at the facility does not provide a true or complete picture of the environmental cost of wastewater treatment. The concept of Life Cycle Assessment (LCA) is the idea of taking into consideration all inputs and outputs of an activity and accounting for the environmental cost of each individual component from its origin to its final disposal. The collective sum of all environmental costs of each component of an activity is, therefore, the net environmental cost of the activity. A standardized method of LCA has been developed under the auspices of the ISO (International Organization for Standardization). This standardized method for LSA is referred to as ISO 14040.

The extent and the manner which wastewater is treated in New Zealand varies widely. Some small to medium metropolitan areas continue to discharge municipal and industrial wastewater directly to receiving waters with only primary treatment. Oxidation ponds are widely distributed around the country servicing rural population centres, and major metropolitan areas have modern wastewater treatment facilities. Although large volumes of sludge solids continue to be disposed of to landfill, there has been a trend to reducing the landfill burden by thermal sludge drying, composting and land application. The majority of WWTP's are of medium size, which is what was simulated for this study.

One component of wastewater treatment operations, the role of flocculants in wastewater life cycle optimization, is the focus of this investigation. The application of flocculant and coagulant chemicals play an important role in optimizing wastewater treatment processes. Beneficial uses of coagulants and flocculants includes enhancing sedimentation processes, binding up nutrients such as phosphorus for subsequent removal and binding up suspended solids for dewatering by mechanical processes such as centrifuge or belt filter press.

There are numerous grades of flocculants available and for any particular operation there may be several different polymers that can perform satisfactorily. It can be shown that selection of the most appropriate flocculant as well as its dose rate can have a direct impact on the environmental life cycle optimization. The wastewater treatment operator is, therefore, able to use flocculant selection and dose rate as a tool to achieve the optimum balance between environmental cost and economic cost for the operation.



