Dynamic Simulation of an Organic Compound Release in Wastewater Treatment

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Abstract
Transient or intermittent releases of specific volatile or semi-volatile organic compounds are not managed well by existing predictive fate models such as TOXCHEM+ or Water9 because they are based on steady-state conditions. In this paper, dynamic modeling of a wastewater treatment system treating an accidental release of acetone is analyzed to determine peak emission rates and total mass loadings to air and effluent. Remedial actions such as nutrient addition to promote biomass growth for biodegradation, and use of off-line storage with slow return pumping to treatment are compared to passive acceptance of the release in treatment. Certain remedial strategies prove more effective in minimizing air emissions and effluent releases than others, demonstrating the benefits of the dynamic modeling approach.

Key Words: dynamic model, wastewater, fate, organic compound

Introduction

Wastewater treatment plants are subjected to fluctuating concentrations of trace organic and metal contaminants. (Monteith, 1986). In industrial settings, batch operations in different processing areas are common, and contribute short-term waste loadings of variable composition to the industry's wastewater treatment facilities. The mix of industrial solvents, process materials and reaction by-products from different production schedules can result in a highly variable mix of contaminant concentrations. While such variations are "normal" operation, industrial wastewater treatment facilities may also be subject to treatment of accidental releases of product or raw material to mechanical failure, disaster or human error.

General fate models (GFMs) such as TOXCHEM+ (Hydromantis, Inc.) and WATER9 (U.S. EPA) are used to predict the fate of specific organic and metal contaminants in wastewater treatment. To date, these GFMs are constructed as steady-state models. As such, they represent an average condition, rather than a more accurate and realistic assessment incorporating time-dependent dynamic conditions. Steady-state modeling is accepted by regulatory agencies for reporting emission rates on a monthly or annual basis, as this application represents the "average" conditions for the time period.

There are other applications, however, that require an assessment beyond the capability of steady-state models. Incidents of a short-term variable nature, such as an accidental release of materials used in a process (e.g. valve left open, ruptured gasket or a crack in heat exchanger elements) can affect the operation of a treatment system or the health and safety of personnel employed in the wastewater treatment area. At such times, a dynamic process simulator may provide a much more useful to determine the appropriate response or strategy for dealing with the transient release.

This paper describes the benefits of combining the TOXCHEM+ predictive fate software with the dynamic general purpose simulator (GPS-X) for investigating and responding to a contaminant release in wastewater treatment, based on an actual release situation at a petrochemical plant.

Objective

The goal of this paper is to demonstrate the importance of coupling of a dynamic wastewater treatment simulator with models for (a) predicting the fate of volatile organic compounds or hazardous air pollutants during wastewater treatment; and (b) providing guidance for the optimal method of treating the accidental release of an organic compound in wastewater treatment

Background on Wastewater Treatment Modeling and Simulation

Numerical modeling of the activated sludge process is a common engineering analysis tool that has gained popularity and acceptance over the past two decades. There are two commonly-used, and essentially different, approaches to modeling treatment systems in use today: steady-state and dynamic. Steady-state simulation is a more straight-forward approach that assumes all inputs to the system are constant, and solves for a result that is representative of the system at equilibrium. Dynamic models allow for time-varying input, and can simulate how a system responds to changes in driving forces, internal operation or other external stimuli.

TOXCHEM+ predictive fate software employs the steady-state approach. It uses mass balance and kinetic rate expressions to estimate the behaviour of specific trace organic contaminants in wastewater treatment. The mathematical models in TOXCHEM+ are written in a steady-state format, and therefore are not suitable for evaluating dynamic conditions in wastewater treatment systems, as typified by a temporary spill condition. The basis for the modeling equations in TOXCHEM+ have been discussed by Melcer, et al. (1994).

GPS-X is a wastewater process simulator that employs the dynamic modeling approach. It includes a number of robust biological treatment process models, such as the ASM1 (e.g. Henze et al., 1987). The ASM1 biological model, developed by the International Water Association in 1987, uses 13 constituent components to mechanistically describe the transformation and removal of carbon and nitrogen in activated sludge systems. Because the model is dynamic-mechanistic in nature, it can be used to study the complexities of a spill situation. However, ASM1 (and its subsequent derivatives ASM2, ASM2D and ASM3) deals only with BOD, COD, TSS and nitrogen compounds, and does not address the fate of trace organic contaminants such as those included in TOXCHEM+.

Combining the Two Approaches

Supplementing the dynamic activated sludge modeling approach used in GPS-X with the trace organic contaminant fate models of TOXCHEM+ provides modelers with a tool that can be used to evaluate the treatment of traditional waste streams containing intermittent releases of specific volatile and semi-volatile organic compounds The dynamic modeling capabilities also allow users to investigate more types of simulation scenarios than could be achieved with the steady-state approach.

Example Scenario

We present a situation based on a real event, which illustrates the benefit of the dynamic modeling to address procedures for dealing with the release of a concentrated organic substrate to the wastewater treatment system. A spike of a highly concentrated product to the process wastewater (typical during an accidental release), can result in several process-related concerns. For example, the spike of material to the biological system can result in a nutrient deficiency (e.g., nitrogen and phosphorus) that will limit the ability of the microbes in the mixed liquor to utilize the organic substrate. Without nutrient supplementation, the incomplete utilization of the organic spike can result in elevated concentrations of the compound emitted to air and discharged in the plant effluent. A second issue that may arise is that the very substantial organic loading may exceed the capacity of the aeration equipment to maintain the required minimum dissolved oxygen concentration.

