

Seasonal ammonia losses from spray-irrigation with secondary-treated recycled water

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ABSTRACT

This work examines ammonia volatilization associated with agricultural irrigation employing recycled water. Effluent from a secondary wastewater treatment plant was applied using a center pivot irrigation system on a 12 ha agricultural site in Palmdale, California. Irrigation water was captured in shallow pans and ammonia concentrations were quantified in four seasonal events. The average ammonia loss ranged from 15 to 35% (averaging 22%) over 2-h periods. Temporal mass losses were well-fit using a first-order model. The resulting rate constants correlated primarily with temperature and secondarily with wind speed. The observed application rates and timing were projected over an entire irrigation season using meteorological time series data from the site, which yielded volatilization estimates of 0.03 to 0.09 metric tons NH₃-N/ha per year. These rates are consistent with average rates (0.04 to 0.08 MT NH₃-N/ha per year) based on 10 to 20 mg NH₃-N/L effluent concentrations and a 22% average removal. As less than 10% of the treated effluent in California is currently reused, there is potential for this source to increase, but the increase may be offset by a corresponding reduction in synthetic fertilizers usage. This point is a factor for consideration with respect to nutrient management using recycled water.

Key words | ammonia volatilization, emissions rate, mass transfer rate model, recycled water

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INTRODUCTION

Ammonia is a common inorganic nitrogen species in solid and liquid waste streams that enters the atmosphere from a variety of natural and anthropogenic sources. Excessive atmospheric ammonia can produce both human health hazards (Makari *et al.* 2009) and aquatic or terrestrial ecosystem degradation (Elser *et al.* 2007). Global emissions inventories have revealed that domestic livestock is the largest source of atmospheric ammonia (Beusen *et al.* 2008).

Ammonia emissions rates from livestock facilities have been well-studied in terms of manure spreading, slurry injection, irrigation with lagoon wastewater, and other application modes (Petersen & Sommer 2011; Todd *et al.* 2011). These rates are sensitive to the application method as well as the meteorological and soil conditions, including water and air temperature, wind speed, soil pH and antecedent moisture content. Observed ammonia losses from spray irrigation with livestock wastewater can range from 5 to 25% during and within the first few

hours of the irrigation event (Al-Kaisi & Waskom 2002; Whalen & DeBerardinis 2007).

Ammonia emissions from humans via municipal wastewater treatment facilities are less well-documented (Anderson *et al.* 2003; Parnaudeau *et al.* 2009), and are the subject of this work. Specifically, this work focuses on estimating ammonia volatilization for irrigation with recycled secondary effluent, a common practice where water is scarce. The estimates can help understand the fate of ammonia in irrigation with recycled water. This research effort determines field-based volatilization rates using a mass balance approach for an experimental field site, which is irrigated with recycled water applied via a center pivot irrigation system. The resulting seasonally observed ammonia volatilization rates are correlated with air temperature and wind speed. Lastly, site geometry, meteorological data and irrigation schedules are used to estimate hourly flux values, which are integrated to yield annual ammonia volatilization estimates.

EXPERIMENTAL SITE AND METHODS

The project was conducted at a 12 ha experimental agricultural site located in the high desert (elev. 770 m) near Palmdale, California. The source of the irrigation water was secondary recycled water from the Palmdale Water Reclamation Plant (WRP), which is owned and operated by the County Sanitation District No. 20 of Los Angeles County (CSDLAC). The recycled water is pumped to the site through a pipeline, and applied to a rotation of forage crops (alfalfa, sudangrass and 3-way grain, which consists of a blend of corn, barley and oats). This study used 1 of 27 center-pivots over a circular site (radius 200 m). The Palmdale climate is characteristic of a high desert, favoring high evaporation and volatilization rates most of the year with high temperature, low humidity and windy conditions. Winter conditions are significantly cooler. Site soil is loamy fine sand, alluvial in origin (Soil Survey NRCS 2008).