**Figure 1.** System LCA Model for Municipal Waste Water Treatment

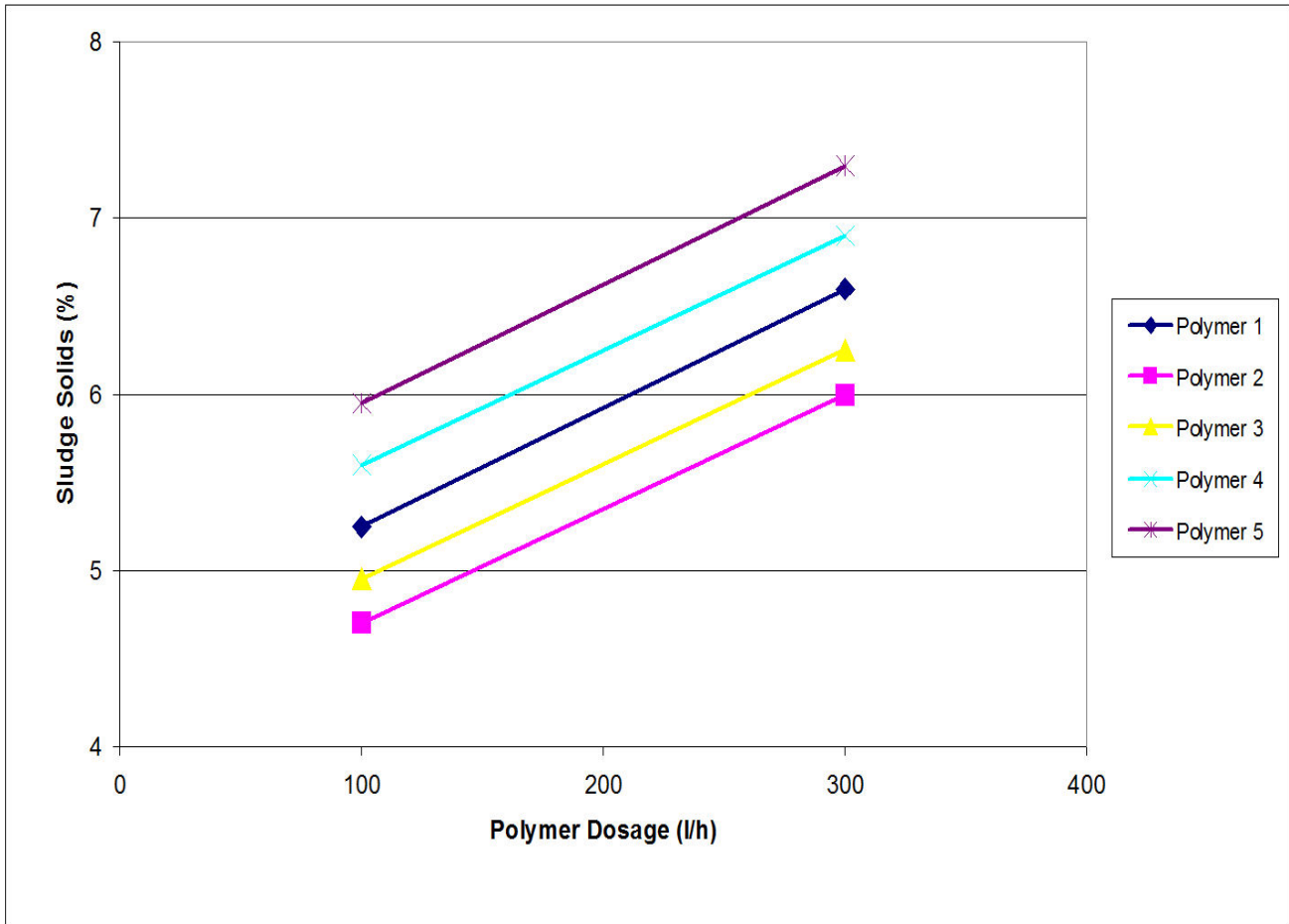
## 2 EXPERIMENTAL

Life Cycle Assessment (LCA) is a, now well established, methodology which evaluates the environmental impacts of products, or services. This includes production and use, as well as upstream impacts, such as resource extraction and pre-processing, as well as those occurring downstream, typically transport and either disposal, recycling or reuse (Curran, 2008). In this study a life cycle inventory model developed at the ETH (Swiss Federal Institute of Technology in Zurich) (ETHZ, 1996) was used to assess the impacts of municipal waste water treatment. The modeling included the evaluation of the composition of the inlet and discharge waters, as well as the energy requirement. One person-equivalent of water, per annum, as the basis for calculation (functional unit). Figure 1 is a schematic of the life cycle model used by Braune (Braune, 2002). Impacts on water, such as aquatoxicity, air (ozone depletion) and land, including resource depletion and eutrophication, were quantified for different scenarios as is summarized in Table 1. The later scenarios (3a, 3g and 3m) included an evaluation of the effect of the transport distance of the dewatered sludge to ultimate disposal as well as the dryness of the cake. A sensitivity analysis identified the transport distance, disposal method (incineration, land) and cake solids and the key variables in terms of environmental impacts (Rebitzer et al., 2003; Rebitzer, 2005).

**Table 1. Water Treatment Scenarios Investigated in the LCA**

Scenario	Description
0	Base case, no water treatment.
1	Water treatment in the absence of chemicals with only gravitational sedimentation. Sludge is disposed to land.
2	Water treatment using only inorganic coagulants (ferric sulphate).
3a	Water treatment using inorganic coagulants (ferric sulfate) as well as organic flocculants (cationic polyelectrolytes) with energy recovery of the sludge (incineration).
3g	Water treatment using inorganic coagulants (ferric sulfate) as well as organic flocculants (cationic polyelectrolytes) with mechanical dehydration and filtration of the sludge followed by disposal to land.
3m	Water treatment using inorganic coagulants (ferric sulfate) as well as organic flocculants (cationic polyelectrolytes) with disposal to land.

A second life cycle assessment study (Stoffregen, 2002) examined, specifically, the effect of flocculant performance on environmental impacts in a municipal water treatment plant, in general of a medium size, with the treatment of 10-50,000 person-equivalents of water. Five flocculants having different performances, as measured by cake solids as a function of dose rate, were compared, as is shown in Figure 2. Figures 3 and 4 provide examples of the extent of the modeling, showing the upstream materials used in the production of a key raw material, the cationic monomer, as well as one of the surfactants used to stabilize the emulsion. The integration, respectively, into the crude oil and natural product cycles is evident. The results of Braune (Braune, 2002) and Stoffregen (Stoffregen, 2002) are presented, in this paper, for the first time outside of the framework of their respective dissertations.



**Figure 2.** Comparison of five flocculants, at two dosage rates, on the sludge thickness. These five polymers were used in all simulations.

Life Cycle Costing (LCC) is an emerging method for the quantification of all costs linked with a product. It has, generally, an analogous system boundary (Figure 1) and functional unit (person-equivalent of water in this case), to LCA. LCC is based on the concept of real monetary flows and includes costs borne at all stages of the product preparation, use and disposal. It can include costs which are expected to become relevant in the economic life time of the product, such as a carbon or disposal tax. LCC does not, however, monetize non-financial items such as indirect costs for education or social impacts. Other techniques, such as Societal Life Cycle Assessment are deemed best for such quantification. To avoid double counting and serve as a compliment to LCA, LCC does not quantify any environmental impacts (Rebitzer et al., 2003; Hunkeler et al., 2008).

### 3 RESULTS

#### 3.1 Life Cycle Assessment of Various Flocculant/Coagulant Options

Figure 5 is the aquatic eutrophication potential in phosphate equivalents (kg) for the six scenarios noted in Table 1. Clearly, the chemical options result in significantly lower environmental impacts than the case with no water treatment or only physical sedimentation. In the case of aquatoxicity, the end-of-life sludge scenario (land disposal, incineration) does not have a major influence on the ultimate impact. Figure 6 shows the complimentary terrestrial eutrophication potential which has no impact when water is not treated, as there is no sludge generation. Terrestrial eutrophication is relatively

insensitive to the chemical strategy employed in treating the water, offer essentially neither advantages nor disadvantages, environmentally speaking, to the addition of either coagulants or flocculants.

The effect of the chemical strategy employed has an important influence on atmospheric impacts. Specifically, Figure 7 examines the ozone depletion potential, as estimated by CFC-11 equivalents. While coagulants have a minimal effect on the ultimate sludge concentration, impacting more on the speed of settling and water quality, flocculants do result in dryer sludges. The indirect consequence of dryness is less water transport to ultimate disposal. Reducing the number of trucks used for sludge disposal is the main factor in the lower ozone depletion potential. Therefore, the key parameter is the product of the sludge dryness and the transport distance. Reducing either has a virtually linear decrease in the CFC-11 equivalent production.

The resource depletion potential (RDP, expressed in kg of crude-oil equivalents) is quite sensitive to the use of coagulants and flocculants with the Scenarios 3g and 3m, involving land application of sludge after mechanical dewatering using flocculants, resulting in credits (Figure 8). Coagulants alone are basically in balance, with a very slight credit, while incineration has a relatively important contribution to resource depletion. When there is land disposal of sludge there is a substitution effect as less fertilizers are required and this is the reason for the credit. As is the case for ozone depletion, resource depletion is sensitive to transport as well as phosphorous removal, the latter predominantly the effect of the inorganic coagulant while the former related to the flocculant. The dual use of the coagulants and flocculants, in regards to this environmental indicator, is essential.