Other concerns from an accidental release of concentrated organic material relate to the wastewater treatment facility achieving the required effluent concentrations of air emission rates stipulated by operating permits. Effluent quality, in terms of $CBOD_5$ as well as the specific organic substrate involved in the release may exceed mandated levels. As well, air emissions will increase from the wastewater treatment system, from stripping of the organic substrate due to aeration, and volatilization from open basin surfaces. The emission rate and mass emitted may pose an environmental risk, although actual exposure of plant and neighbouring people to the air emissions can only be determined by coupling the dynamic model to an air dispersion model. Such projects have been accomplished using a steady-state model coupled to an air dispersion model (Monteith and Thompson, 1993).

Modeling Scenario– Offline treatment for accidental release management

The model can also be used to evaluate and optimize the treatment of an industrial wastewater containing a temporary concentrated acetone spike in the process wastewater stream. The high concentration of acetone resulted from an accidental release due to a crack in a pump casing on a pad in the process area. Process wastewater is collected for treatment separately from stormwater run-off. To meet effluent quality limitations imposed by regulating agency, the treated effluent cannot exceed a concentration of 50 ug/L. The amount of time required to reduce the acetone concentration is a function of the incoming acetone concentration, incoming flow, and process operation. This combination of factors can lead to a complex treatment system that cannot be addressed with a steady-state model.

Using the combined GPS-X/TOXCHEM+ approach, modelers can address questions such as:

- At what rate can the wastewater with elevated acetone levels directed to off-line storage be returned to the main liquid treatment train?
- What will be the maximum mass air emission rate and total emission loading to the atmosphere from the combined off-line basin and aeration basin?
- Are there nutrient limitations that govern the rate of pumping back the elevated acetone stream from the off-line basin?
- Are there limitations on the aeration capacity of the activated sludge system that would effect the rate of pumping back the acetone stream from off-line storage?

Baseline and Accidental Release Scenario

The wastewater treatment plant receives a consistent flow and organic loading on a daily basis, with some diurnal fluctuation evident. Under normal conditions the wastewater treatment facility receives an average flow of 2,000 m^3/d (0.5 MGD), with a typical COD value of 150 mg/L. The acetone concentration, as determined by GC methods, is typically 0.5 mg/L.

The accidental release of acetone lasted for a 12 hour period, and was released from the faulty pump at a constant rate of 34 L/min (9 gal/min). The total loss of acetone escaping to the process wastewater from this release was estimated as 1434 m^3 (379 gal). The schematic of the treatment system, as described in the above scenario, is depicted in Figure 1.

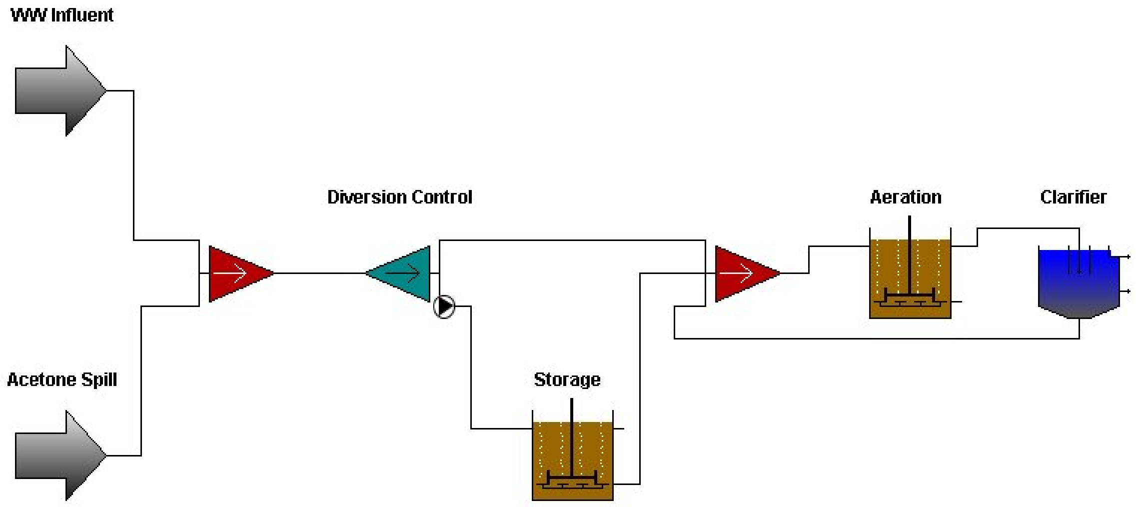

Figure 1. Process Schematic for Modeling of Accidental Release of Acetone

For simplification, the modeling units of interest include an open off-line storage basin, and a coupled conventional activated sludge aeration basin and secondary clarifier. Details of the Process Units are provided in Table 1.

Table 1. Input Parameters of Process Modeling Units

Parameter	Storage Basin	Aeration Basin	Clarifier
Volume (m^3)	10,000	1,000	300
Surface Area (m^2)	270	125	100
HRT (hours) under default spill simulation scenario	-	6	1.8
RAS flowrate (m^3/d)	-	-	2,000
WAS flowrate (m^3/d)	-	-	40
Airflow (m^3/d)	0	25,840	-

Results

Baseline without release

The Effluent carbonaceous biochemical oxygen demand ($CBOD_5$) and total suspended solids (TSS) concentration profile over a period of 5 days is presented in Figure 2. The slight diurnal fluctuations are present in the TSS profile, ranging from 10-18 mg/L. Effluent $CBOD_5$ remains low at about 4-5 mg/L through this period.