Historical monitoring of the recycled water used at the site indicates that ammonia is the predominant nitrogen species (CSDLAC 2011). The three-year average effluent total ammonia (ammonium, NH_4^+ plus ammonia, NH_3) concentration during the period of this study was 21 mg-N/L and represented over 60% of the total nitrogen, which averaged approximately 30 mg-N/L. The balance is primarily organic nitrogen associated with suspended solids. As the recycled water tends to be slightly basic pH (7.4 to 8.4) and the pK_a of ammonia is 9.3, the NH_4^+ concentrations are typically one to two orders of magnitude greater than the NH_3 concentrations. However, because NH_3 tends to volatilize during irrigation, NH_4^+ rapidly dissociates to maintain equilibrium. Hence, the total ammonia concentration contributes to volatilization during irrigation.

Ammonia volatilization was monitored over four consecutive quarters (Q1, Q2, Q3 and Q4) using shallow pans placed on the ground to collect samples from the sprinkler

heads located 0.5 to 1 m above ground level. The timing and meteorological conditions for the four sampling events are summarized in Table 1. Water depth in each pan was kept below 2 cm to simulate observed surface water on the ground (estimated depth of 0.5 to 1.5 cm based on field observations). Samples from the pans were collected over time using 10-mL bottles. All bottles received a drop of sulfuric acid prior to sampling in order to reduce the sample pH to below 5 and minimize further volatilization. The samples were transported to the laboratory and analyzed using colorimetric spectrometry (Hach Models DR/2500 and DR/5000).

Because evaporation potential was high at the field site, a water balance was maintained during each ammonia sampling effort. This information was used to correct the observed ammonia losses for water evaporation. Evaporation rates were estimated by adding recycled water to a small open container with similar geometry as the pans, and using a digital scale to record mass readings at specific times. Measured rates agreed well with volumetric spot checks using the pans. The rates of evaporation varied non-linearly with time (not shown), and were fit using the following power-law model:

$$(M_{\text{wo}} - M_{\text{we}})/M_{\text{wo}} = K_{\text{we}}t^n \quad (1)$$

where M_{wo} is the initial mass of water (g), M_{we} is the mass of evaporated water (M), t is time (T), and K_{we} and n are empirical constants obtained from regression of mass ratio data and time data. The power regression relationship was found to be more appropriate than linear regression, because temperature and wind changed over the several hours that each sampling event lasted. Non-linear regressions were developed for each quarter ($r^2 > 0.98$) and used to estimate water loss with time from the pans.

Ammonia volatilization losses for each season were calculated based on observed temporal changes in

Table 1 | Average (range) conditions during quarterly sampling events

Sampling event	Air temp. (°C)	Initial water temp. (°C)	u_2 , wind speed at 2 m ht. (m/s)	Water evap. (v/v)	Crop status (ht)	Initial conc. (C_{wo}) (mg N/L)
Q1 11/18/05	16.9 (12–18)	15 (12–17)	6.9 (6.4–7.2)	0.16	Sudan grass (30 cm)	16.2
Q2 02/24/06	20.2 (10–21)	13 (11–15)	2.3 (1.6–2.7)	0.08	3-way grain (5 cm)	21.1
Q3 05/12/06	30.2 (28–33)	25 (23–27)	6.6 (6.4–7.0)	0.15	3-way grain (130 cm)	21.4
Q4 08/18/06	32.5 (30–38)	28 (26–30)	4.1 (2.4–6.3)	0.19	3-way grain (75 cm)	15.9
					Averages:	18.6

ammonia concentration from the evaporation pans while accounting for the concentration effect caused by water evaporation. In addition to estimating total losses, ammonia loss with time was modeled using an air-water mass transfer expression (e.g. [Schwarzenbach et al. 2003](#)):

$$F_{a/w} = -k_{a/w}(C_w - C_w^{eq}) \quad (2)$$

where $F_{a/w}$ is the ammonia flux (from air to water arbitrarily positive here) across the air-water interface [$ML^{-2}T^{-1}$], $k_{a/w}$ is the air-water exchange velocity (mass transfer coefficient) [L/T], C_w is the aqueous ammonia concentration, and C_w^{eq} is the interfacial aqueous concentration (ML^{-3}), which was assumed to be in equilibrium with the atmospheric ammonia concentration. The mass transfer coefficient in Equation (2) depends on physical processes on liquid and gas phase resistances in series, but the liquid resistance dominates in this case due to the high volatility of ammonia. The atmospheric ammonia concentration is expected to be in the 1 to 10 ppb range ([Wilson & Serre 2007](#)). Such levels can be neglected here relative to the much greater aqueous concentrations (20 ppm as N), and the ammonia flux from the water to the air becomes:

$$F_{a/w} = -k_{a/w}C_w \quad (3)$$

On the basis of the specific interfacial surface area $a_{a/w}$ [L^{-1}], in this case the surface area of pooled irrigation water divided by the pool volume, Equation (3) can be expressed in terms of the change in aqueous ammonia concentration with time:

$$\frac{dC_w}{dt} = -k_{a/w}a_{a/w}C_w \quad (4)$$

where the mass transfer coefficient and the interfacial area combine to act as a first-order mass transfer rate constant $k_{a/w}a_{a/w}$ [T^{-1}]. Equation (4) assumes that the pools are shallow and well-mixed such that internal gradients do not limit interfacial transfer. Integrating Equation (4) leads to the following expression:

$$\frac{C_w}{C_{w0}} = \exp(-k_{NH_3}t) \quad (5)$$

where $k_{NH_3}(=k_{a/w}a_{a/w})$ is the empirically determined ammonia mass transfer rate constant. Logarithmic

transformation of Equation (5) yields the following form:

$$\ln\left(\frac{C_w}{C_{w0}}\right) = -k_{NH_3}t \quad (6)$$

For each sampling event, observed ammonia losses were normalized by the initial observed mass (normalized concentration) in the evaporation pan, and the resulting time series was fitted with Equation (6) to yield an estimate of the rate constant. The quarterly first-order rate values were then normalized to a common temperature (20 °C) using the following van't Hoff-Arrhenius type expression:

$$k_{NH_3}(T) = k_{NH_3}(20)\theta^{T-20} \quad (7)$$

where T is the temperature (°C), and the empirical parameter θ ranges from 1.02 to 1.10 for wastewater ([Metcalf & Eddy 2003](#)), assumed to be 1.06 here. The average air temperature was employed in Equation (7) under the assumption that ponded water rapidly equilibrated with the air temperature.

While temperature is a key thermodynamic driver of ammonia volatilization, other meteorological conditions (e.g., wind) can also impact the process. Meteorological variables (air temperature, humidity, wind speed) for each sampling event were obtained from the California Irrigation Management Information System ([CIMIS 2010](#)) station 197, which is located less than 1 km from the experimental pivot site. These variables were tested along with temperature for correlation with observed ammonia volatilization rates.

In order to develop an emission factor based on the observed batch ammonia volatilization rates, we used Equation (3) and (4) to calculate hourly aqueous ammonia concentration changes and ammonia volatilization fluxes, respectively. The computations required estimates for the volatilization rate constant (k_{NH_3}), which was based on results from the pan study, and the specific interfacial surface area ($a_{a/w}$), which was based on an assumed surface pool geometry similar to the pans (diameter constant and depths ranging from 0.5 to 1.5 cm). Volatilization rate constants were continuously updated using local meteorological conditions according to multiple regression analyses developed in the next section. The applied ammonia concentration was taken as the average of the four quarterly measurements (from [Table 1](#), 18.6 mg/L). For these calculations, the pool concentration was renewed every six hours during irrigation, simulating the rotational speed of the irrigation pivot; it was set to zero between irrigation events. Soil moisture content sensors (HydraProbe II,

Stevens Water Monitoring Systems, Portland, OR) installed at the site were used to indicate the onset and completion of irrigation events. Here we employed the observations for a typical irrigation season, from 7/28/2008 to 5/10/2009. The resulting hourly flux time series was integrated to yield daily and annual ammonia emission factors for pivot-based irrigation using secondary WWTP effluent.

RESULTS AND DISCUSSION

The observed ammonia remaining with time is plotted for the quarterly tests as fractional concentration in Figure 1. Two-hour evaporation water losses from the samples ranged from 8 to 19% in the samples. Accounting for water loss, the two-hour ammonia volatilization averaged 22% over the range of field conditions, with lesser (15%) and greater (35%) losses occurring during the cooler and hotter sampling conditions, respectively. These results are relatively consistent with reported ammonia volatilization losses for irrigation with livestock waste lagoon water (Al-Kaisi & Waskom 2002; Whalen & DeBerardinis 2007).