Braune (Braune, 2002) has shown that the main life cycle material uses linked to water treatment include CO<sub>2</sub>, SO<sub>x</sub>, NO<sub>x</sub>, N<sub>2</sub>O, CN, NH<sub>3</sub>, P as well as heavy metals and, the infrastructure-related, cement. The latter is noteworthy as a Japanese study has indicated, examining life-cycle energy, that the net breakeven point for the treatment of rural waste water is approximately 2000 person-equivalents. Below this, the net benefits of treating the water never exceed that of constructing and operating the plant. It is certainly also noteworthy that small plants have highly varying flowrates and are very difficult to operate, often functioning at as low as 10% efficiency versus a norm of 80+% for larger facilities.

Rebitzer (Rebitzer et al., 2003) has observed that the life cycle cost to treat one person-equivalent of water, of one year, is on the order of two hundred USD, if the sludge has a consistency of 15% and is transported 100 km. This is reduced to USD 130 for sludge transport of 40 km and to USD 80 if the sludge has a consistency of 25%. Therefore, the economic cost is even more sensitive to the environmental impact in regards to cake solids and transport. The flocculant cost is never more than five percent of the total life cycle cost. Transport accounts for two-thirds of the life cycle cost for wet sludges, the balance being the energy used in drying. As the sludge thickness exceeds thirty five percent, an excellent target which is obtained in some plants, the drying and transport costs become approximately equal, at 35 USD/pe/y.

### ***3.2 Life Cycle Assessment of Water Treatment with Five Different Flocculant Scenarios***

Table 2 summarizes the characteristics of the five polyelectrolytes investigated (Braune, 2002; Stoffregen, 2002). All polymers tested, and subsequently simulated, were medium-high charged cationics based on acrylamide and dimethylaminoethyl acrylate, commonly referred to in the trade as Q9 and described in Figure 3. For the sludge type investigated (digested sludge, with an average age of five weeks) increasing the mol% of cationic monomer in the flocculant, from 35-65%, increased the solids level of the sludge. This effect was slightly smaller than the influence of polymer dose rate for a given flocculant.

**Table 2. Polyelectrolytes Physical-Chemical Characteristics and Performance**

<b>Polyelectrolyte</b>	<b>Charge on the Flocculant (mol% cationic groups)</b>	<b>Flocculant Consumption (kg/TDS)</b>	<b>Sludge Dry Material (wt%)</b>
1	50	3.00	34.66
		4.00	35.34
2	35	3.08	34.33
		4.04	35.00
3	45	3.02	34.50
		4.02	35.17
4	55	2.99	34.83
		3.98	35.50
5	65	2.97	35.00
		3.96	35.67

Figure 9 shows the normalized eco-indicators for all five flocculants listed in Table 2. The most significant effect is on nitrification potential with a slight, opposite, tendency in terms of resource depletion potential. A sensitivity study was carried out (Stoffregen, 2002) revealed that the effect of residual polymer in the environment mostly influenced the aquatic ecotoxicity. This implies that polymer overdosing should be avoided and the optimal application is at or near the point of electroneutrality (neutralizing the sludge to have near zero zeta potential). However, the impact of the material used is quite secondary compared to transport and disposal and the optimum environmental, and economic, strategy coincide with the polymer providing the highest sludge consistency. The polymer's direct effect is, therefore, less important than its indirect contribution to the sludge dryness (Stoffregen, 2002; Rebitzer et al., 2003).