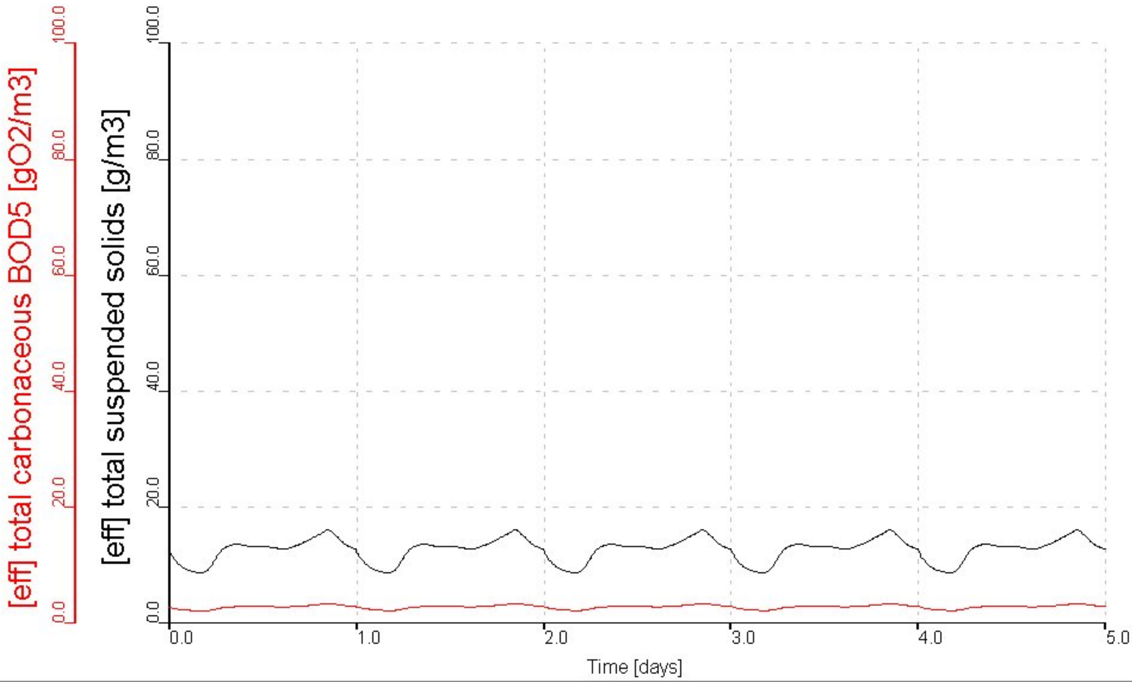

Figure 2. Effluent Quality Profile during Baseline Operation

Accidental Release - Scenario 1, No action taken

The effect of an accidental release on the operation of a treatment system can be onerous; a release of a substrate such as acetone, will exert a very large organic load to the secondary treatment system, resulting in concerns about aeration capacity and partial substrate utilization due to nutrient limitations.

The release of acetone due to the mechanical pump failure occurs at day 1.0 in Figure 3, and lasts for 12 hours (0.5 days). As a result of the influx of acetone, with no mitigating action, the concentration of the compound expressed as COD in Figure 3, rises dramatically, to a value of 835 mg/L (off-scale). The effluent concentration does not return to a more normal value until approximately 1.5 days have passed, or a full day after the release ended.

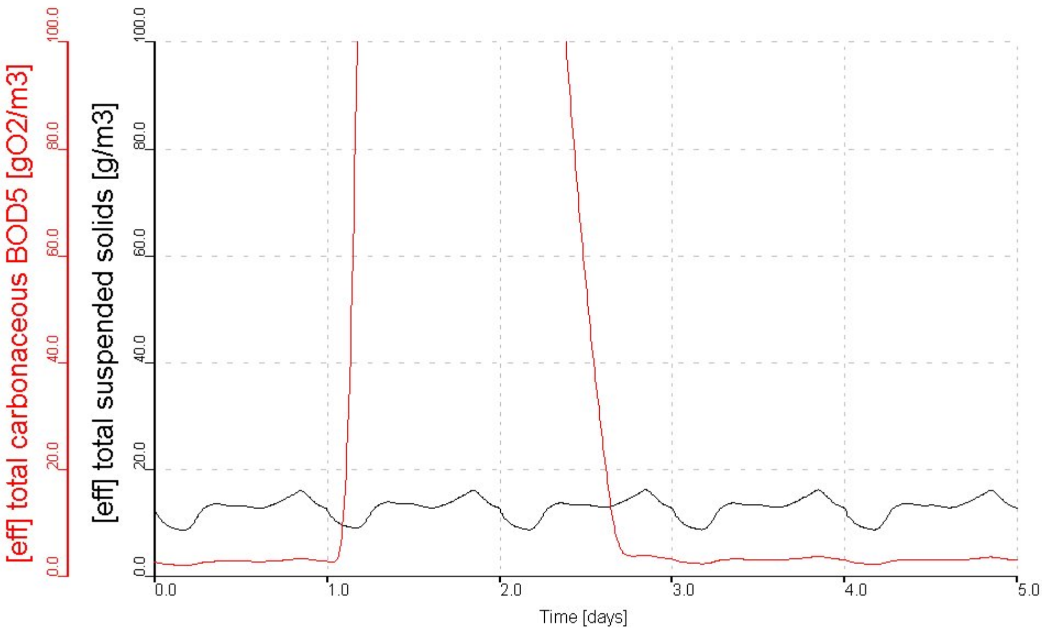

Figure 3. Effluent Response to Acetone Release with No Mitigating Action.

The impact of the release on the acetone emission to air, without any action at the treatment system, is provided in Figure 4. The liquid phase measurement reflects the extra detention time provided by the secondary clarifier. In this scenario, the off-line storage basin was not utilized for mitigation of the release, and so there is no predicted acetone emission from the basin. The maximum emission rate from the aeration basin is 240 kg/d expressed as COD.

