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Extent, Cause and Management of Salinity in the USA

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ABSTRACT

Increasing demands for high quality water by municipal and industrial users can no longer be met with development of new water supplies in the western U.S. These demands are occurring at the same time that there are increasing constraints on discharge of drainage waters. Environmental concern and regulation of off site impact of drainage water is presently a major constraint to sustainable irrigation systems. If irrigated agriculture in the western U.S. is to maintain its important role in food production, agriculture will have to utilize lower quality water for irrigation, including reuse of drainage water, use of treated municipal waste waters and development of brackish waters presently considered undesirable for irrigation.

At present the actual impact of salinity on agricultural production in the U.S. is not well known. It is estimated that 20-30% of all irrigated lands are impacted by salinity, but this is based on very limited data. The causes of salinity problems in the U.S. are varied, ranging from the presence of saline geologic formations, such as the shales of Colorado and Utah, presence of saline ground water in the upper Great Plains (Dakotas, and north western Colorado) and irrigated areas with either insufficient drainage or non- optimum water management. The large Central Valley of California saw a large increase in irrigated acreage in the 1950's through the 1970's. Initial reclamation was successful, however the long term needs for drainage have not been met and thus the long term viability of irrigated agriculture in the valley is presently questioned. In these regions as well as in the dryland areas of the Great Northern Plains, salinity problems have been aggravated by excessive rather than insufficient irrigation or infiltration. In the lower Colorado River Basin the problems are related to non-uniformity of water infiltration, which is only partially caused by insufficient drainage.

Increased use of low quality water and implementation of drainage water reuse will require not only improved water management but also application of periodic salinity monitoring and prediction of the impact of management changes on salinity, crop production and soil physical properties. Until recently rapid salinity monitoring equipment was not available, thus it was not practical to monitor salinity changes either through a cropping season or through a cropping sequence. New advances make it possible to obtain detailed information rapidly and at low cost. Generalized water quality criteria are not adequate for predicting site specific needs based on local climate, soils, growing season, crop, irrigation practices etc. Changes in management practices, such as cyclic reuse of drainage water or supplemental irrigation with low quality waters can now be evaluated using process- based computer models that consider the dynamics of water flow including irrigation amounts and timing, crop water requirements, and sensitivity to water and salt stress, and solution chemistry including cation exchange, mineral precipitation/dissolution and the effects of chemistry on soil physical properties.

Additional information is needed to predict the sensitivity of crops to salinity at various stages of growth. Incorporation of irrigation infiltration models into the root zone simulation models would allow for a more comprehensive evaluation of the options available to the producer. New management practices are needed for minimizing the adverse impact of drainage return flows including toxic anions as well as management practices for reuse of saline drainage waters.

IRRIGATION AND SALINITY-EXTENT OF THE PROBLEM

The total acreage of land in agricultural production in the U.S. was calculated at 390 million hectares in 1987 with 115 million hectares being harvested croplands (Bajwa et al.,1992). Irrigated agricultural land in turn consisted of 14.8% of the harvested cropland (National Research Council, 1996). Total agricultural acreage in the U.S. has remained relatively constant in the past few decades, with gains in total production being ascribed to increased productivity per acre. Increased productivity is due to increased use of fertilizers, increased pest management, improved crop varieties with increased yield and disease- resistant traits and increased use of irrigation. It appears unlikely that there will be further dramatic improvements in fertility or pest management and increased productivity with new varieties is uncertain.

A disproportionate amount of the value of food production is generated by irrigated land. Bajwa et al. (1992) estimated that irrigated lands comprised about 15 % of the harvested cropland in the U.S. (About 20.6 million hectares in 1992) and produced about 38 % of the total cropland value. Irrigated lands produce an even higher percentage of the food production consumed by humans. The high value from irrigated lands is attributed to the higher value of irrigated crops, as well as the capacity for multiple cropping in the southwestern U.S., where most of the irrigated land is located. Total irrigated acreage in the U.S. increased rapidly in the 1970's but there has been no net increase since 1981. Presently the 17 western states and Arkansas, Louisiana, and Florida account for 91 % of the total irrigated acreage. There is potential to increase irrigation use in the eastern U.S., but farm prices have not been sufficient to allow for the economic development of the needed infrastructure (including artificial drainage systems).

Due to increasing and competing water demands by an expanding population, increased industrial needs, as well as increased environmental restrictions, the amount of high quality water available to agriculture will decline. As shown in Figure 1, irrigation water use in the U.S. has increased slightly since 1950, but industrial water use has increased dramatically. There is no possibility for increased diversion of surface waters for irrigation in the western U.S., since most

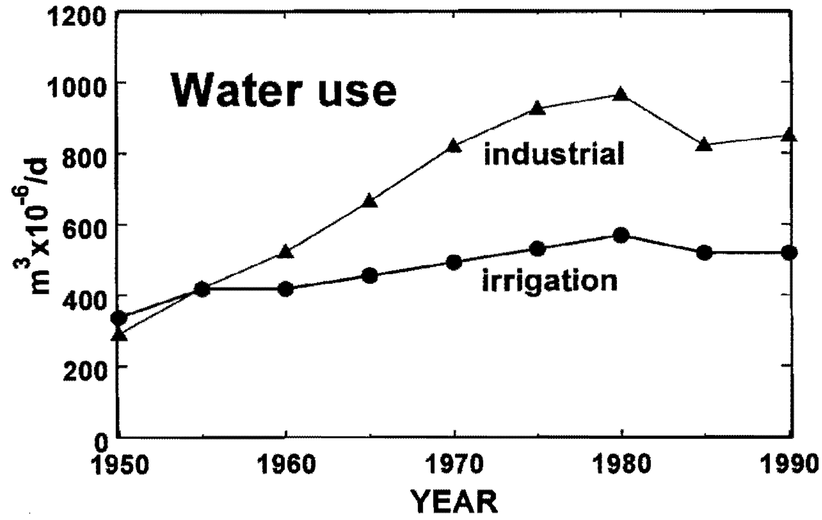

Figure 1

Irrigation and industrial water use in the U.S. for the years 1950 to 1989. Data taken from National Research Council, 1989

river resources are over-allocated. It is estimated that the amount of additional waster required to meet environmental requirements or concerns in California alone are on the order of $37x10^{12}$ m^3 (3 million acre-feet). California law has expanded the public trust uses of land and surface water from the traditional ones of navigation, fishing and commerce to include protection of fish and wildlife, scenic and recreational use, and preservation in a natural condition for scientific study (California Dept. of Water Resources, 1994). Surface water diversions in California have already been reduced to restore stocks of endangered fish species. Dams constructed for water storage and hydroelectric power have also been removed in an attempt to restore fisheries, with a resultant loss in usable surface water.

Irrigation in the U.S. utilizes both surface and ground water. In 1990 surface water represented 63 % of the water used for irrigation (National Research Council, 1992). Table 1 (modified from Solley et al.,1993) provides information on water use on a regional basis. It is clear that most irrigation occurs in the western U.S., with California, Pacific Northwest and Missouri Basins representing 62 % of the irrigation water used. The Lower Colorado represents only 4.5 % of the water use but is disproportionately important, as it has been the major source of winter vegetables in the U.S. It is not straightforward to evaluate drainage water reuse in the various hydrologic systems. Drainage waters either return to the surface systems (such as the Colorado River) or result in ground water recharge. In many instances the return flows are utilized down gradient. Improving irrigation efficiency may result in loss of water supply to down gradient users dependent on the excess recharge of drainage waters. Major rivers especially the Colorado and Rio Grande, undergo multiple diversions and return flows, with decreasing water volumes and increasing salinity downstream.