### **3.3 Life Cycle Costing of Flocculant Options for Wastewater Treatment**

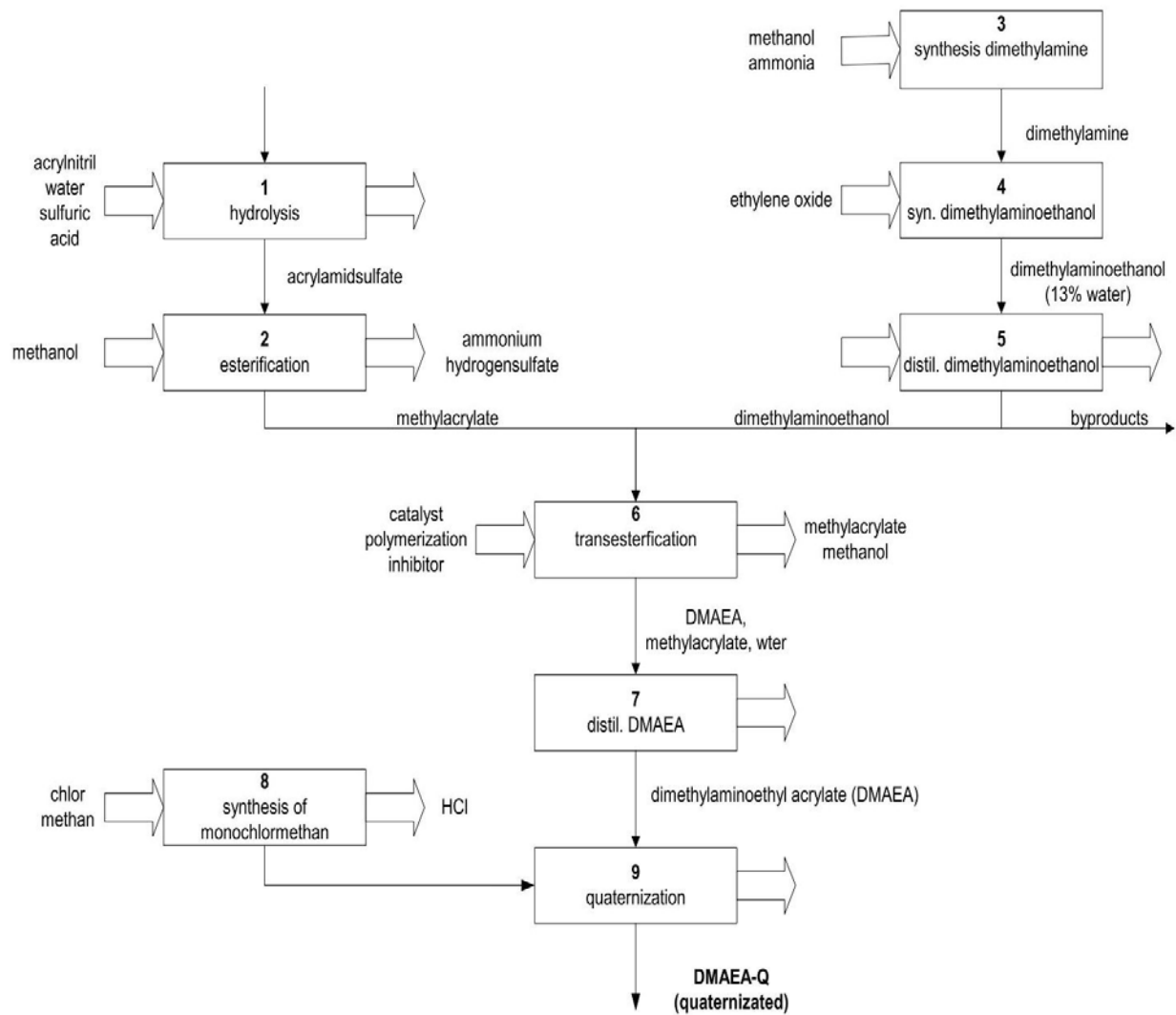
The life cycle cost of the treatment of has been shown to be dominated by solid waste with sludge drying account for over 32 USD per person-equivalent of water, per annum (Hunkeler et al., 2008). Sludge transport from the water treatment plant to the ultimate landfill contributes 24 USD/pe/y at a 40 kilometer transport distance. Electricity to run the plant is 4 USD/pe/y, of which half (2 USD/pe/y) is compensated by natural gas production in the digestion of sludges. When sludges are incinerated this increases the life cycle cost by 5 USD/pe/annum, while the overhead management of the plant typically costs USD 2/pe/annum. The chemical consumption is typically 3 USD/pe/annum, sixty percent of which is coagulants (3 USD/pe/year) with the balance being the flocculant (2 USD/pe/year). Overall, the flocculant contributes 4.3% to the life cycle cost of the water treatment (Rebitzer et al., 2003) for a scenario of a plant in a community of 50,000 inhabitants.

Independent of the transport distance each 1% increase in sludge solids reduces the life cycle cost by 2.5%, and increases polymer consumption by only 0.2%. At a 100 km transport distance the savings amount to over 2 USD/pe/annum for each percent in solids, while at a transport distance of 40 km these savings are slightly over 1 USD/pe/annum. The additional polymer cost to achieve those savings, at 40 km, is 0.02 USD/pe/annum. Therefore, when a flocculant can increase the dry material of the sludge by 1.6% (for example from 16% to 17.6%) it has no, net, life cycle cost.

Each percentage increase in sludge concentration reduces global warming potential, as measured in CO<sub>2</sub> equivalents by 0.2 kg/pe/annum (Rebitzer et al., 2003). A flocculant which would increase the dry solids by 1.6%, as per the example in the previous paragraph, would reduce the global warming potential contribution of the flocculant itself by one-third. Therefore, both the life cycle cost and the environmental impact, as measured by the life cycle assessment, are both highly sensitive to the solids level of the sludge prior to transport, or in the case of incineration, drying.