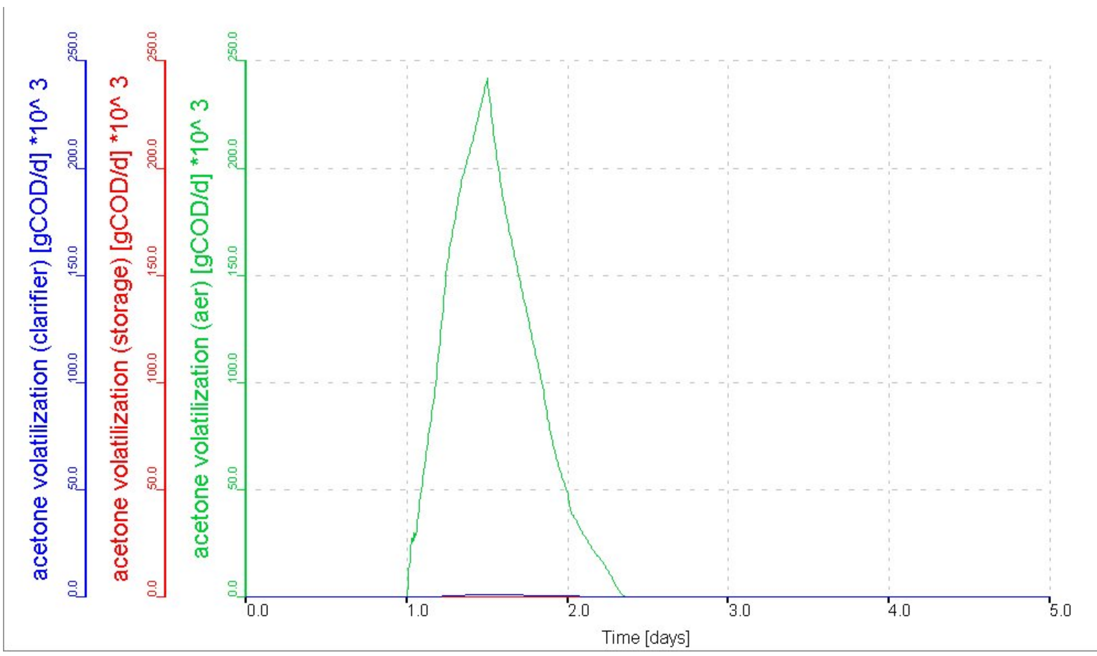

Figure 4. Emission of Acetone from Wastewater Treatment with No Mitigating Action

Although the emission of acetone to atmosphere from the aeration basin is substantial, the greatest portion of the release would be expected to pass through the treatment system in the effluent.

Scenario 2 – Addition of Nutrients

Due to use of online instrumentation such as TOC or respirometers, some action can be taken to reduce the impact of the acetone release on the environment. As a first mitigating action, a nitrogen supplement is added to assist the utilization of the acetone as a substrate by the mixed liquor biomass. Figure 5 indicated the effect of the nitrogen supplementation on levels of dissolved oxygen, mixed liquor suspended solids and the aeration rate. When the biomass is not nitrogen-limited, the MLSS concentration increases substantially while utilizing the acetone as its substrate. As a result more air is required to maintain oxic conditions in the reactor. Based on dissolved oxygen control, there is an initial sag in the D.O. concentration until the control takes over.

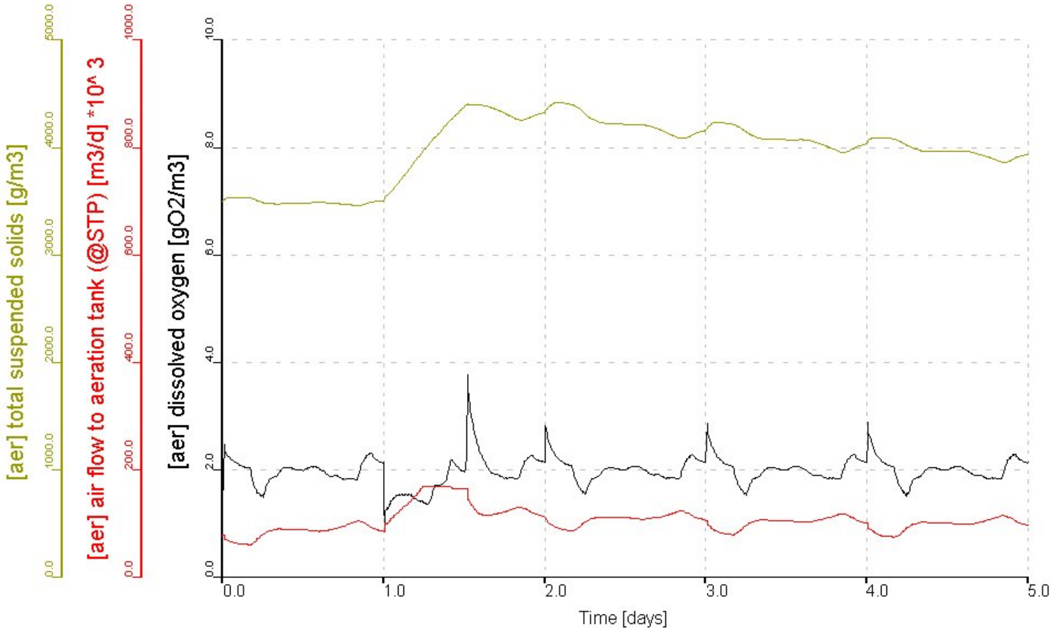

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Figure 5. Effect of Acetone Release on Air Flow, Dissolved oxygen and Mixed Liquor Suspended Solids

The effect of the nitrogen supplement on the mass emitted to the atmosphere is provided in Figure 6. Because biomass growth is not limited by nutrients, a higher biomass concentration results in greater biodegradation of the acetone. As a result, the maximum emission rate from the aeration basin for acetone declines to 100 kg/d as COD. The double peak is a result of the combination of organic loading and the diurnal flow pattern.