Table 1 Irrigation Water Use in U.S., 1990 (m^3 x 10^{-9})

Region	Fresh Water			Reclaimed Wastewater	Consumptive Use
	Ground	Surface	Total		
New England	0.119	1.49	1.61	0	0.168
Mid-Atlantic	1.37	1.27	2.64	0	2.26
South Atlantic-Gulf	30.96	29.04	60.00	3.17	42.84
Great Lakes	1.78	2.12	3.90	0	3.70
Ohio	0.372	0.540	0.91	0.004	0.80
Tennessee	0.050	0.312	0.362	0.005	0.25
Upper Mississippi	4.76	0.504	5.26	0.001	4.90
Lower Mississippi	83.88	15.48	99.36	0.010	73.92
Souris-Red-Rainy	0.756	0.564	1.32	0	1.18
Missouri Basin	96.84	236.4	333.24	0.041	147.6
Arkansas-White-Red	88.80	24.12	112.92	0.12	93.0
Texas-Gulf	53.40	15.24	68.64	0.41	57.84
Rio Grande	21.72	49.44	71.16	0.008	42.84
Upper Colorado	0.432	88.2	88.63	0.006	30.12
Lower Colorado	30.12	51.36	81.48	2.46	54.72
Great Basin	18.96	65.76	84.72	0.70	41.88
Pacific Northwest	105.6	321.6	427.2	0.144	157.2
California	142.8	237.6	380.4	1.72	260.4
Alaska	0.001	0.006	0.007	0	0.004
Hawaii	2.68	7.46	10.14	0.083	7.03
Caribbean	0.72	1.16	1.88	0	1.22
Total	686.4	1151	1836	8.88	1025

Source: Solley et al., 1993

As mentioned above, ground water constitutes about 37 % of the irrigation water used in the U.S. In the western states, further net expansion of irrigation by ground water pumping is not possible. Postal (1989) estimates that about 21% of the irrigated land in the U.S. is irrigated by overpumping, and is thus not sustainable. This value represents more than 50% of the land irrigated by ground water.

As shown in Table 1, reclaimed waste water use in the U. S. is currently very low, comprising an insignificant fraction of the total irrigation water use. Nonetheless reclaimed waste water use (secondarily treated) is increasing rapidly, especially in the southwest, where it has been utilized primarily for landscaping purposes. The consumptive use and water diversion values shown in Table 1 indicate that the individual water use efficiency in the various irrigation projects is surprisingly low. The average consumptive use for all agricultural irrigation projects is only 56 % of the water diverted. This value while greater than the world average project efficiency of 30% listed by Ghassemi et al.(1995) is surprising in view of the relatively large capitalization and high degree of sophistication of U.S. irrigation projects and high level of expertise available to the farmers. As mentioned above, this water use efficiency value is misleading in terms of overall water use. For example in the Colorado River Basin, Table 1 indicates an overall water use efficiency of 50 %. Nonetheless, consumptive use is likely closer to 90% if we consider the volumes of water that actually leave the Colorado River Basin as drainage in comparison to the available water supply. Upper basin agricultural projects return their drainage water to the river, thus it is utilized downstream. Urbanization of the major agricultural valleys is resulting in decreased agricultural land available for irrigation. This issue will be increasingly important in the future.

Major irrigated crops in the U.S. are corn, wheat, soybeans, cotton, alfalfa and rice (National Research Council, 1992). Crop yields are significantly higher on irrigated land as compared to rain-fed land. It is estimated that irrigated yields exceed whose for rain-fed lands by 54 % for grain corn, 97 % for wheat, 33 % for soybeans and 67 % for cotton (U.S. Department of Agriculture, 1986). As mentioned above vegetable crops are economically important but comprise a relatively small amount of the total irrigated acreage.

Salt affected soils in the U.S. have been traditionally defined as soils whose electrical conductivity of a saturation extract exceeded 4 dS/m (U.S. Salinity Laboratory Staff, 1954). More recently the term has been used to denote any soil whose salinity is limiting crop productivity. This definition is not entirely satisfactory since producers shift to more salt tolerant crops as salinity increases. Unfortunately salt tolerant crops are almost always lower value crops than are the salt sensitive crops. Estimates of salt damage in the U.S. do not usually take into account the income lost by the restriction in crops that can be grown as salinity increases.

Postal (1990, in Ghassemi et al, 1995) estimated that 27% of the irrigated land in the U.S. was damaged by elevated salinity. This value is comparable to the cited world average of 24% and in reasonable agreement with the value of 23% given by the U.S. Department of Agriculture (1989) for salt-affected irrigated land in the U.S. The U.S. value has to be considered a very rough estimate, due to the varied hydrologic systems, and varied management practices of a decentralized agricultural system. Table 2 presents the regional distribution of the salt affected-irrigated lands. As expected, essentially all the salinity problems are located in the western U.S.. Large acreages affected by salinity are located in the Colorado, Rio Grande and Central Valley CA basins in the southwestern U.S., as well as in the Northern Great Plains (Missouri River Basin).

In the U.S., there is great variation in the management from farm to farm within an irrigation project, ranging from extent of artificial drainage, fertilizer use, irrigation system utilized etc. These management differences result in differences in the extent of salinity problems across a project, in addition to the variations caused by spatial variability of physical properties of the soils. Farmers in various projects have organized drainage districts, or combined drainage and irrigation responsibilities into one organization, with the objective of coordinating construction of water drainage works. On farm drainage remains an individual responsibility thus drainage spacing and efficiency vary widely.

Table 2 Salt-affected Soil Under Irrigation in the U.S., 1982[1]

Water Resources Regions	Total Irrigated Land (1000 ha)	Salt-affected or Sodic (1000 ha)	Affected portion of Irrigated Soils (%)
Upper Mississippi	373	2	0.4
Lower Mississippi	2109	178	8.5
Souris-Red-Rainy	39	10	24.5
Missouri	5637	837	14.8
Arkansas-White-Red	3039	151	5
Texas-Gulf	2816	422	15
Rio Grande	782	591	75.5
Upper Colorado	651	269	41.3
Lower Colorado	616	407	66.1
Great Basin	997	581	58.3
Pacific Northwest	3411	746	21.9
California	4048	1435	35.4
Total	24517	5628	23

[1] U.S. Department of Agriculture (1989)

Despite the present uncertainty in the extent of salt affected soils and lack of knowledge about the long-term tends in these areas, the potential presently exists to develop a comprehensive inventory. Recent technology allows for rapid measurement of salinity using remote electromagnetic (EM) sensing of the soil (Rhoades et al., 1999). Rhoades et al.(1999) estimated that a typical 64 ha field could be intensively mapped using the sensing equipment in approximately 3 hours. Including survey time and data processing the entire working time was estimated at 4.5 hours. Greatly improved estimates of the extent of salt affected lands will be available at least in the lower Colorado River Basin within a few years due to an organized effort by the U.S. Bureau of Reclamation in coordination with the Salinity Laboratory utilizing such mobile EM sensing technology developed by the Salinity Laboratory.

Damages due to salinity also have to be regarded as rough estimates at best. Ghassemi et al. (1995) indicate that in the Colorado River Basin alone, annual damages are more than $750 million per year. However, these damages are almost completely associated with municipal use and damages to domestic appliances, primarily water heaters. Also, these damages are primarily due to water hardness not salinity. Decreased salinity in the Colorado River system would not significantly reduce these values since the river remains calcite saturated independent of salinity levels (Suarez, 1982). Recently the U.S. Bureau of Reclamation correlated crop productivity in Imperial Valley with variations in the yearly salinity level in the lower Colorado River. The irrigation water salinity was still below levels that unavoidably result in yield losses, nonetheless significant yield losses are suggested for various crops. This information indicates that producers did not compensate for the increased salinity by changes in management such as increased leaching. It is not certain that management changes can be made to adjust for the yearly salinity fluctuations. For example in Imperial Valley the primary irrigation system is furrow, and the summer evapotranspiration requirements of most crops are equal or greater than the achievable infiltration rates for many of the valley's soils.