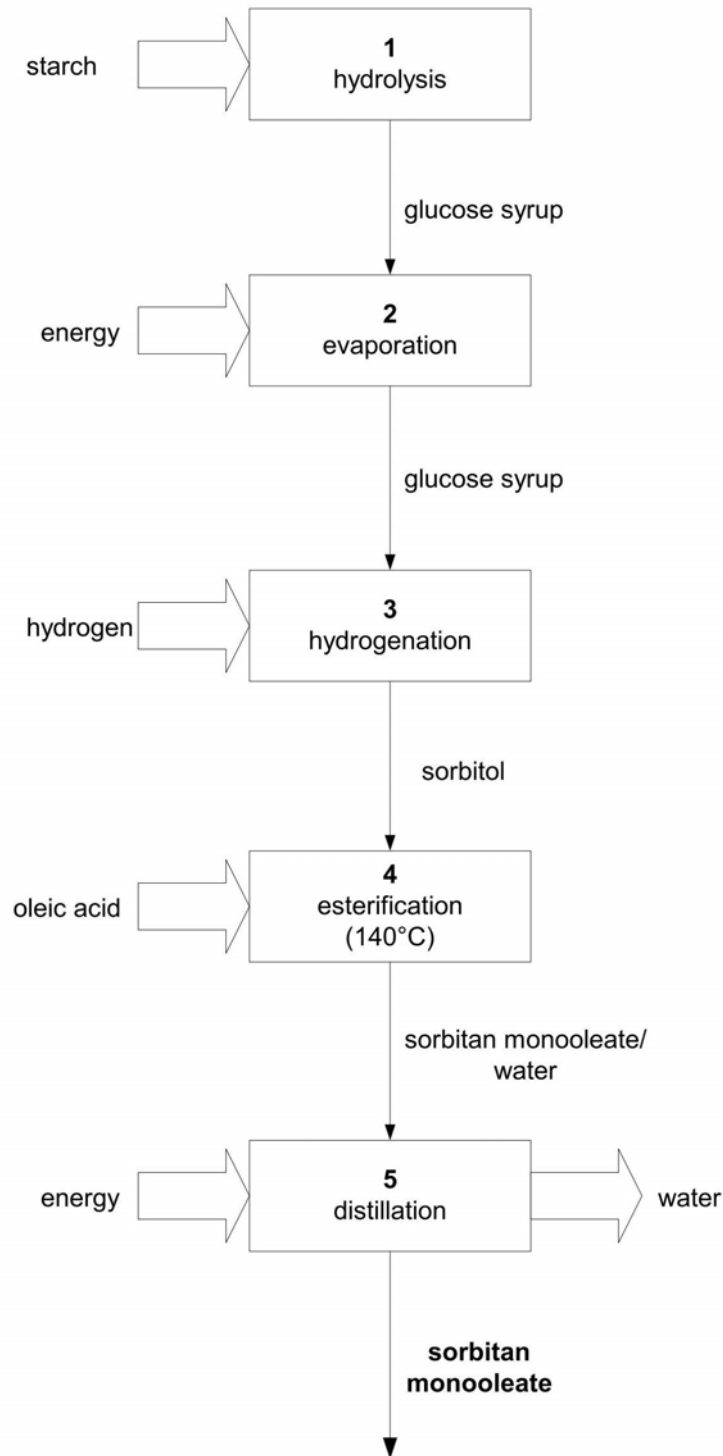
#### **4 SUMMARY**

In this study a life cycle inventory model was used to assess the impacts of municipal waste water treatment. A base case with no water treatment was compared to scenarios where coagulants and flocculants were employed with ultimate disposal either by landfill or incineration. Five polymeric flocculants were also compared, having cationic charges between 35 and 65 mol%. The effect of the flocculants was to influence the dry material of the final filter cake, which in turn altered the eutrophication and resource-depletion potential. Sludge dryness was also found to have an important impact on the life cycle cost, in particular via reduction in the transport and drying expenses.

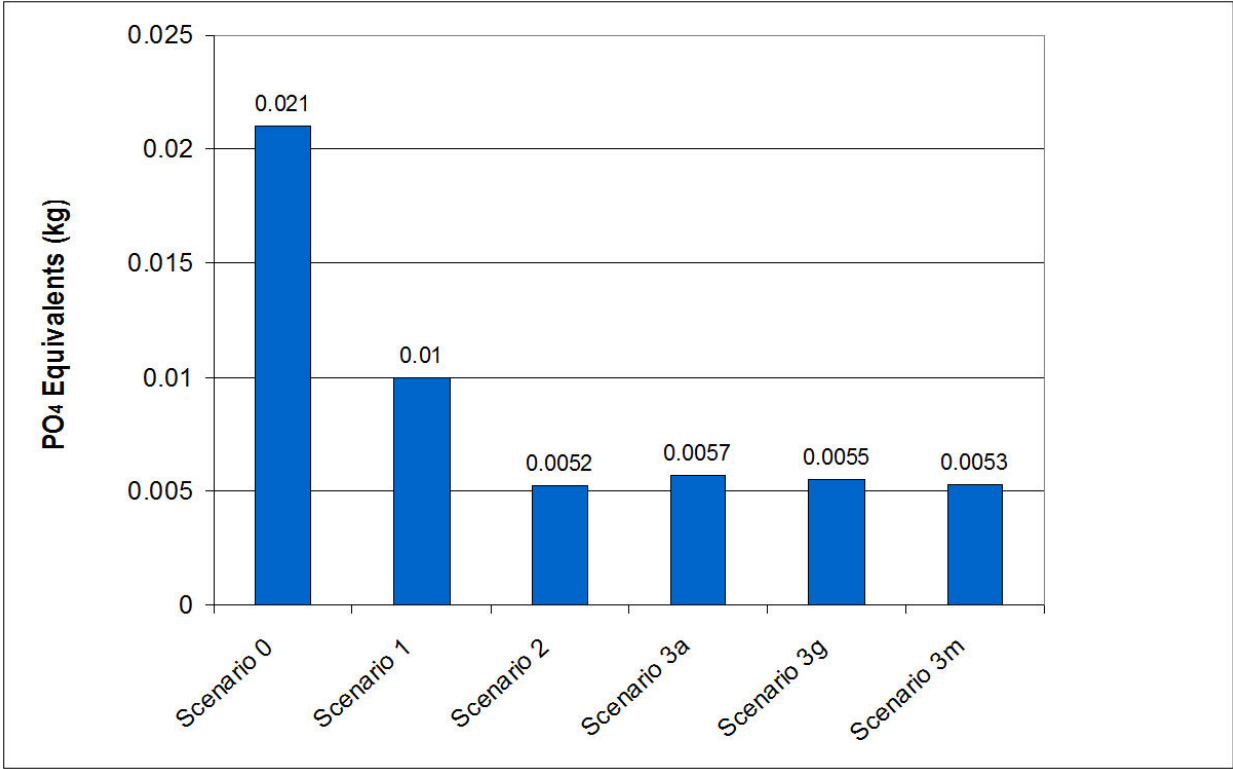


**Figure 3.** Upstream materials used in the production of the cationic monomer, the main ingredient in dewatering flocculants. A diverse set of raw materials are observed, the majority of which are linked to crude oil.