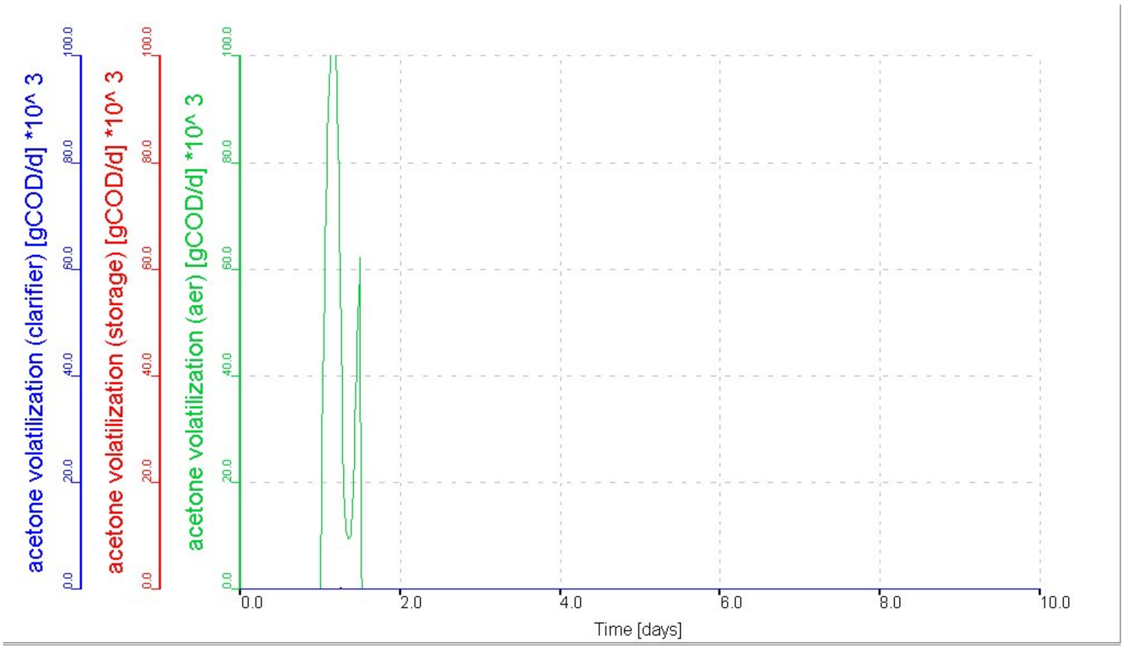

Figure 6. Emission of Acetone from Wastewater Treatment with Nitrogen Addition

The effluent concentration profile for acetone resulting from nitrogen addition is presented in Figure 7. The maximum effluent $CBOD_5$ concentration resulting from the release is now only 80 mg/L, far less than the maximum concentration of 835 mg/L when no action was taken. The double peak in the effluent concentration profile results from the combination of the high strength wastewater and maximum daily flow rate of the diurnal flow pattern.

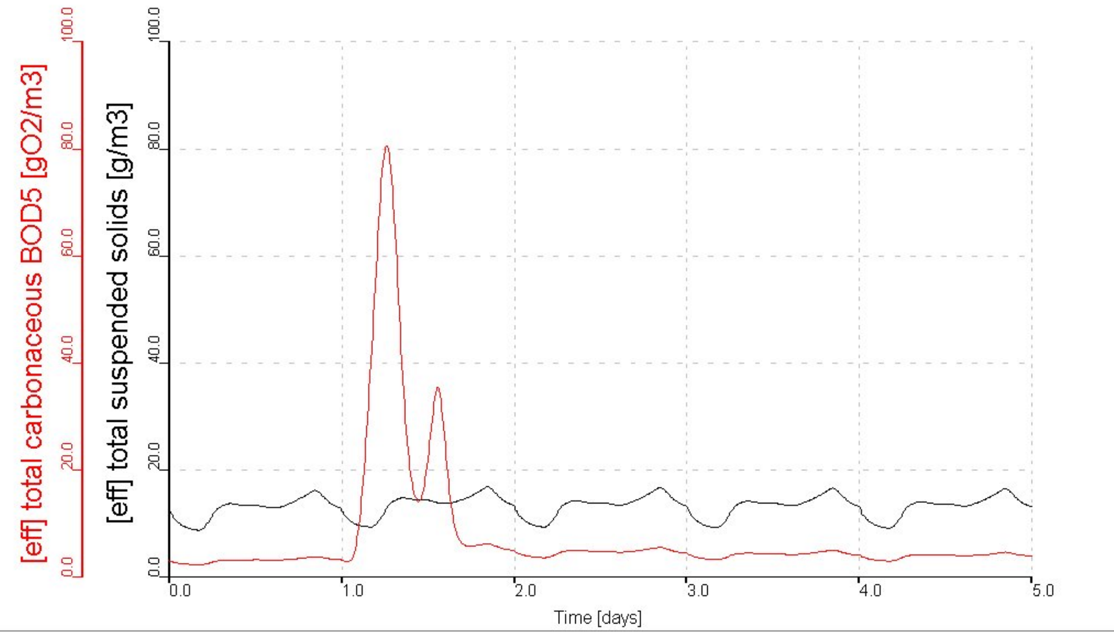

Figure 7. Effect of Acetone Release on Effluent $CBOD_5$, Supplemental Nitrogen Addition

Scenario 3 – Off-line Storage of Accidental Release Wastewater
Rather than simply accepting the wastewater through the existing treatment facility, the manufacturing site has the capability of diverting the acetone-contaminated wastewater to an off-line storage basin. This protective action is implemented when on-line sensors (e.g., total organic carbon (TOC), dissolved organic carbon (DOC), or respirometer) alert operators to the presence of a challenging wastewater. The remedial action is to divert some or all of the wastewater to the off-line basin, then to subsequently pump back the acetone-contaminated wastewater to the main treatment train at a controlled rate so as not to overload the system. The proportion of the contaminated flow to divert is 1500 m^3/d, with a controlled return rate of 150 m^3/d to the main treatment system flow.

