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IMPACT OF SODIUM AND POTASSIUM ON ENVIRONMENTAL SYSTEMS*

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ABSTRACT

Health effects associated with sodium-cycle water softening has led to the consideration of potassium-cycle ion exchange as an attractive alternative. Regulatory agencies, however, have expressed concern regarding the environmental impacts associated with discharge of potassium-laden brine. To assist in providing guidance regarding the relative environmental impacts deriving from discharge of sodium- and potassium-cycle softener regeneration brine, this article summarizes available literature exploring systems potentially impacted by brine discharge. The literature indicates that replacing sodium chloride with potassium chloride as a water softener regenerant appears to result in a more environmentally benign scenario and may, in certain circumstances, be environmentally beneficial. Some areas where potassium chloride may be advantageous are land application of sewage sludge, viral inactivation, mobility in soil, effects on soil properties and impacts on plant life. There are no significant differences between sodium chloride and potassium chloride in effect on engineered physicochemical processes of in aquatic life systems. The impact of sodium may be detrimental to the environment because the uptake of phosphorus by algae was reportedly enhanced by sodium. Potassium, on the other hand, was not reported to enhance phosphorous uptake. Some questions remain about the impact of potassium and sodium on septic tank bacteria, biological waste treatment processes, and effects on natural flora. The literature reviewed on these topics was somewhat conflicting. Further efforts to assess the impact of potassium and sodium should be directed at resolving these literature discrepancies.

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1. INTRODUCTION

Health effects associated with sodium-cycle water softening have led environmental engineering and public health communities to explore the use of potassium as a regenerative cation for ion exchange systems. However, environmental impacts of potassium-cycle regeneration brine in comparison to sodium-laden brine are unclear. This article reviews the available literature regarding the impact of potassium and sodium on environmental systems.

In cation exchange softening, the hardness-producing elements of calcium and magnesium in the water are removed and replaced with a cation bound to a resin [1]. After the ability of the bed to produce soft water has been exhausted, the unit is flushed with a regenerant. A popular regenerant of cation exchange resins has predominantly been sodium chloride [2, 3]. In considering health effects associated with sodium, potassium chloride has surfaced as an alternate regenerant. Potassium chloride, as a water softener regenerant, costs one and a half to two times as much as sodium chloride [4]. Inconsequential differences were reported in hardness removal when potassium and sodium ion exchange cycles were compared. An advantage of potassium chloride regeneration is that 11 to 21 percent less chloride is discharged from backwashing operations [5]. Current estimates (1992) on the quantities of potassium chloride and sodium chloride used for water conditioning are fifteen to twenty thousand tons and 2.332 million tons, respectively [4, 6]. Cole indicates that potassium chloride is a viable alternative for domestic water softeners, particularly in areas where effluent levels of sodium are a concern [5].

A variety of environmental systems may be impacted by the discharge of water softening regeneration brine. Discharges from water softeners may be directed to either on-site wastewater treatment systems (i.e., septic systems), or to publicly-owned treatment works. Regeneration brine may impact process efficacy and may eventually be discharged, in varying concentrations, to the environment via drain fields or receiving water bodies. At this point, should the cations accumulate in a potable water supply, mobility of the sodium and potassium in the environment, and potential impacts on environmental systems become important issues.

Although the major objective of this study was to investigate the impact of replacing sodium with potassium in various operations, there was no significant information available that directly addressed this impact. Available information was consequently extrapolated to explore possible consequences of the substitution.

2. WASTEWATER TREATMENT

There are many types of treatment facilities used to treat domestic wastewater. Primarily wastewater is directed to either septic systems for on-site treatment or publicly-owned treatment works (POTWs). Many times the wastewater contains regeneration brine from water softeners, which may affect the facilities differently. The microbial activity in a septic system may be affected by regeneration brine. Additionally, leaching from septic tank may effect the surrounding soil, plant, and microbial activity. At POTWs, the regeneration brine could effect biological treatment processes if in sufficient concentration.

2.1 Septic Systems

The only work directly addressing the impact of sodium in water softener regeneration waste on septic systems is that of Tyler et al. [7]. Based on a literature search and analysis, Tyler et al. concluded that it is beneficial, both to seepage drain fields and septic tank bacteria, to add sodium-laden softener regeneration waste to septic tanks [7]. The major conclusions of this study included the following:

1. Softener effluents contain significant amounts of calcium and magnesium, which counteract the effect of sodium and sustain soil permeability by maintaining proper sodium absorption ratios (SAR);
2. Reduction in hydraulic conductivity (HC) might be expected if water of low salt concentration such as rainwater is applied after septic tank effluent; and
3. Reduction in HC might be expected if all water passing through the septic tank were softened, and the regeneration water were not passed through the septic tank.