Regressions of the ammonia data provided estimates of the first-order volatilization rate model (Figure 1). The regression results are presented with time in hours (h). The first-order rate values ranged from about 0.09 (Q1) to

0.23 h^{-1} (Q4) and described the ammonia loss well for Q1, Q3, and Q4 data, ($r^2 \geq 0.77$). The model fit to the Q2 data was less robust ($r^2 = 0.66$), a result that may be attributed to lower temperatures resulting in reduced volatilization magnitudes, which may have amplified experimental errors. Normalization of the rate constants to 20 °C (using Equation (7) and average air temperatures from Table 1) resulted in a value of $0.09 \pm 0.02 h^{-1}$ ($2.2 \pm 0.5 d^{-1}$), which is consistent with values estimated for similar gas-liquid systems, such as reaeration and evaporation processes in shallow ponds (Ro et al. 2007)

The results of a linear regression of the seasonal rates with temperature are illustrated by the plot in Figure 2. With the exception of the rate constant estimated for sampling event Q2, which is more uncertain relative to the others, the correlation between the rate constant and temperature is good ($r^2 = 0.76$). This result is expected given the degree of success in normalizing the seasonal rate constants to a single temperature. As a first approximation, for the temperatures of this study, these results are summarized in the following restrictive equation:

$$k_{NH_3} = 8.1 \times 10^{-3}T - 0.068 \quad (8)$$

where k_{NH_3} is the ammonia volatilization rate (h^{-1}) and T is the temperature (°C). As was noted above, and is evident in

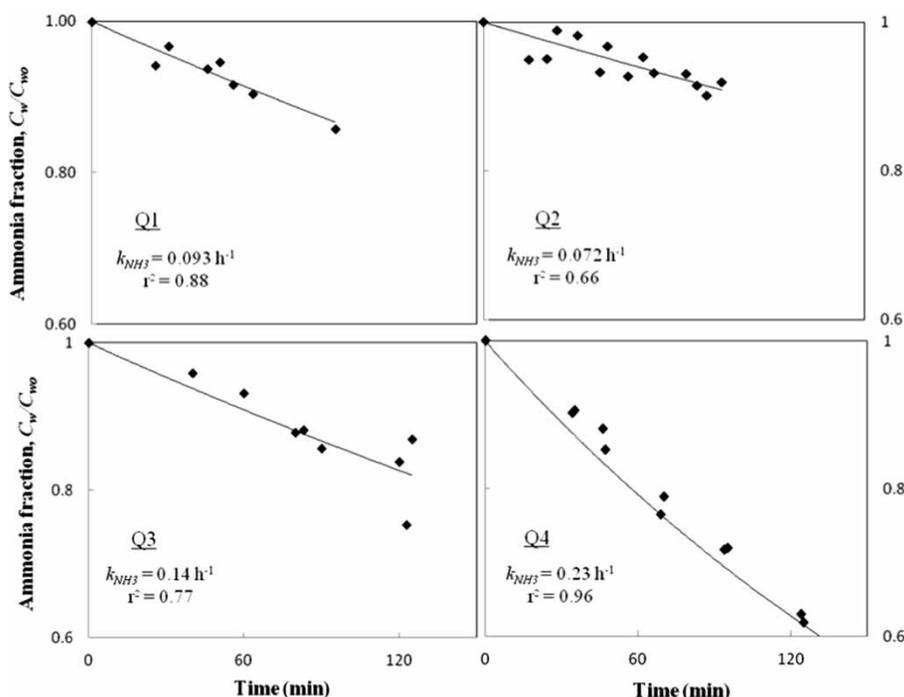


Figure 1 | Observed fractional ammonia concentrations (C/C_o) over time for Q1 through Q4 with best-fitting first-order rate model results.

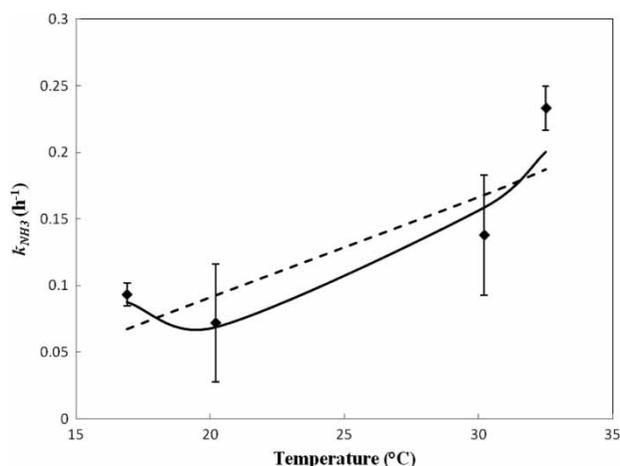


Figure 2 | Estimated first-order ammonia volatilization rate constant (k_{NH_3}) values (error bars represent 95% CI), best-fitting regression with temperature only (dashed line, Equation (8)), and multi-regression with temperature and 2-m elevation wind speed (solid line, Equation (9)).