The effect of this operation on the acetone emission rate from the treatment system (including aeration and off-line storage basins) is provided in Figure 8. In this treatment scenario, the emissions from off-line storage are significantly higher than from the aeration basin. The large open surface of the off-line storage is vulnerable to emissions due to surface volatilization, which is a function of wind speed and temperature. The emissions from the storage basin continue for an extended period of time following the release of acetone, declining to a negligible rate after approximately 17 days of storage.

Figure 8. Emission of Acetone from Wastewater Treatment with Off-Line Storage

Figure 9 presents the effect of the flow diversion to off-line storage, with subsequent feed back to treatment, on effluent acetone concentration. The maximum effluent concentration is predicted to be 135 mg/L (off-scale). Given the rate of returning of the wastewater from storage to treatment, the peak concentration occurs approximately one day after the release began.

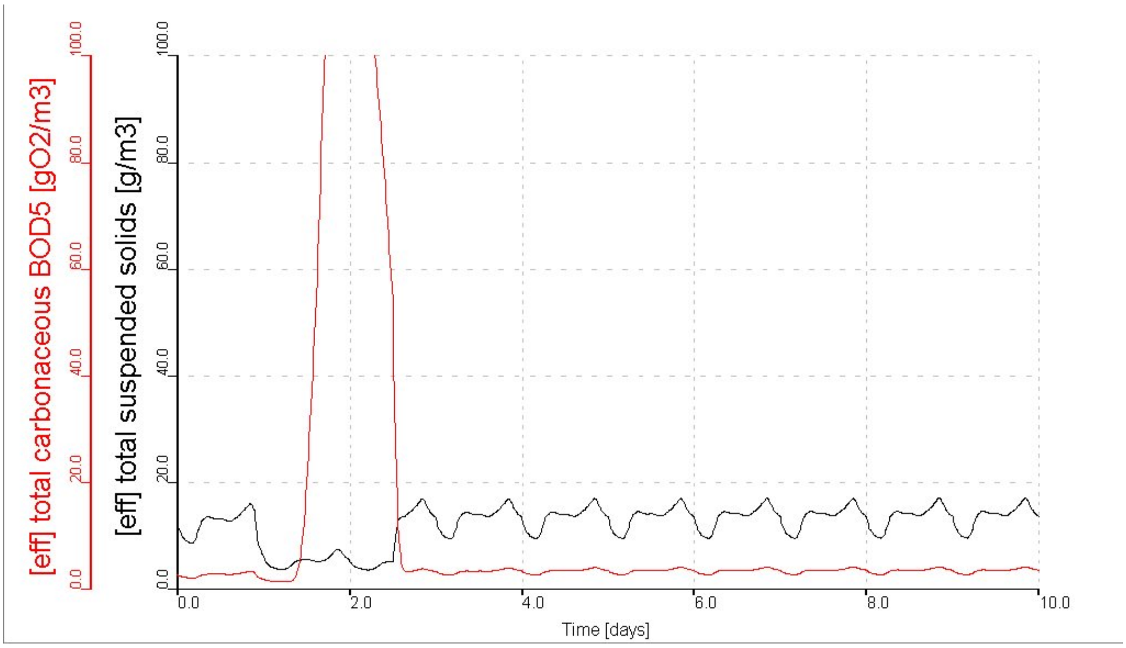

Figure 9. Effect of Acetone Release on Effluent CBOD$_5$, Off-Line Storage and Return Pumping

One of the main advantages of dynamic modeling of organic contaminant fate is the ability to determine the optimum return pumping rate to treatment, given the initial diversion rate of 1500 m^3/d. Figure 10 is a sensitivity analysis of the total environmental fate of acetone based on varying the return pumping rate from off-line storage. Nutrient supplementation was not practiced for this scenario evaluation. The figure is interesting from a number of perspectives. Below a return pumping rate of 300 m^3/d, the situation is relatively stable, with constant amounts released to both the air and in the treated effluent. Above the pumping rate of 300 m3/d, more acetone is discharged in the treated effluent, and less is stripped/volatilized from aeration and off-line storage. As the pumping rate becomes higher and higher, the capacity opf the biological treatment system to utilize the substrate is exceeded, and the effluent concentration rises. The figure reveals that there is an optimum point for minimizing the total environmental release of acetone, at a return pumping rate of approximately 550 m^3/d.

Scenario 4 – Off-line Storage of Accidental Release Wastewater with Optimized Return Pumping Rate

Under the optimized return pumping rate of 550 m3/d the emission rates are predicted as shown in Figure 11. BY this optimized treatment schedule, the emission from the storage basin have been reduced to a maximum rate of 56 kg/d of acetone as COD, while the peak emission rate from the aeration basin is only 30 kg/d of acetone. Moreover, the emissions end after 6 days of storage, compared to 15 days in the un-optimized scenario. The effect of this optimization on treated effluent acetone concentration is depicted in Figure 12.