The major salinity damages in the U.S. are associated with saline soils or rising saline ground waters rather than by irrigation with saline water. In the San Joaquin Valley of California crop yields were calculated to have decreased by 10% since 1970 for a loss of $31 million and projected to increase to $321 million by the year 2000 if no action was taken to complete the drainage system for the valley (El-Ashry et al. 1985). Salinity damages occur primarily in the western portion of the valley, an area of more approximately 0.9 million ha. The valley was originally irrigated by ground water, resulting in rapid declines in the water table and severe problems of subsidence. Introduction of California Aqueduct water (surface water from the Sierra and Cascade Ranges) in the late 1960's reversed this trend and from 1967 to 1984 the potentiometric surface rose 30-60 m across the western part of the valley (Belitz and Phillips, 1995). As of 1999, damages are likely not much greater than those of the early 1980's despite the lack of completion of the drainage system. The projected losses assumed that the quantities of irrigation water brought into the valley would remain constant. Due primarily to water shortages during several drought years and increased use of water for habitat maintenance, less water was imported into the Valley, more ground water was pumped and thus water table levels did not rise as projected. This development illustrates that salinity problems are mostly due to insufficient drainage, often caused by over- irrigation.

Belitz and Philips (1995) proposed an alternative to the needed drainage outlet. They proposed a reduction in surface water use of 160,000 acre-feet/y (197 million m^3) with improved water application and replacement of 54,000 acre-feet/y (66 million m^3) of surface water imported into the basin with ground water available at depth in the basin. Under this plan they maintained that the need for an outlet drain could be delayed for up to 50 years without crop losses and with the potential to release sufficient water to municipal users to support a population of 1.8 million people. Under-irrigation may result in short term yield loss but it will not result in dramatically high salinity levels unless a shallow water table exists. Increased salinity decreases yield but also decreases water consumption by the crop thus moderating further increases in salinity. Despite the reprieve caused by the water shortage in the San Joaquin Valley a long term solution to the problem will likely require either a limited drain system or an extensive sequence of re-use of drainage water, which would require a high level of planning and coordination.

Salinity problems in the U.S. are both natural and man–induced. Naturally occurring saline soils were present in the Northern Great Plains, Upper Colorado River Basin and portions of the Central Valley in California. The primary sources of salinity in the Colorado River Basin are Cretaceous shales, deposited in shallow inland seas and containing evaporite minerals. Soils and shallow ground water in the Upper Colorado River Basin are generally highly saline. These salts were slowly flushed into the Colorado River, but only to a limited extent, since recharge in these valleys depended on the limited rainfall. An example of the impact of irrigation on the salt loading is the case of Grand Valley CO where it is estimated that irrigation contributes about 90% of the present recharge thus increasing dramatically the salt load to the river. This increased salinity affects the downstream irrigation projects in California, Arizona and Nevada. In addition to the increased salt loading to the river, secondary salinization occurred within the valley. Over-irrigation in the upland areas, coupled to poor drainage and shallow depths to bedrock, resulted in rising perched water tables and surface soil salinization. The lower portions of the valley were also affected by increased upslope recharge and displacement of salts into the alluvial basin. In addition to recharge from the valleys the upper Colorado River also has recharge from numerous saline springs. In this instance the solution is not increased drainage but increased irrigation efficiency, especially in the upper portions of the valley where the soils are underlain by the saline formations. Starting in the mid 1970's, the U.S. Bureau of Reclamation undertook an extensive program of canal lining, development of an improved water scheduling system and demonstration projects to improve irrigation efficiency. Reductions in salt loading have been stated but quantification of the magnitude is difficult in the short term as the salt loading is also dependent on yearly fluctuations in the climatic conditions (such as rainfall totals, spring temperature and snowmelt runoff) which are highly variable in that region.

Increased river salinity downstream in the Colorado River Basin and in the Rio Grande are caused by return of drainage water to the river from up-stream irrigation projects. The concentration of salts in the river increases as the drainage waters are returned to the river. Downstream users in Imperial and Coachella Valley experience salinity problems as a result of the increased salinity of the irrigation water and insufficient drainage or infiltration. In contrast to upstream users, increased irrigation efficiency in the lower basin projects is not always possible. Additional leaching is required in the lower basin due to the increased irrigation water salinity and increased evapotranspiration in lower basin valleys.

In the upper Northern Great Plains (and extending into Canada) saline geologic formations are also present. This region is underlain by saline shale rock over much of its area. The area was glaciated within the past 10,000-50,000 years thus the surface is covered by glacial till, unconsolidated sediments with poor hydraulic characteristics but high water holding capacity. Conversion of native prairie land to dryland farming, primarily wheat, has resulted in increased recharge to the subsurface. The institution of fallow rotations, implemented to protect against total crop failure, resulted in higher moisture content at planting time but also significantly increased recharge during the fallow. The relatively shallow- rooted wheat planted following the fallow is unable to utilize the deeper unsaturated zone moisture which is recharged to the ground water.

Since drainage systems are poorly developed and there are numerous non continuous restrictive clay layers, lateral displacement of water and salts is common. Brown et al. (1983) described seven common types of saline seeps. All saline seeps include lateral movement of water and salts to lower lying areas where the water emerges at the surface. These seeps remain wet and with evaporation and further discharge, the salts are further concentrated. Under these marginal, rain-fed agricultural conditions, installation of artificial drainage is not economically feasible.

The solution to controlling and reducing saline seeps has been to reduce the use of fallow and maintain crop rotations that utilize more water. Alfalfa has been used as a perennial crop in the recharge area. In addition to greater water use the deeper rooted alfalfa has the ability to extract water that would otherwise result in recharge. Flexible cropping systems have been developed that take into account the existing and predicted moisture status of the land, thereby increasing water utilization. Reduction of recharge gradually results in decreases in water table elevation and allows for restoration of downward movement of water and salts in the lower lying areas.

Salinity in the Central Valley of CA has resulted from the accumulation of salts due to natural weathering processes over geologic time, as well as dissolution of salts from marine shale formations, on the west side of the valley. Natural drainage via the San Joaquin River flowing north to the San Francisco Bay, is limited. Large areas were saline before the development of irrigation, some with high water levels. Installation of drainage systems and high ground water pumping rates allowed for reclamation of these soils. Large increases in the amount of irrigated land were accompanied by the importation of large volumes of surface water and reduction in the use of ground water, dramatically altering the balance between water inflow, outflows and consumptive use. Rising water tables, failure to complete a discharge drain due to environmental concerns and restrictions on the discharge of drainage water to the San Joaquin River have caused the salinity problems to reappear.

In the Central Valley salinity has been keep in check for the past 10 years by a combination of reduced area of irrigation, reduced importation of irrigation water due to drought and environmental concerns, use of evaporation ponds for reduction in drainage water volume and limited reuse of drainage water for irrigation. Pumping of drainage water into evaporation ponds is not considered a viable long term solution to the drainage problem.

WATER QUALITY MODELING

The water quality model FAO Soil Water Salinity (Suarez et al., 1999) is intended to evaluate the suitability of a water for irrigation, primarily in arid and semiarid regions. The suitability of a water is evaluated in terms of its utility for crop growth. Thus the criteria is not only water salinity but the existing soil chemical and physical properties, the water requirements of the crop and its salt tolerance, adequacy of drainage and amount of water that can be infiltrated. The model does not presently consider nitrogen chemistry; it is assumed that all nutrient levels are adequate for optimum plant growth.