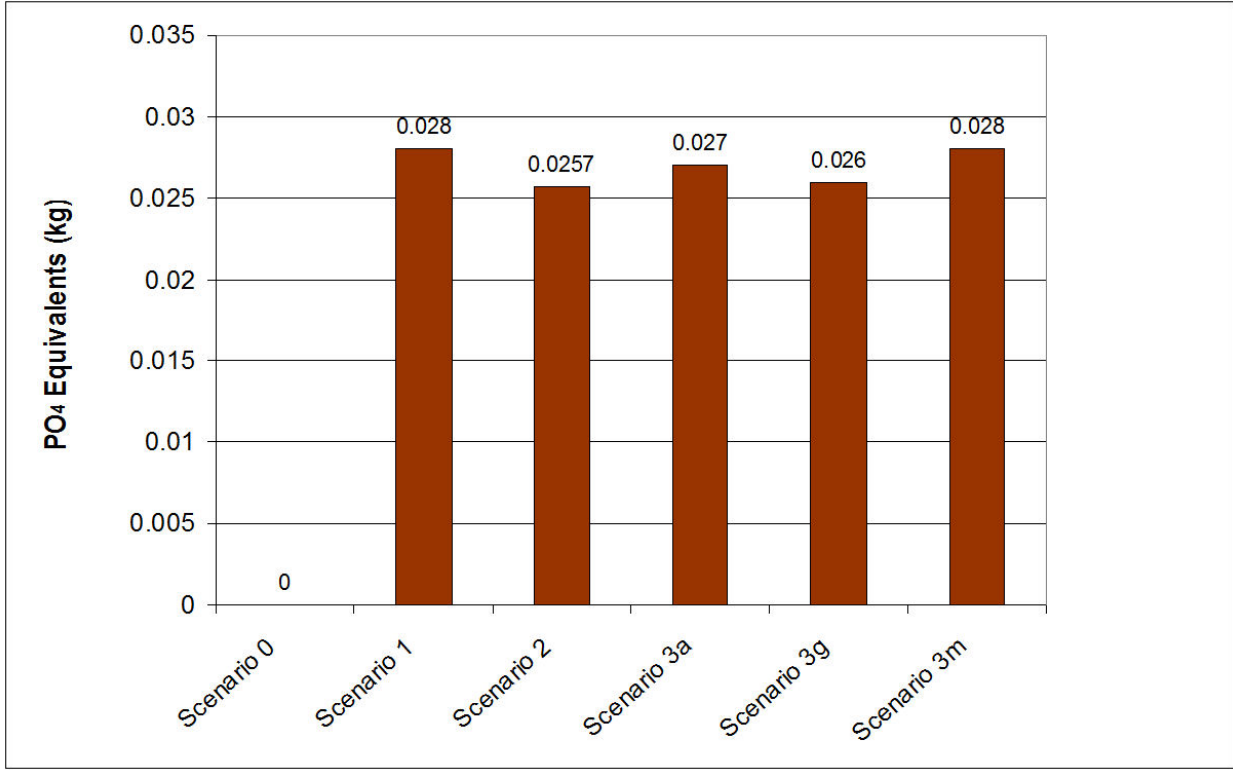




**Figure 4.** Upstream materials used in the production of a surfactant used to stabilize the emulsion-based flocculants. The derivation of many products of natural origin (e.g. starch, oleic acid) is evident, as is the by-product (water).