the plot in Figure 2, the relationship is affected by other variables, particularly wind (Ro et al. 2007). A multiple regression with respect to temperature and wind speed resulted in the non-linear curve in Figure 2, which provided better correlation with volatilization rate than temperature alone ($r^2 = 0.94$):

$$k_{\text{NH}_3} = 7.7 \times 10^{-4}T + 1.3 \times 10^{-3}u_2 - 0.13 \quad (9)$$

where u_2 [m/s] is the wind speed at 2 m above the ground and the other variables are defined in Equation (8).

Figure 3 summarizes the effects of temperature and wind velocity on k_{NH_3} . As expected, the higher temperatures

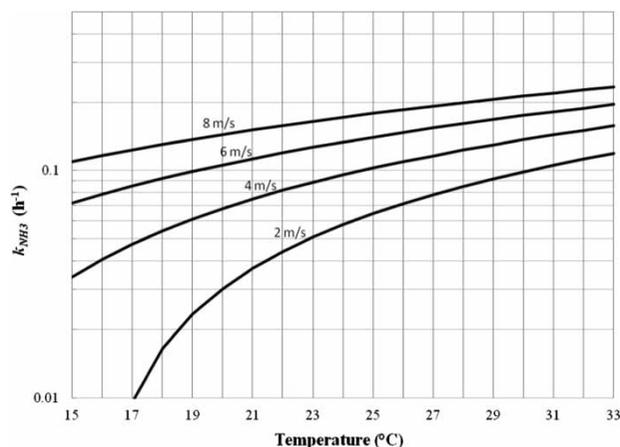


Figure 3 | Diagram for estimating first-order ammonia emissions rate constants as a function of air temperature and wind speed (u_2); based on Equation (9).

and wind velocities resulted in higher ammonia volatilization and first-order mass transfer rates.

Using Equation (9) in conjunction with Equations (3) and (4) (as discussed in the previous section) allows one to estimate an hourly ammonia flux time series based on local meteorological conditions. Recall that the simulations mimic the pivot's rotational cycle, resetting the applied ammonia concentration to the effluent level every six hours. This situation results in peak flux rates, as the thermodynamic driving force ($C_w^{\text{eq}} - C_w$) is at its maximum at these instances. As expected, the higher temperatures and wind velocities result in higher ammonia volatilization and first-order volatilization rates. It is interesting to note that, due to the high variation in temperature and wind speed in this desert climate, hourly volatilization rate estimates may vary by a factor of five over a 24-h period.

The plots in Figure 4 project the time-variant k_{NH_3} values and fluxes over an entire irrigation season, demonstrating seasonal variation atop the noted daily variations. Following the passing of the pivot, the flux tends to decrease as the magnitude driving force decreases. Based on (9), the k_{NH_3} values track the temperature and wind speed, generally increasing to a maximum each afternoon and a minimum overnight. For the range of assumed pool geometries (constant diameter, depths 0.5–1.5 cm, based on field observations), integrating the hourly volatilization rates leads to a range of cumulative estimates of 0.4 to 1.1 MT $\text{NH}_3\text{-N/yr}$ (0.03 to 0.09 Mg N/ha/yr).

A gross estimate of ammonia volatilization can be estimated as approximately 22% using the average removal fraction over 2 h. Average effluent flow rates to the experimental site ranges from 1,160 to 2,320 m^3/d , depending on weather conditions, crop demands and periods of no irrigation. With an average total ammonia concentration of about 20 mg N/L (Table 1), this finding suggests an annual ammonia loss for the 12 ha site range from 0.49 to 0.98 Mg $\text{NH}_3\text{-N/yr}$ (0.04 to 0.08 Mg N/ha/yr), which is consistent with the range estimated using the more complex model.