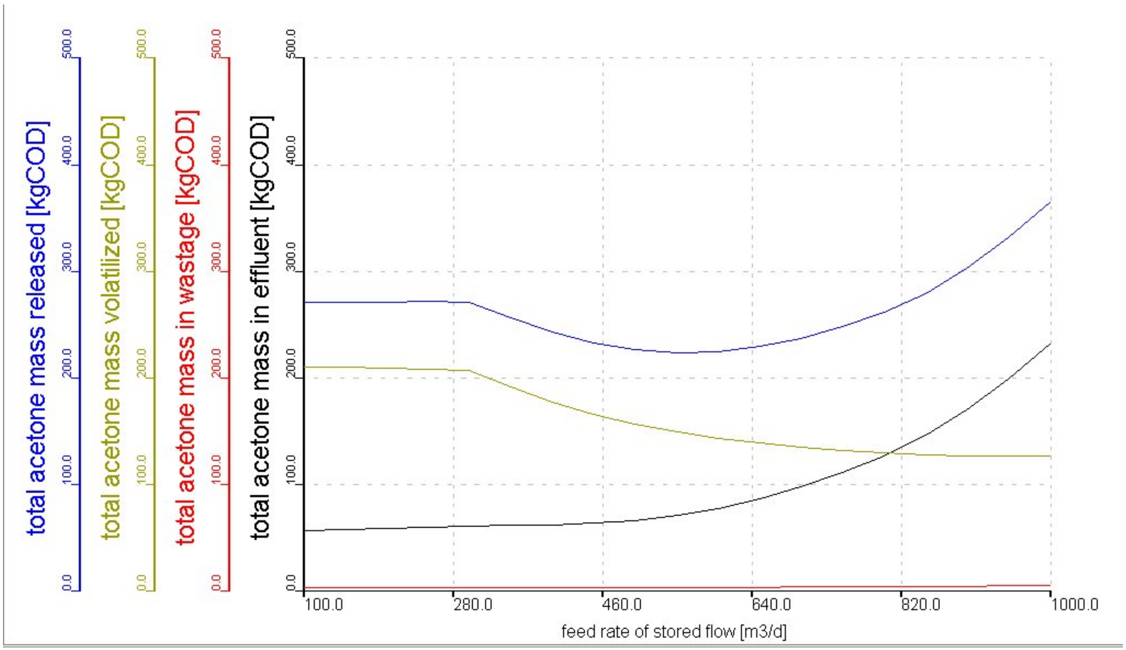

Figure 10. Effect of Return Pumping Rate on Total Environmental Release of Acetone

Figure 11. Emission of Acetone from Wastewater Treatment with Off-Line Storage Optimized for Return Pumping Rate

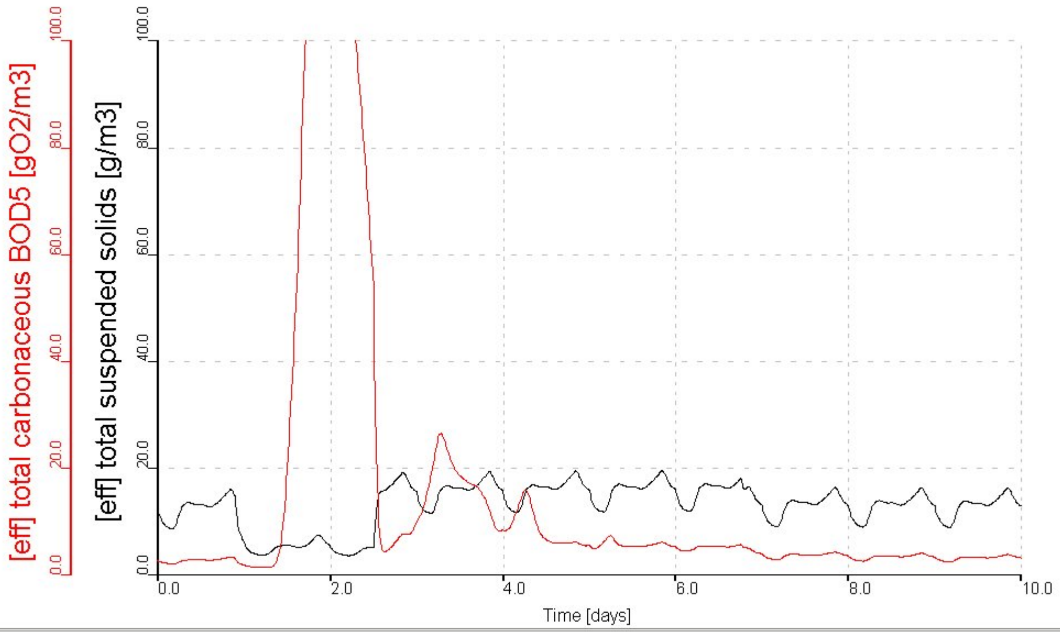

Figure 12. Effect of Acetone Release on Effluent $CBOD_5$, Off-Line Storage and Optimized Return Pumping

Scenario 5- Optimization of Diversion Rate to Off-Line Storage and Return Pumping
With dynamic modeling, it is possible to optimize (i.e. minimize) the environmental release of acetone in both treated effluent and air emissions. By performing this scenario, the simulation reveals that the optimized diversion rate to off-line storage is 1914 m3/d, with a return pumping rate of 582 m3/d.

The air emission rates from this optimized scenario are provided in Figure 13. The emission rates are not that different from those of Figure 11, although the emission rate from the aeration basin is reduced. The optimized scenario does have a more significant effect on the treated effluent concentration of acetone however, as indicated in Figure 14. In this scenario, the maximum acetone concentration does not exceed 32 mg/L as COD.