The FAO soil water quality model is a modification of the UNSATCHEM model (Suarez and Simunek, 1997, Simunek et al., 1996), with addition of a plant growth module, upgraded to 32 bit and with a Windows 95 user interface. The UNSATCHEM model in turn is based on the SOILCO2 model (Simunek and Suarez, 1993, Suarez and Simunek, 1993) with addition of a chemical speciation routine (Suarez, 1977), calculation of exchangeable cations as described in Robbins et al.,(1980), and calculation of osmotic activity coefficients using the Pitzer routines of GMIN (Felmy, 1990). Water flow is simulated with a variably saturated water flow model which considers the effects of salinity, sodicity and pH on hydraulic conductivity. Plant water uptake takes into consideration the dynamic water and salt stress occurring in the root zone. This calculation requires the input of crop-specific salt tolerance information, which is readily available. The relative yield of a crop is calculated as the ratio of the water uptake to the optimum water uptake of the crop in the absence of water or salt stress. The model also includes a generic plant growth model which provides output of absolute yield, green biomass, root biomass etc, as a function of time, as related to the temperature, solar radiation, and water availability. The output from this plant model must be regarded as a representation, since it has not been optimized for each crop, planting regime and soil fertility, and locality. Until further testing the model should be used as a guide to specific management decisions rather than an absolute predictor of future conditions.

The UNSATCHEM and FAO models includes prediction of carbon dioxide production and transport in both the liquid and gas phases, thus providing dynamic simulation of CO_2 concentrations. This information can be used to evaluate aeration problems as well as for use in the chemical routines for calculation of pH, Ca and alkalinity concentrations. This is a unique feature of these two models that is especially important when considering gypsum requirement or "green manuring" as an option for sodic soil reclamation. The utility of this feature of the model is demonstrated in the results of reclamation simulations shown in Simunek and Suarez, (1997) where enhanced CO_2 coupled with calcite dissolution was shown to be an effective reclamation practice. Accurate prediction of water movement, carbon dioxide concentration and heat transport may require detailed soil information, however for the objectives of this model default criteria can be readily utilized.

Since it is a dynamic model the irrigation inputs should be specific time events of specified duration and intensity with corresponding entry of ET_0. The plant submodel can be utilized in either of two ways; either for a perennial crop, such as a grass with a fixed root distribution or an annual crop with a growing root distribution. In the case of a perennial crop the crop yield is expressed as a relative yield-meaning the ratio of the crop biomass under the simulated conditions to the crop biomass under unstressed conditions. In this instance we assume that the relative yield is equal to the actual water consumed divided by the optimum (unstressed) water consumption.

The user friendly interface utilizes default parameters and pull down menus. Additional options are available by changing the input file after initially creating the files with the interface. The help files provide information for the preparation of the input files.

Water Flow

The model uses a modified version of the one-dimensional Richards' equation (Richards, 1952)

$$\frac{\partial\theta_w}{\partial t} = \frac{\partial}{\partial z}[K\frac{(\partial h}{\partial z} + \cos\alpha)] - S \qquad \mathbf{(1)}$$

where h is the water pressure head, θ_w is the volumetric water content, K is the hydraulic conductivity function, t is time, z is the spatial coordinate, α is the angle between the flow direction and the vertical axis (0 for vertical flow) and S is the sink/source term(representing water removal by plant roots). The effects of thermal and density gradients are neglected, although they may be important in some instances, and we assume that the gas phase dynamics do not affect water flow. These simplifications are not justified in all instances but consideration of these processes greatly increases the complexity of the calculations and is beyond the scope of these programs.

The unsaturated soil hydraulic properties are described by a modified version of those proposed by van Genuchten (1980). The water retention and hydraulic conductivity functions are given by

$$\theta(h) = \theta_r + \frac{\theta_s - \theta_r}{(1 + |\alpha h|^n)^m} \qquad (2)$$

and

$$K(h) = K_s K_r r = K_s r S_e^{1/2} \left[1 - (1 - S_e^{1/m})^m\right]^2 \qquad (3)$$

respectively, where

$$m = 1 - 1/n \qquad n > 1 \qquad (4)$$

$$S_e = \frac{\theta - \theta_r}{\theta_s - \theta_r} \qquad (5)$$

and where θ_r and θ_s denote residual and saturated water content, respectively, K_s is the saturated conductivity [cm d^{-1}], K_r is the relative hydraulic conductivity, S_e is relative saturation and m [-],

n [-], and α [cm^{-1}] are the empirical parameters of the hydraulic characteristics. Hydraulic characteristics are determined by a set of 5 parameters, θ_r, θ_s, α, n, and K_s and the variable r, representing the effect of soil chemistry on hydraulic properties. Use of the model requires optimizing the 5 parameters from the experimental water retention, pressure head, and saturated conductivity data. This parametrization can be performed using the RETC code (van Genuchten et al., 1991). In keeping with the objectives of this model we do not expect the users to conduct detailed studies on the water retention curve and unsaturated hydraulic conductivity of each soil used. It is considered that for a water quality model the water retention vs pressure head curve is reasonably represented by the functions obtained from soil texture by Carsel and Parrish (1988). The major error of importance for our applications is likely the saturated hydraulic conductivity. In some instances the values presented appear greater than what we observe- for example K_s for a loam soil. A user with more detailed hydraulic information may want to use the interface to set up the initial files and then use a word processor to alter the input file.

Chemical Effects on Hydraulic Conductivity

Equation 3 differs from previous relations in that it includes a reduction term, r, which scales the hydraulic conductivity in relation to the chemical conditions in the soil. Elevated levels of exchangeable sodium result in swelling of smectitic clays, dispersion of clay, migration and subsequent blocking of pores results at low salinity. This process is readily observed in the natural development of clay pan layers in soils and most dramatically in sodic, nonsaline soils. In addition, it has been determined that elevated levels of pH adversely impact saturated hydraulic conductivity, separate from the sodicity and salinity interactions (Suarez et al., 1984).

Suarez and Simunek (1997) represented the chemical effects on hydraulic properties by the use of a reduction function, r, given by

$$r = r_1 r_2 \tag{6}$$

where r_1 is the reduction due to the adverse effects of low salinity and high exchangeable sodium fractions on the clay and r_2 is the adverse effect of pH. The r_1 term is given by McNeal (1968) as

$$r_1 = 1 - \frac{cx^n}{1 + cx^n} \tag{7}$$

where c and n are empirical factors, and x is defined by

$$x = f_m 3.6 * 10^{-4} ESP^* \, d^* \tag{8}$$

where f_m is the mass fraction of montmorillonite in the soil, d^* is an adjusted interlayer spacing and ESP^* is an adjusted exchangeable sodium percentage (percentage of the total negative exchange charge of the soil that is neutralized by Na^+). The term d^* is defined by

$$\begin{aligned} d^* &= 0 && C_0 > 300 \text{ mmol}_c\text{L}^{-1} \\ d^* &= 356.4\,(C_0)^{-0.5} + 1.2 && C_0 \le 300 \text{ mmol}_c\text{L}^{-1} \end{aligned} \tag{9}$$

and the term ESP^* is given by

$$ESP^* = ESP_{\text{soil}} - (1.24 + 11.63 \log C_0) \tag{10}$$

The reduction factor r_2, for the adverse effect of pH on hydraulic conductivity, was calculated,

$$
\begin{aligned}
r_2 &= 1 && for\ pH < 6.83 \\
r_2 &= 3.46 - 0.36\ pH && for\ pH\ \varepsilon\ \langle 6.83, 9.3 \rangle \\
r_2 &= 0.1 && for\ pH > 9.3
\end{aligned}
\tag{11}
$$

from the experimental data of Suarez et al. (1984), after first correcting for the adverse effects of low salinity and high exchangeable sodium using the r_1 values. In view of the differences among soils, these specific values may not be generalized predictors of soil hydraulic conductivity. Soils differ in their reaction to these factors, in ways that are not yet completely understood. Thus although the above equations may not be generalized predictors, they do represent conditions of arid land soils examined at the U.S. Salinity Laboratory and they illustrate the changes in *K* that affect infiltration and solute movement under various chemical conditions.