SUMMARY AND CONCLUSIONS

Proper management of recycled water irrigation systems requires a good understanding of the fate of the nutrients present in the irrigation water. This study helped quantify average and seasonal ammonia volatilization resulting from center pivot irrigation with recycled water. A first-order mass transfer approach modeled ammonia volatilization well, and fitted rate constants were consistent with

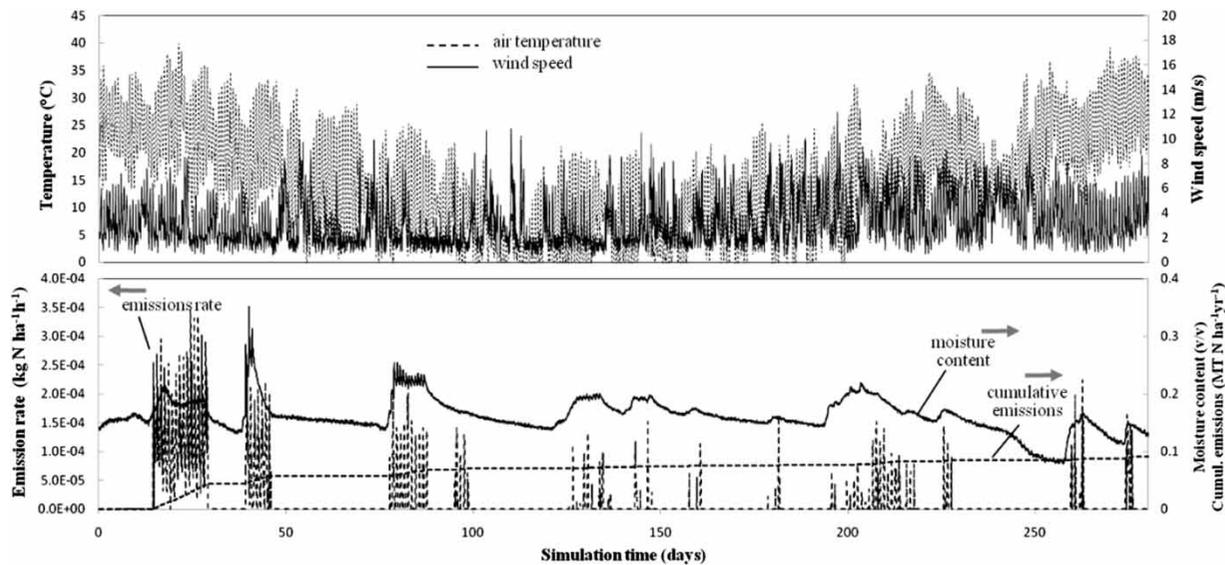


Figure 4 | Observed wind speed and air temperature time series at the experimental site (upper graph) and resulting hourly ammonia emissions rate and cumulative emissions estimates (lower graph) [note: moisture content observations (lower graphs) were used to identify irrigation event timing].

literature values. This model demonstrated that meteorological conditions at the site could cause hourly volatilization flux values to vary by a factor of five over the course of the day. Integrating the hourly flux over the entire irrigation season resulted in an annual mass transfer rate estimate (0.03 to 0.09 Mg/ha/yr) on the same order as that estimated using the average volatilization loss (22%), suggesting that the simpler approach is useful for inventory purposes. Nevertheless, the dynamic model may be useful for estimating ammonia losses in terms of their timing and magnitude. Future work should focus on evaluating ammonia volatilization rates for different climates, soils, crops and fertilization methods (e.g., recycled water vs. groundwater with synthetic fertilizers).

In terms of regional implications of this activity, consider that California reused about 10% of its secondary effluent flow in 2003, with about 66% of the reuse being for agricultural and landscape irrigation (CA DWR 2003). This situation amounts to an irrigation flow of approximately 430 Mm³/yr. Assuming that effluent ammonia concentrations range from 10 to 20 mg/L, and 22% volatilization losses, this figure amounts to losses of 900 to 1,900 Mg NH₃-N/yr. As the use of recycled water for irrigation increases, there is potential for higher ammonia volatilization. However, the increase may be offset by a corresponding reduction in synthetic fertilizer usage. This potential shift plus an understanding of the fate of nutrients are relevant factors to consider in irrigation with recycled water.

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