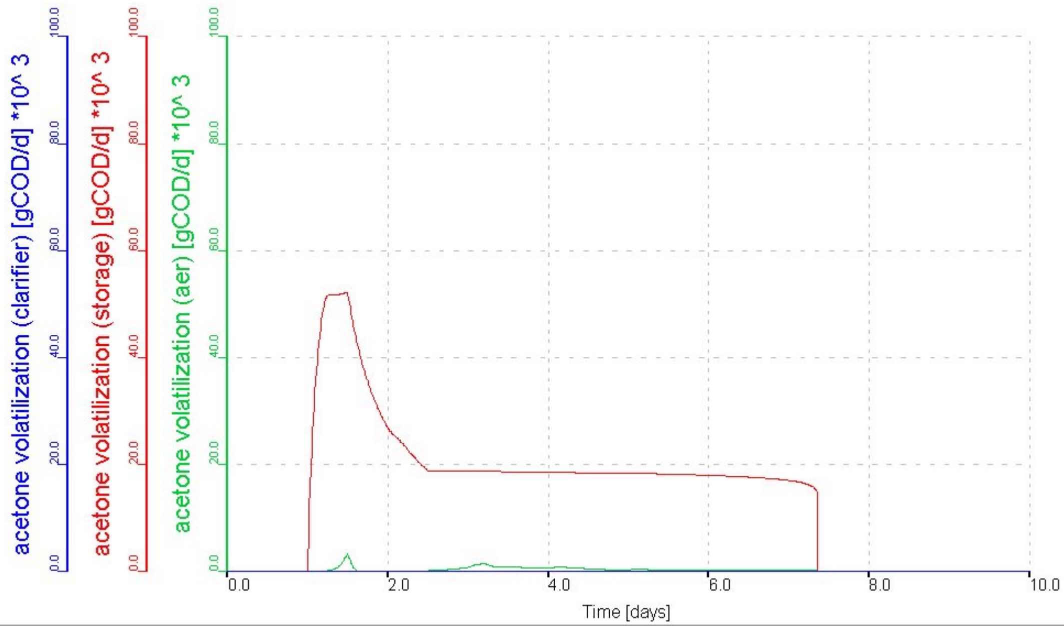

Figure 13. Emission of Acetone from Wastewater Treatment with Off-Line Storage Optimized for Diversion Rate and Return Pumping Rate

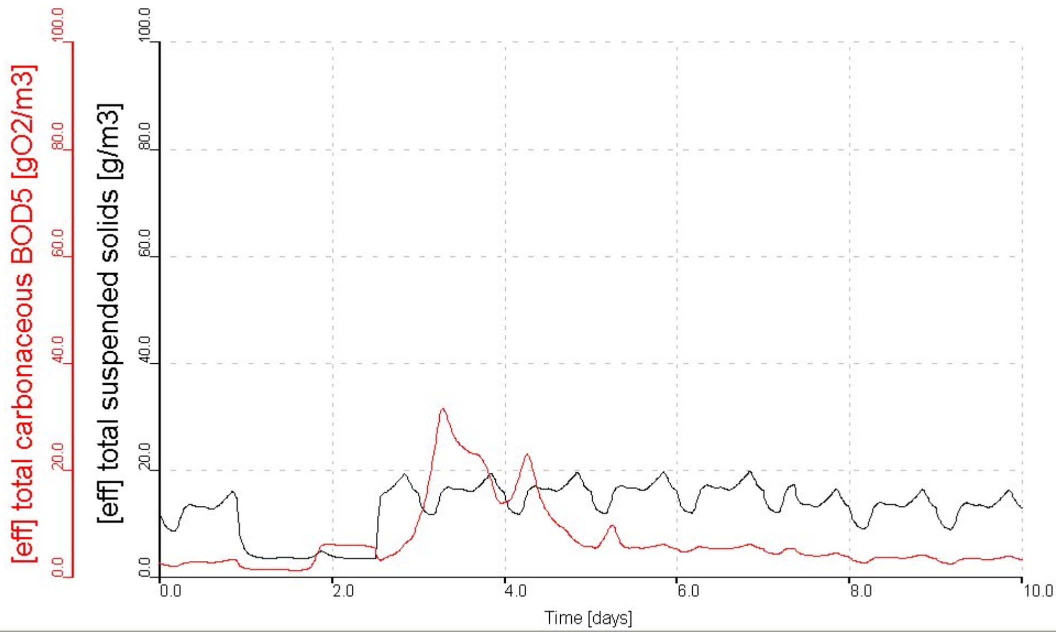

Figure 14. Effect of Acetone Release on Effluent CBOD$_5$, with Off-Line Storage Optimized for Diversion Rate and Return Pumping Rate

Fate Summary of Scenarios

The mass fate distributions of acetone from the different simulation scenarios, as presented in Table 2, indicate that optimal treatment of an accidental release can be significantly mitigated by taking the appropriate actions. Acceptance of the acetone release to treatment with no action results in 1668 kg of acetone as COD released to the environment, mostly in the liquid effluent. Nutrient (nitrogen) addition to promote biomass growth and biodegradation of the acetone is the best overall strategy investigated, with 80 kg of acetone discharged in total of the original 2500 kg released, and only 26 kg released as air emissions. Optimization of the off-line storage and return pumping is also an effective strategy, achieving an overall total release of 165 kg/d of acetone as COD, although most of the discharge is from air emissions from the off-line storage

Table 2. Mass Fate of Acetone from Different Treatment Scenarios.

Scenario	Description	Acetone (kg COD) in				
		Effluent	Wasted in solids	Volatilized	Biodegr.	Total released
1	no spill	0	0	0	0	0
2	Spill	1496	30	143	832	1668
3	spill with nutrient addition	52	1	26	2420	80
4	spill with diversion (1500m^3/d in and 150 m^3/d out)	60	3	336	2100	400
5	sensitivity with fixed diversion - optimal results: 550m^3/d feedback	71	4	149	2276	224
6	optimization of diversion and feedback	22	1	142	2335	165

Summary

Until now, fate simulations of specific organic compounds has been under steady-state conditions. In reality, most treatment plants accept intermittent, dynamic and/or discontinuous releases of organic materials that do not lend themselves to steady-state analysis. The dynamic fate simulation of organic compounds is a powerful tool than can be used to investigate, analyze and optimize treatment systems to minimize total environmental releases resulting from incidents such as accidental releases of materials.

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