Tyler et al. viewed conclusions 1 and 2 as separate events and recommended that it would be beneficial to add brine solution to septic tanks [7]. However, it appears that they failed to analyze the combined effect of these two factors in the long term. Although softener waste would improve the soil permeability temporarily, at some point rainwater would deteriorate soil hydraulic conductivity according to conclusion 2. Therefore, there appears to be no rationale to the conclusion that application of softener waste would maintain soil HC. Supporting current practice, the authors stated in the third conclusion that the failure to add regeneration waste to seepage fields may destroy the soil HC by increasing soil SAR due to the elimination of calcium and magnesium. This recommendation was made by calculating the increases in swelling pressures of a soil system with constant calcium and magnesium content and increasing sodium levels. Although these evaluations indicate that continuous addition of sodium would deteriorate soil HC, the authors do not identify the situations in relation to septic systems where this is true. Further, it is inconsistent with sound engineering practice to add regeneration waste to a seepage field that has never been exposed to softener regeneration waste and unnecessarily increase salt content of a virgin soil.

Addressing the beneficial effects of brine on septic tank bacteria, the authors concluded that softener regeneration waste would increase the osmotic potential of septic tank effluents bringing it closer to optimum values required for bacteria.

This conclusion was made without experimental validation and was based on studies conducted on pure bacterial cultures under controlled laboratory conditions. Such an extrapolation is somewhat speculative since septic tank ecology is complex and less controllable. In arriving at the above conclusion, the authors have used osmotic potential as the sole criteria to evaluate the impact of brine on septic tank ecosystem. Further, no attempt was made in this study to discuss the impact of ionic strength on the biological solids. A study by Winneberger and Weinberg reported that adding sodium chloride or potassium chloride improved sludge settleability [8]. Such an observation may have been a result of increased double layer compression of the bacterial cells due to increased ionic strength.

The results of a study cited in the Tyler et al. report [7] indicated that addition of salt required an acclimation time and also increased the lag time for gas production [9]. These results clearly contradict the conclusion that the addition of salt enhances the bacterial environment. If the environment was enhanced there would not be a need for acclimation. However, all the studies cited in this article [7] have indicated that the final performance of septic tanks subjected to brine solutions revived after a period of acclimation [9, 10]. Studies conducted on the effects of sodium and/or potassium on bacteria indicate that the preference of sodium or potassium by bacteria is a function of a number of factors such as type of bacteria, substrate, growth environment, etc. [11-15]. In certain situations these ions are interchangeable with equal effect and other times they are not [14, 16].

Although the work of Tyler et al. supports the practice of adding softener regeneration waste to septic tanks, there are other studies that suggest otherwise [7]. A number of studies have been cited that reported deterioration of groundwater quality as a result of septic tank effluent [17-22]. In all cases, sodium and/or potassium were invariably found to be the contaminant that caused deterioration. In a study by DeWalle et al., it was reported that sewage effluent from septic tank drain fields resulted in increased calcium concentrations in the groundwater [19]. Cation exchange between sodium and calcium was explained as the mechanism for the phenomena. This hypothesis was supported by measuring constant sodium concentrations over a thirty-year period. Such an observation is plausible as the soil surface can act as a cation exchange site and the increased sodium concentration can replace calcium from soil surface. Based on conservation of mass, the sodium passing through soil and adsorbing would eventually lead to increased sodium concentrations. Increased sodium concentrations, as a result of continuous application of septic tank effluent, would make the seepage drain field hard and impermeable [19]. A case study by Mancino and Pepper demonstrated this phenomenon [22]. Retardation of potassium through soil as a result of cation exchange was reported by Ceazan et al. [23] and Roda et al. [24].

A potential case of nutritional imbalance in septic systems may be due to insufficient concentrations of calcium and magnesium to prevent uptake and accumulation of sodium [25]. As sodium levels in soil increase, the likelihood for nutritional problems may increase. Another effect of high sodium content is poor soil physical conditions, for example soil permeability, clay swelling and dispersion [25]. For favorable soil conditions, a proper balance between sodium, calcium and magnesium is essential. If calcium and/or magnesium ions are lost from a soil system as a result of cation exchange, the continued application of sodium rich septic tank effluent water may deteriorate soil properties.