Plant Modeling

There are two options in the model relating to plant water uptake and root modeling, a fixed root distribution and root growth. In the case of a fixed rooting distribution, the root distribution is input by the user and remains constant throughout the simulation. This option is suited for use when simulating perennial crops such as alfalfa and pasture grasses. In this instance, water uptake depends only on input ET, and water and salt stress simulated by the model. The model predicts relative yield based on the ratio of T_p to T_a.

The root growth option is suitable for simulation of annual crops and initiates the generic crop submodel. In this case the user inputs an initial root distribution from which the roots will develop. This option requires additional inputs such as maximum rooting depth, solar radiation growing degree days etc. Additional features can be utilized by changing the crop input file after creating the file with the default parameters in the interface.

Water uptake by plant roots-fixed root distribution

The sink term in Eq. 1 is defined as the volume of water removed from a unit volume of soil per unit of time as a result of plant water uptake. In the case of a fixed rooting distribution, the root water uptake in response to water and salinity stress is expressed as

$$S = S_p \alpha_s(h)\, \alpha_\varphi(h_\varphi) \tag{12}$$

where S_p is the potential water uptake [$cm^3cm^{-3}d^{-1}$] and $\alpha_\varphi(h_\varphi)$ is the osmotic stress function for water uptake and h_φ is the osmotic head [cm]. The water stress response function, $\alpha_s(h)$, is a dimensionless function of the soil water pressure head ($0 \leq \alpha_s \leq 1$) described by van Genuchten (1987) as

$$\alpha_s(h) = \frac{1}{1 + (\frac{h}{h_{50}})^b} \tag{13}$$

where h_{50} [cm] and b [-] are empirical constants. The default parameter of the model is set at h_{50}

equal to -7000 cm and b equal to 3. The parameter h_{50} represents the pressure head at which the water extraction rate is reduced by 50%. This water stress response function, $\alpha_s(h)$, does not consider transpiration reduction near saturation which is related to oxygen stress and is more properly considered based on gas phase composition.

The potential water uptake rate in the root zone is expressed as the product of the potential transpiration rate, T_p [LT^{-1}], and the normalized water uptake distribution function, $\beta(z)$ [L^{-1}], which describes the spatial variation of the potential water uptake rate, S_p, over the root zone, as follows

$$S_p = \beta(z)\, T_p \tag{14}$$

The function $\beta(z)$, in the case of a fixed root distribution, is specified by the user in the input file. The actual transpiration T_a is given by

$$T_a = \int_{L-L_r}^{L} S(h,h_\varphi,z)\,dz = T_p \int_{L-L_r}^{L} \alpha_s(h)\alpha_\varphi(h_\varphi)\beta(z)\,dz \tag{15}$$

The total actual transpiration at each time step is calculated by summation of the transpiration amounts for each of the root zone depth intervals. The transpiration in each of the depth intervals is based on the root distribution function and the stress calculated in that depth interval. There is no compensation at other depths for reduced water uptake within any depth interval. The total transpiration for the simulation is the sum of the actual transpiration time steps. The ratio of actual transpiration to potential transpiration is taken as the relative yield. The h_{50} and p values are input for each crop.

The stress reduction function (on transpiration) given in equation 15 is obtained by multiplication of the product of the water and osmotic stress functions. It is also possible to use this fixed root option for predicting the water uptake and relative crop yield for an annual crop. In this instance the input values are ET_0 x the crop coefficient. Values for these coefficients are crop and locally specific as well as varying with time during growth, thus must be provided by the model user. Use of this option bypasses the more detailed crop model but may provide more accurate prediction of water requirements and use if the crop factors are known for the crop and locality to be simulated.

Water uptake by plant roots-root growth option

A specification of the root growth option enables use of a generic crop growth model. In this instance the input is ET_0 and solar radiation. Additional plant specific information is required including planting date, heat units to maturity and harvest date. The plant is divided into 5 stages of phenology, seedling, vegetative, reproductive, mature and dead, with transitions determined by heat units. Production of biomass is partitioned into root and canopy fractions depending on the phenological state. Among the plant adjustable parameters are canopy extinction coefficient, leaf area index at which maximum transpiration can occur, maintenance respiration, maximum root penetration, exponential root distribution factor, maximum nodal root density, thickness of layer for averaging stress, as well as plant parameters for the Hoogenboom et al. (1987) plant model. In this instance the input ET values are those of the ET_0, referenced well- watered grass, with full canopy cover and is equal to T_p. The actual transpiration rate, T_a, predicted by the model takes into account the water and salinity stress. The rate is calculated by first averaging the water and salinity potential and then calculating stress, and partitioning the plant water requirement in accord with the rooting distribution. The root growth model considers stress, allowing for limited compensation of the root distribution to water and salt stress.

Root growth-UNSATCHEM

The root depth, L_r, can be either constant or variable during the simulation. For annual vegetation the plant submodel is required to simulate the change in rooting depth with time. In UNSATCHEM (Simunek and Suarez, 1994 and Suarez and Simunek, 1996) the root depth is the product of the maximum rooting depth, L_m [L], and the root growth coefficient, $f_r(t)$ [-]:

$$L_r(t) = L_m f_r(t) \tag{16}$$

To calculate the root growth coefficient, $f_r(t)$, Simunek and Suarez (1993b) combined the Verhulst-Pearl logistic growth function with the growth degree day (*GDD*) or heat unit concept (Gilmore and Rogers, 1958). The heat unit model cannot be used directly to predict biomass during the growth stage since it would predict a linear growth with time at constant temperature.

For the growth degree day function the model utilizes a modified version of the relation developed by Logan and Boyland (1983), which can be expressed by a sine function to approximate the daily temperature cycle, and by the three temperature limits, T_1, T_2, and T_3 [K]. Below the base value T_1, plants register little or no net growth. The plant growth is at a maximum level at temperature T_2, which remains unchanged for some interval up to a maximum temperature T_3, above which increased temperature has an adverse effect on growth. Based on this information, Simunek and Suarez (1993b) proposed the following dimensionless growth function

$$g(t) = \begin{cases} g(t) = 0 & t \leq t_p ; t \geq t_h \\ \frac{1}{T_{Bas}} \left[\int \delta (T - T_1) dt - \int \delta (T - T_2) dt - \int \delta (T - T_3) \right) & \\ g(t) = 1 & t \varepsilon (t_m, t_h) \end{cases} \tag{17}$$

where T_{Bas} are the heat units [KT] necessary for the plant to mature and the roots to reach the maximum rooting depth, t_p, t_m, and t_h represent time of planting, time at which the maximum rooting depth is reached and time of harvesting, respectively; and parameter δ [-] introduces into the heat unit concept the reduction in optimal growth due to the water and osmotic stress. The expression inside the parenthesis of equation (17) reaches value T_{Bas} at time t_m when roots reach the maximum rooting depth. The individual integrals in equation (17) are evaluated only when the particular arguments are positive. Parameter δ [-] is defined as the ratio of the actual to potential transpiration rates:

$$\delta = \frac{T_a}{T_p} \tag{18}$$

Biomass or root development during the growth stage can also be expressed by the Verhulst-Pearl logistic growth function

$$f_r(t) = \frac{L_0}{L_0 + (L_m - L_0)e^{-rt}} \tag{19}$$

where L_0 is the initial value of the rooting depth at the beginning of the growth period [L] and r is the growth rate [T^{-1}].