**Figure 5.** Aquatic eutrophication potential, over the life cycle, for six water treatment scenarios.



**Figure 6.** Terrestrial eutrophication potential, over the life cycle, for six water treatment scenarios.

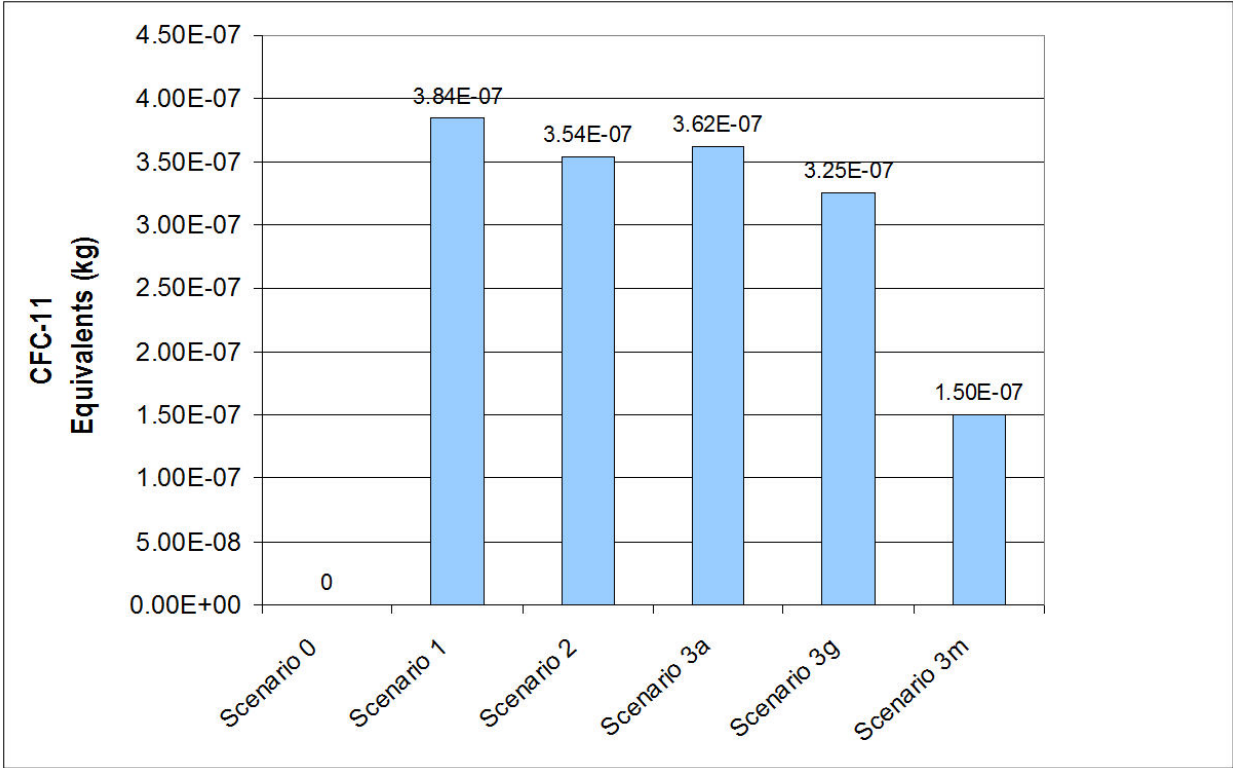


Figure 7. Ozone depletion potential, over the life cycle, for six water treatment scenarios.

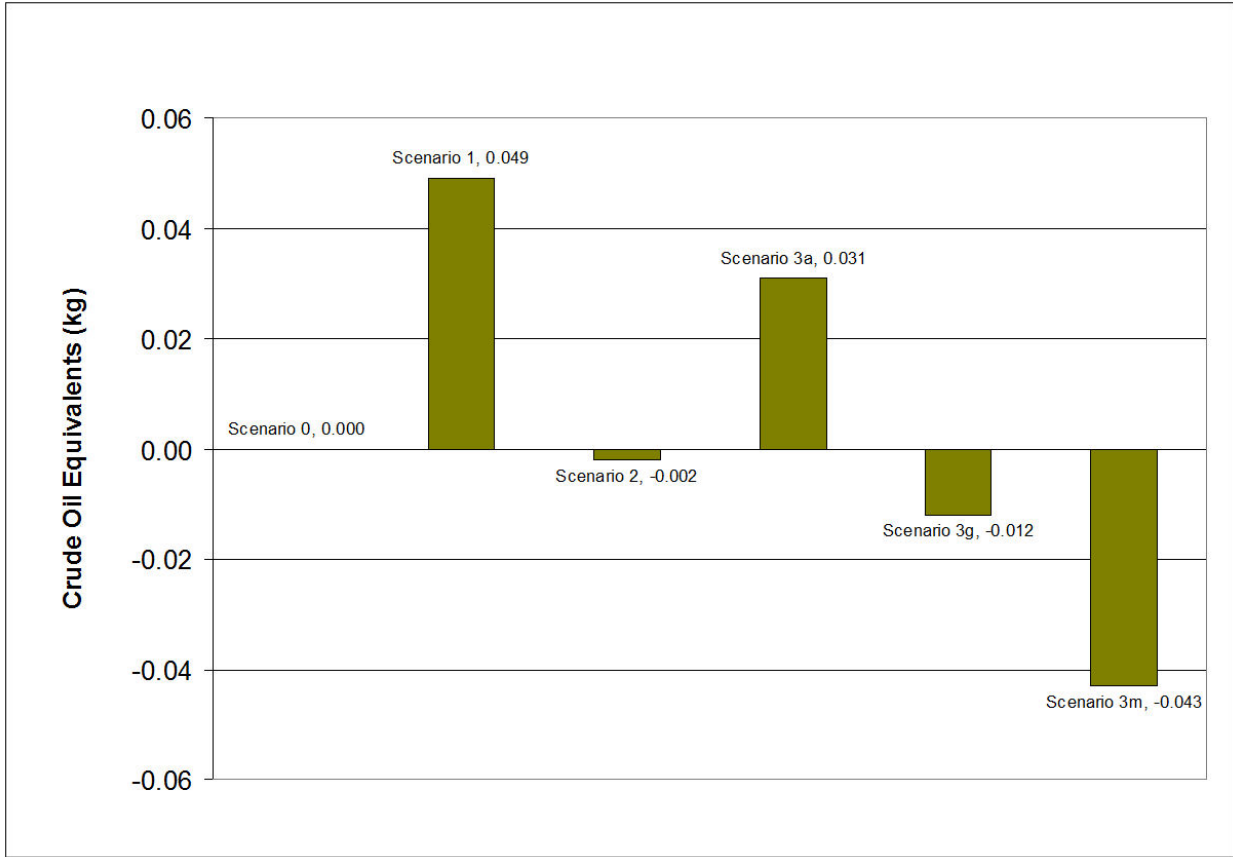
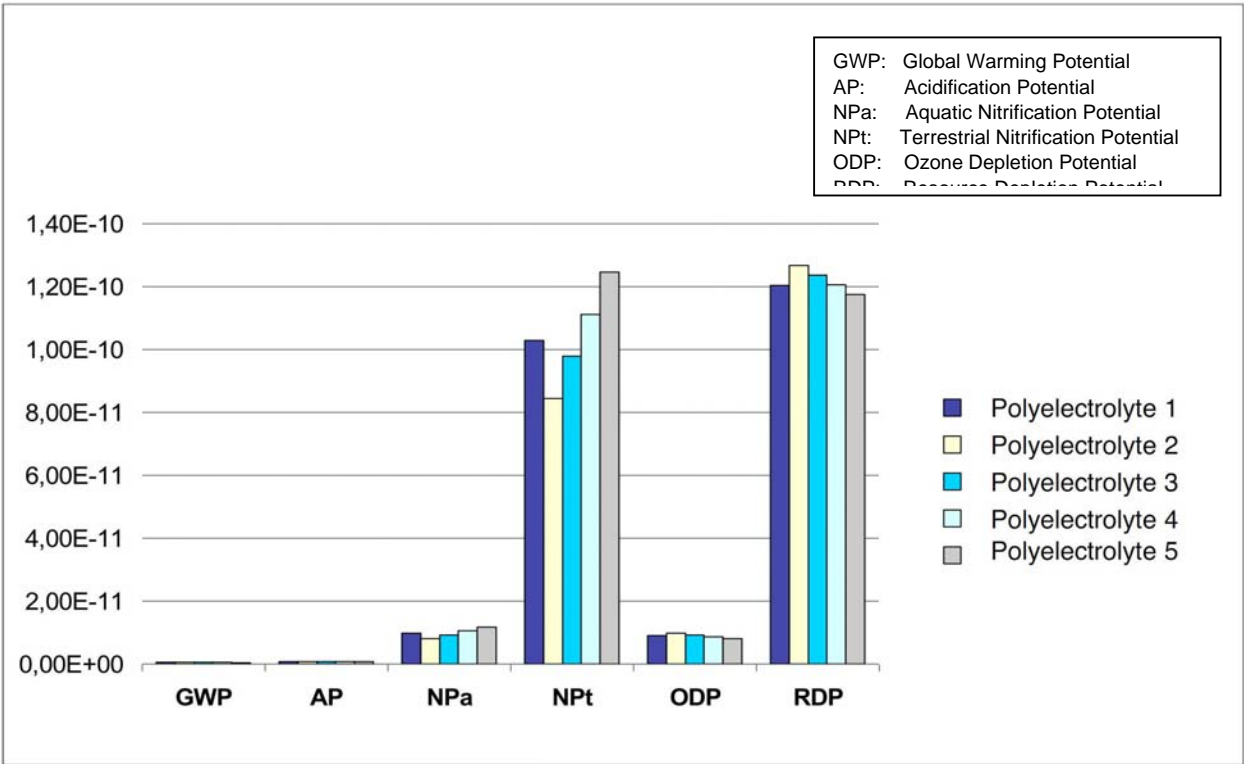