Simunek and Suarez (1993) combined these equations, substituting the growth function calculated from the heat unit concept (17) for the time factor in the logistic growth function (19):

$$t = t_m g(t) \tag{20}$$

where t_m is the time when *GDD* reaches the required value for the specific plant species (T_{Bas}).

Heat Transport

Prediction of temperature in the unsaturated zone is required for prediction of water movement and water content. Plant growth, extraction of water by plant roots and evaporation of water at the soil surface are all highly dependent on temperature. In addition, soil temperature is required for calculation of the temperature dependence of the chemical kinetic and equilibrium reactions and for prediction of CO_2 production. UNSATCHEM and FAO include a heat transport routine which is used for prediction of the factors discussed above.

Concentration/Production/Transport of Carbon Dioxide

Unsaturated zone models typically either consider a closed system with constant inorganic carbon, as is also commonly considered for ground water systems, or assume an open system at fixed CO_2. The first assumption is clearly not desirable as large amounts of CO_2 are produced by plant decomposition as well as plant root respiration. Specification of a fixed CO_2 is a marked improvement over the closed system assumption but still does not consider the spatial and temporal fluctuations. These changes are due to both changes in production of CO_2, as well as changes in the transport of CO_2, which is mostly related to changes in the air-filled porosity of the soil, but can also be related to the flow of water.

Carbon dioxide production

Simunek and Suarez (1993b) described a general model for CO_2 production and transport. Production of CO_2 is the sum of the production rate by soil microorganisms, γ_s [$L^3L^{-3}T^{-1}$], and the production rate by plant roots, γ_p [$L^3L^{-3}T^{-1}$]

$$P = \gamma_s + \gamma_p = \gamma_{s0} \prod_i f_{si} + \gamma_{p0} \prod_i f_{pi} \tag{21}$$

where the subscript s refers to soil microorganisms and the subscript p refers to plant roots, $\prod f_i$ is the product of reduction coefficients dependent on depth, temperature, pressure head (the soil water content), CO_2 concentration, osmotic head and time. The parameters γ_{s0} and γ_{p0} represent, respectively, the optimal CO_2 production by the soil microorganisms or plant roots for the whole soil profile at 20°C under optimal water, solute and soil CO_2 concentration conditions [$L^3L^{-2}T^{-1}$]. The individual reduction functions are given in Simunek and Suarez (1993) and the discussion of selection of the values for optimal production as well as coefficients for the reduction functions is given in Suarez and Simunek (1993).

Carbon Dioxide Transport

Gas transport in the unsaturated zone includes three general transport mechanisms (Massmann and Farrier, 1992): Knudsen diffusion, multicomponent molecular diffusion and viscous flow. However, Massmann and Farrier (1992) showed that gas fluxes in the unsaturated zone can satisfactorily be simulated using the single-component transport equation, neglecting Knudsen diffusion, as long as the gas permeability of the media is greater than about 10^{-10} cm^2. They also showed that CO_2 concentrations and fluxes can be described by Fick's law to within 5% accuracy.

The one-dimensional carbon dioxide transport model presented by Simunek and Suarez (1993a), assumed that CO_2 transport in the unsaturated zone occurs in both the liquid and gas phases. The CO_2 concentration in the soil is governed by convective transport in the aqueous phase and diffusive transport in both gas and aqueous phases, and by CO_2 production and/or removal. The one-dimensional CO_2 transport is described by the following equation:

$$\frac{\partial c_T}{\partial t} = -\frac{\partial}{\partial z}(J_{da} + J_{dw} + J_{ca} + J_{cw}) - Sc_w + P \qquad \textbf{(22)}$$

where J_{da} is the CO_2 flux caused by diffusion in the gas phase [LT^{-1}], J_{dw} the CO_2 flux caused by dispersion in the dissolved phase [LT^{-1}], J_{ca} the CO_2 flux caused by convection in the gas phase [LT^{-1}], and J_{cw} the CO_2 flux caused by convection in the dissolved phase [LT^{-1}]. The term c_T is the total volumetric concentration of CO_2 [L^3L^{-3}] and P is the CO_2 production/sink term [$L^3L^{-3}T^{-1}$]. The term Sc_w represents the aqueous CO_2 removed from the soil by roots water uptake. Substituting expressions for the fluxes into (22) we obtain

$$\frac{\partial(c_a\theta_a + c_w\theta_w)}{\partial t} = \frac{\partial}{\partial z}\theta_a D_a \frac{\partial c_a}{\partial z} + \frac{\partial}{\partial z}\theta_w D_w \frac{\partial c_w}{\partial z} - \frac{\partial}{\partial z}q_a c_a - \frac{\partial}{\partial z}q_w c_w - Sc_w + P$$

(23)

where c_w and c_a are the volumetric concentrations of CO_2 in the dissolved phase and gas phase [L^3L^{-3}], respectively, D_a is the effective soil matrix diffusion coefficient of CO_2 in the gas phase [L^2T^{-1}], D_w is the effective soil matrix dispersion coefficient of CO_2 in the dissolved phase [L^2T^{-1}], q_a is the soil air flux [LT^{-1}], q_w is the soil water flux [LT^{-1}] and θ_a is the volumetric air content [L^3L^{-3}]. The total CO_2 concentration, c_T [L^3L^{-3}], is defined as the sum of CO_2 in the gas and dissolved phases

$$c_T = c_a\theta_a + c_w\theta_w \qquad \textbf{(24)}$$

The total aqueous phase CO_2, c_w, is defined as the sum of $CO_2(aq)$ and H_2CO_3, and is related to the CO_2 concentration in the gas phase by

$$c_w = K_H R T c_a \tag{25}$$

where K_H is the Henry's Law constant, R is the universal gas constant and T is the absolute temperature [K]. Aqueous carbon also exists in the form of HCO_3^-, CO_3^{2-} and other complexed species, such as $CaCO_3^o$, and these species should be included in the definition of c_w. Substituting into (23) gives

$$\frac{\partial R_f c_a}{\partial t} = \frac{\partial}{\partial z} D_E \frac{\partial c_a}{\partial z} - \frac{\partial}{\partial z} q_E c_a - S^* c_a + P \tag{26}$$

where R_f is the CO_2 retardation factor [-], D_E is the effective dispersion coefficient for the CO_2 in the soil matrix [L^2T^{-1}], q_E is the effective velocity of CO_2 [LT^{-1}], S^* is the CO_2 uptake rate [T^{-1}] associated with root water uptake and θ_a is the volumetric air content [L^3L^{-3}].

Under most conditions, the compressibility of the air can be neglected. Then, with the assumption that the air flux is zero at the lower soil boundary and that the water volume changes in the soil profile caused by the water flow must be immediately matched by the corresponding changes in the gas volume, Simunek and Suarez (1993) obtained

$$q_a(z) = q_w(0) - q_w(z) + \int_{L-L_r}^{z} S(z)dz \tag{27}$$

This assumption seems to be reasonable, since when water leaves the soil system due to evaporation and root water uptake, air enters the soil at the surface and, vice versa, when water enters the soil during precipitation and irrigation events, soil air is escaping. Only in the case of saturation (typically at the soil surface) does the condition arise that air can not escape and is compressed under the wetting front.

Chemical Routines

Transport

The governing equation for one-dimensional advective-dispersive chemical transport under transient flow conditions in partially saturated porous media is taken as (Suarez and Simunek, 1996)

$$\frac{\partial \theta c_{T_i}}{\partial t} + \rho \frac{\partial \bar{c}_{T_i}}{\partial t} + \rho \frac{\partial \hat{c}_{T_i}}{\partial t} = \frac{\partial}{\partial z}[\theta D \frac{\partial c_{T_i}}{\partial z} - q c_{T_i}] \qquad i = 1, n_s \tag{28}$$

$$D = \tau D_m + \lambda \frac{|q|}{\theta} \tag{29}$$

where c_{T_i} is the total dissolved concentration of the aqueous component i [ML^{-3}], $\bar{c}_{T_i}$ is the total adsorbed or exchangeable concentration of the aqueous component i [MM^{-1}], $\hat{c}_{T_i}$ is the non-adsorbed solid phase concentration of aqueous component i [MM^{-1}], ρ is the bulk density of the soil[ML^{-3}], D is the dispersion coefficient [L^2T^{-1}], q is the volumetric flux [LT^{-1}], and n_s is the number of aqueous components. The second and third terms on the left side of equation (28) are zero for components that do not undergo ion exchange, adsorption or precipitation/dissolution.

The coefficient D is the sum of the diffusion and dispersion components
where τ is the tortuosity factor [-], D_m is the coefficient of molecular diffusion [L^2T^{-1}], and λ is the dispersivity [L]. This representation is a relatively simplified treatment of the diffusion process.

Solution Species
The FAO and UNSATCHEM (Suarez and Simunek, 1996) models include equilibrium chemistry for the aqueous species and either equilibrium or kinetic expressions for the solid phase controls. Seven major aqueous components, consisting of Ca, Mg, Na, K, SO_4, Cl, and alkalinity are defined, along with SO_4, CO_3, and HCO_3 complexes. The reactions in the CO_2-H_2O system and complexation reactions for major ions have been described in numerous publications.

Calcite and gypsum
The equilibrium condition of a solution with calcite in the presence of CO_2 is described by the expression

$$(Ca^{2+})(HCO_3^-)^2 = \frac{K_{SP}^C K_{CO_2} K_{a_1}}{K_{a_2}} P_{CO_2}(H_2O) = K_{SP}^C K_T \quad \textbf{(30)}$$

where parenthesis denote activities, and K_{CO2} is the Henry's law constant for the solubility of CO_2 in water, K_{a1} and K_{a2} are the first and second dissociation constants of carbonic acid in water, and $K_{SP}{}^C$ is the solubility product for calcite. To obtain equilibrium, i.e., when the ion activity product (IAP) is equal to the solubility product K_{sp}, we solve the following third order equation

$$[Ca^{2+} + x]\,[HCO_3^- + 2x]^2 = \frac{K_{SP}^C K_T}{\gamma_{Ca^{2+}} \gamma_{HCO_3^-}^2} \quad \textbf{(31)}$$

The equilibrium condition has been shown to not be valid for soil systems due to poisoning of crystal surface by dissolved organic matter, thus the FAO model uses an apparent K that corresponds to the point at which no further nucleation occurs. The UNSATCHEM model uses a kinetic option (Lebron and Suarez, 1996) that considers the effects of dissolved organic carbon both on crystal growth and heterogeneous nucleation. The combined rate expression is given by

$$R_T = R_{CG} + R_{HN} \quad \textbf{(32)}$$

where R_T is the total precipitation rate, expressed in mmol $L^{-1}s^{-1}$, R_{CG} is the precipitation rate related to crystal growth, and R_{HN} is the precipitation rate due to heterogeneous nucleation. The R_{CG} term is given by

$$R_{CG} = s\,k_{CG}\left[(Ca^{2+})(CO_3^{2-}) - K_{SP}\right]\left[-0.14 - 0.11\log[DOC]\right] \quad \textbf{(33)}$$

where s is the calcite surface area, k_{CG} is the precipitation rate constant due to crystal growth, and DOC is the dissolved organic carbon in mmol L^{-1}. The R_{HN} term is given by

$$R_{HN} = k_{HN} f(SA)(\log\Omega - 2.5)(3.37x10^{-4} DOC^{-1.14}) \quad \textbf{(34)}$$

where k_{HN} is the precipitation rate constant due to heterogeneous nucleation, *f(SA)* is a function of the surface area of the particles (e.g. clay) upon which heterogeneous nucleation occurs (= 1.0 if no solid phase is present), Ω is the calcite saturation value, and 2.5 is the Ω value above which heterogeneous nucleation can occur. The presence of calcite (varying surface area) does not affect the calcite precipitation rate when DOC is $\geq$ 0.10 mM

Precipitation/dissolution of gypsum is described by. Equilibrium is obtained by solving the resultant quadratic equation.

$$[Ca^{2+}][SO_4^{2-}] = \frac{IAP}{\gamma_{Ca^{2+}} \gamma_{SO_4^{2-}} (H_2O)^2} \quad \textbf{(35)}$$

Magnesium precipitation

The model considers that Mg precipitation can occur as a carbonate (either nesquehonite or hydromagnesite), or as a silicate (sepiolite). Dolomite precipitation is not considered, as true dolomite appears to very rarely form in soil environments. The dissolution rate of dolomite is very slow, especially as the solution IAP values approach within 2-3 orders of magnitude of the solubility product. If nesquehonite or hydromagnesite saturation is reached, the model will precipitate the predicted Mg carbonate. The model allows precipitation of a mixed precipitate (calcite+magnesium carbonate) under conditions of approximately three orders of supersaturation with respect to dolomite. This result is consistent with the high levels of dolomite supersaturation maintained in high Mg waters (Suarez, unpublished data). Precipitation (or dissolution, if present in the soil) of sepiolite is also considered by the model. Sepiolite will readily precipitate into a solid with a K_{SP}^S greater than that of well crystallized sepiolite. Formation of this mineral requires high pH, high Mg concentrations and low CO_2 partial pressure. We utilize the precipitated sepiolite solubility value rather than the well crystallized equilibrium value.

Relatively little information exists on the controls on Si concentrations in soil waters, especially in arid zones. In soil systems Si concentrations are controlled by dissolution and precipitation of aluminosilicates and Si adsorption onto oxides and aluminosilicates. As a result of these reactions Si concentrations in soil solution follow a U shaped curve with pH, similar to Al oxide solubility with a Si minimum around pH 8.5 (Suarez 1977b).

There are two options in UNSATCHEM to predict Si concentrations in solution. In arid land soils it is assumed that Si in solution is a simple function of pH, fitted to data from 8 arid land soils reacted at various pHs for two weeks by Suarez (1977b), as follows

$$\Sigma SiO_2 = 0.001(6.34 - 1.43pH + 0.0819pH^2) \quad \textbf{(36)}$$

where SiO_2 is the sum of all silica species expressed in mol L^{-1}. This relationship likely provides only a rough estimate of Si concentrations, but we consider it acceptable because it is used only to restrain Mg concentrations at high levels of evapotranspiration, when Mg concentrations become very high at low CO_2 and elevated pH. An additional option is to consider the Si concentration to be controlled by inputs from mineral weathering and concentrated only by processes of evapotranspiration. In this case UNSATCHEM utilizes kinetic expressions for the weathering of selected silicate minerals.

Cation Exchange

Cation exchange is generally the dominant *chemical* process for the major cations in solution in the unsaturated zone. Generally cation exchange is treated with a Gapon-type expression of the

$$K_{ij} = \frac{\bar{c}_i^{y+}}{\bar{c}_j^{x+}} \frac{(c_j^{x+})^{1/x}}{(c_i^{y+})^{1/y}} \quad \textbf{(37)}$$

form (White and Zelazny, 1986)

where y, and x, are the respective valences of species i, and j and the overscored concentrations are those of the exchanger phase (concentration expressed in $mol_c\,kg^1$). It is assumed that the cation exchange capacity c_T is constant.