Figure 8. Resource depletion potential, over the life cycle, for six water treatment scenarios.



**Figure 9.** Summary of the main, normalized environmental indicators linked with the life-cycle of five flocculants (polyelectrolyte 1-5). Nitrification potential (NPt) is the most influenced with resource depletion also significantly varying.

## **GLOSSARY**

**Coagulants** are small molecules which can be inorganic or organic in nature. Metal based coagulants include the ferric sulphate and chloride as well as aluminum based materials. The monomeric aluminum sulphate can be polymerized to yield polyaluminum chloride (PAC), generally with a molecular weight in the 5,000 to 12,000 g/mol range. PACs are available with slightly different chemistries as expressed by the degree of basicity. Organic coagulants are generally with a molecular weight in the low hundreds of thousands of daltons and based on polyamines and polyDADMACs. Coagulants work well on the pre-treatment of water, removing fines and color. Many coagulants can be blended, including iron and aluminum as well as PAC with either polyamines or pDADMACs. They are applied in decanters in water treatment works and can have a physical-chemical role, in addition to their influence on sedimentation, in lowering phosphorous.

**Eutrophication Potential** is the potential nutrients to cause over-fertilization, both of water and land, which can result in increased biomass. It is expressed in terms of an emission such as NO<sub>x</sub>, ammonia, chemical oxygen demand or phosphate. These are all converted in phosphate equivalents using classification factors. As an example, 0.42 kg of nitrate are considered equivalent to 1 kg of phosphate and 0.022 kg of COD.

**Flocculants** are large molecules, soluble in water, with a size on the hundred nanometer scale. They are used to separate solids from liquids based on charge-charge interactions which induce adhesion. Depending on the density of the solid and media, either sedimentation or floatation. Flocculants are part of a family of molecules called "polyelectrolytes" indicating that they are both polymers, of Greek origin meaning something of many (poly) parts (mer) as well as charged (electrolyte, indicating a salt).

**ISO** is an abbreviation for the International Organization for Standardization

**ISO 14040** is a an international standard, last revised in 2006, describing norms for environmental management and product life cycle assessment.

**Life Cycle Assessment (LCA)** is a tool to compare the environmental impacts of alternative products. It includes all impacts linked with the up-stream activities of the product, including the extraction and transport of raw materials and any pre-processing. The impact of the product during production, use and end-of-life disposal is also considered. The method, in its most evolved form, was developed by the Society of Environmental Toxicology and Chemistry (SETAC).

**Life Cycle Costing** summarizes all costs associated within the life cycle of a product that are directly covered by one, or more, of the actors in the product life cycle (e.g. supplier, producer, user/consumer, End-of-Life actor). These costs must relate to real money flows and as they can be referred to as "internal". Costs that are not presently part of the product system (i.e. external costs or "externalities) though anticipated to be internalized in the decision relevant future are to be included as well. A complementary product system, with equivalent system boundaries and the equivalent functional unit to LCA is also required. Life Cycle Costing is performed on an analogous basis as Life Cycle Assessments, with both being steady-state in nature (Hunkeler et al., 2008).

**Person Equivalent** can be defined as 60 g BOD/day or 200 l/day of water.

**Resource Depletion Potential (RDP)** is an environmental impact measured as part of a Life Cycle Assessment. Abiotic RDP can include estimations of the depletion of both non-renewable or renewable (wind, flowing water) resources as the result of a transformation, generally upstream of the product, of a material.

**Sustainable Development** is defined by the World Commission on Environment and Development, chaired by Gro Harlem Brundtland, former Prime Minister of Norway, was mandated by the United Nations in 1983. Specifically, "Sustainable development is development that meets the needs of the

*present without compromising the ability of future generations to meet their own needs” (UN World Commission on Environment and Development., 1987).*

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