Existing chemical models require either input of a soil specific selectivity value or use a generalized value for the selectivity coefficient. We observe that the experimentally determined selectivity values are not constant, nor is the cation exchange capacity which varies as a function of pH, due to variable charge materials such as organic matter. It has been observed that soils have an increased preference for Ca^{2+} over Na^{+}, and Ca^{2+} over Mg^{2+}, at low levels of exchanger phase Ca^{2+}. Suarez and Wood (1993) developed a mixing model which is able to approximate the nonconstant values of the soil selectivity coefficient by taking into account the organic matter content of the soil and using the published constant selectivity values for clay and organic matter. Calcium preference decreases as the organic matter exchanger sites (which have higher Ca preference than clays) become Ca saturated. UNSATCHEM uses this approach by solving 2 sets of equations for cation exchange (clay and organic matter).

REFERENCES

Bajwa, R.S., W.M. Crosswhite, J.E. Hostetler and O.W. Wright. 1992. Agricultural Irrigation and Water Use. ERS/USDA, Agricultural Information Bulletin No. 638. U.S. Gov. Printing Office Washington D.C.

Belitz, K. and S.P. Phillips. 1995. Alternative to agricultural drains in California's San Joaquin Valley: Results of a regional-scale hydrogeologic approach. Water Resour. Res.31:1845-1862.

Brown, P.L., A.D. Halvorson, F.H. Siddoway, H.F. Maylan and M.R. Miller. 1983. Saline-seep Diagnosis, Control and Reclamation. Great Plains Research Center Conservation Research Report No. 30. U.S. Department of Agriculture. Washington D.C.

California Department of Water Resources. 1994. California Water Plan Update. Bulletin 160-93. Department of Water Resources. Sacramento, CA.

Carsel, R.F., and R.S. Parrish. 1988. Developing joint probability distributions of soil water retention characteristics. Water Resour. Res. 24:755-769.

El-Ashry, M.T., J. van Schilfgaarde and S.Schiffman. 1985. Salinity pollution from irrigated agriculture. J. of Soil and Water Conservation 40:48-52.

Felmy, A.R. 1990. GMIN:A computerized chemical equilibrium model using a constrained minimization of the Gibbs free energy. Pacific Northwest Lab. Richland, Wash.

Ghassemi,F.,A.,J. Jakeman and H.A. Nix. 1995. Salinisation of Land and Water Resources. Human Causes, extent, management and case studies. CAB International Wallingford. U.K.

Gilmore, E. and J.S. Rogers.1958. Heat units as a method of measuring maturity in corn. Agron. J. 50, 611-615.

McNeal, B. L. 1968. Prediction of the effect of mixed-salt solutions on soil hydraulic conductivity. Soil Sci. Soc. Am. Proc. 32, 190-193.

National Research Council. 1996. A New Era for Irrigation. National Academy Press. Washington D.C.

Logan, S. H. and P.B.Boyland. 1983. Calculating heat units via a sine function. J. Am. Soc. Hort. Sci. 108, 977-980.

Mangold, D. C. and C. Tsang. 1991. A summary of subsurface hydrological and hydrochemical models, Reviews of Geophysics 29(1), 51-79.

Massmann, J. and D.F. Farrier.1992. Effects of atmospheric pressure on gas transport in the vadose zone. Water Resour. Res. 28, 777-791.

Postal, S. 1989. Water for Agriculture: Facing the limits. Worldwatch Paper 93. Worldwatch Institute. Washington D.C.

Rhoades, J.D., F. Chanduvi and S. Lesch. 1999. Soil Salinity Assessment: Methods and interpretation of electrical conductivity measurements. FAO Irrigation and Drainage Paper 57. FAO. Rome.

Robbins, C.W., J.J. Jurinak and R.J. Wagenet. 1980. Calculating cation exchange in a salt transport model. Soil Sci. Soc. Am. J. 44:1195-1200.

Simunek, J. and D.L. Suarez. 1993. Modeling of carbon dioxide transport and production in soil:1. Model development. Water Resour. Res. 29, 487-497.

Simunek, J., and D.L. Suarez. 1997. Sodic soil reclamation using multicomponent transport modeling. J. Irrigation Drainage Engineering. 123:367-376.

Simunek, J., D.L. Suarez and M. Sejna. 1996. The UNSATCHEM software package for simulating the one-dimensional variably saturated water flow, heat transport, carbon dioxide production and transport, and multicomponent solute transport with major ion equilibrium and kinetic chemistry. Ver 2.0 Res. Report N0. 141. U.S. Salinity Laboratory,

USDA-ARS, Riverside CA.
Solley, W.B.,R.R. Pierce and H.A. Perlman. 1993. Estimated water use in the United States in 1990. U.S. Geological Survey Circular 1081. U.S. Government Printing Office . Washington D.C.
Suarez, D. L. 1977a. Ion activity products of calcium carbonate in waters below the root zone. Soil Sci. Soc. Am. J. 41, 310-315.

Suarez, D. L. 1977b. Magnesium, carbonate, and silica interactions in soils. U. S. Salinity Laboratory Annual Report, USDA, 120 pp.
Suarez, D.L. 1983. Calcite supersaturation and precipitation kinetics in the lower Colorado River, All-American Canal and East Highline Canal. Water Resourc. Res. 19:652-661.
Suarez, D. L., J.D. Rhoades, R. Lavado and C.M. Grieve.. 1984. Effect of pH on saturated hydraulic conductivity and soil dispersion. Soil Sci. Soc. Am. J. 48, 50-55.
Suarez, D. L. and J. Simunek. 1993. Modeling of carbon dioxide transport and production in soil:2. Parameter selection, sensitivity analysis and comparison of model predictions to field data. Water Resour. Res. 29, 499-513.
Suarez, D. L. and J. Simunek,. 1996. UNSATCHEM: Unsaturated water and solute transport model with equilibrium and kinetic chemistry. Soil Sci. Soc. Am. J. 61:1633-1646.
Suarez, D.L. and J.D. Wood. 1993. Predicting Ca-Mg exchange selectivity of smectitic soils. Agron. Abst. p. 236. Am. Soc. Agron. Madison WI.
U.S. Department of Agriculture. 1986. Agricultural Resources: Cropland, Water, and Conservation, Economic Research Service pp21-22.U.S. Government Printing Office . Washington D.C.
U.S. Department of Agriculture. 1989. The Second RCA Appraisal, Soil, Water and Related Resources on Nonfederal Land in the United States, Analysis of Conditions and Trends. U.S. Government Printing Office. Washington D.C.
U.S. Salinity Laboratory Staff. 1954. Diagnosis and management of saline and alkaline soils. Handbook 60. U.S. Department of Agriculture. U.S. Government Printing Office. Washington D.C.
van Genuchten, M. Th. 1987 A numerical model for water and solute movement in and below the root zone, Unpublished Research Report, U. S. Salinity Laboratory, USDA, ARS, Riverside, CA.
van Genuchten, M. Th. 1980. A closed-form equation for predicting the hydraulic conductivity of unsaturated soils. Soil Sci. Soc. Am. J. 44, 892-898.
van Genuchten, M.Th., F.Leiji and S.Yates. 1991. The RETC code for quantifying the hydraulic functions of unsaturated soils. EPA/600/2-91/065. 85pp.
White, N. and L.W. Zelazny 1986. Charge properties in soil colloids. p.39-81. *In* :D.L. Sparks (ed.) Soil physical chemistry. CRC Press, Boca Raton, Florida