2.2 Biological Treatment Processes

In POTWs, biological treatment processes are associated with secondary treatment of wastewater. The primary objective of secondary treatment is to reduce the oxygen demand of wastewater achieving a given level of purification. The level of purification of the effluent is selected to ensure that detrimental environmental effects on receiving water bodies are minimized. Unit operations can be classified on the basis of their microbial population, either fixed film processes or suspended growth processes. In a fixed film process, the microorganisms are attached to a stationary matrix that remains in contact with the influent of wastewater. Fixed film processes include trickling filters and rotating biological contactors where the microorganisms are immobilized. In suspended growth processes, the microorganisms intermix with the wastewater. Activated sludge is an example of an aerobic suspended growth process.

To explore the potential impacts of potassium and sodium on biological treatment processes, an intensive review was conducted on the effects of increased potassium chloride (KCl) and sodium chloride (NaCl) concentrations in the secondary treatment of wastewater [26-33]. These reviews cover both aerobic and anaerobic treatment processes and are relatively old. Current research has been drawn away from the effects of KCl and NaCl on the overall treatment process and has moved toward the effects of these two chemicals on specific organisms involved within the various treatment schemes. The effect on the overall process will be discussed first, followed by the specific organisms.

McCarty and McKinney stated that the anaerobic digestion process efficiency is related to cation type, concentration, and possibility for adaptation to cations [27]. Anaerobic digestion is an ancillary process to secondary wastewater treatment. Their studies included sodium and potassium in concentration ranges of 0.1 to 8.0 g/L and 0.1 to 12.0 g/L, respectively. Investigation by Kugelman and McCarty concluded that the effects of cations on the anaerobic digestion process are functions of all cations present and their concentrations [30]. Kugelman and McCarty studied sodium ion concentrations in a range of 0.046 to 9.2 g/L and potassium ion concentrations in the range of 0.195 to 14 g/L [30]. Both studies showed that each cation had some optimum concentration for maximum anaerobic digestion. Sodium had an optimum concentration range of 0.092 to 0.207 g/L, while the optimum range of potassium was 0.195 to 0.390 g/L. The similarity in their optimum concentration was based primarily on the fact that they are both monovalent ions. On a molar basis, the order of inhibition by cations, in excess of optimum concentration, was $K^+ > Na^+$. Initial growth inhibition for sodium was 3.45 g/L, while approximately 2.34 g/L of potassium was enough for inhibition to be observed [30]. In general, toxicity increased with valence and the atomic weight of the cation. Perhaps the most important conclusion from these studies of cation effects is that cations play a nutritional role in the metabolic pathways of all organisms. Metabolic functions of potassium and sodium result from the fact that these cations serve as metallic activators for a wide variety of enzymes, as well as osmotic regulators.

Similarly, Ludzack and Noran investigated the effects of various NaCl concentrations on the activated sludge process [31]. It was found that increasing the NaCl concentration to 5.0 g/L stimulated oxygen uptake. However, NaCl concentration beyond 5.0 g/L decreased flocculation and oxygen demand removal efficiency. Nitrification was also curtailed severely. The higher NaCl concentrations apparently caused a considerable degree of lysis and release of cellular material. In a later article, Kincannon and Gaudy [32] concluded that the biochemical response in an activated sludge process was inversely proportional to both NaCl and KCl concentrations beyond a concentration of 3.5 g/L of each salt. Kincannon and Gaudy [32] only studied the effect from salt ion pairs and not the individual cations. Therefore, no conclusion can be drawn on which component, either the cation or the anion, of the salt caused the inhibition at the higher concentrations. The investigation by Ludzack and Noran revealed a correlation between the chloride (Cl^-) concentration and the efficiency of activated sludge processes [31]. The work of Ludzack and Noran concluded that the inhibitory effect of the NaCl solution on the biochemical response in activated sludge processes can be attributed to the chloride concentration rather than the associated cation [31]. Ludzack and Noran investigated the effects of NaCl and Cl^-, they did not investigate the effect of Na^+ [31]. McCarty studied effects of both the cation and the anion of NaCl and KCl on biological treatment processes [29]. McCarty [29] found, contrary to Ludzack and Noran [31], that the toxicity is normally associated with the cation, rather than the anion portion of the salt.

In a recent study, the effects of potassium on excess uptake of phosphate in an aerobic-anaerobic activated sludge process were examined (Imai and Endoh [33]). Imai and Endoh concluded that the presence of sufficient potassium, a ratio of potassium to phosphate equal to 0.9, was necessary for excess uptake to occur [33]. They also stated that potassium deficiency for phosphate uptake will seldom be encountered in domestic sewage, since approximately 3-10 mg/L of potassium is enough for phosphate removal. The wastewater in their study contained 0.016 g-K/g-VSS. Their results imply that potassium is needed in excess to remove excess amounts of phosphate, and that potassium deficiency inhibits the excess uptake of phosphate. The effect of potassium on phosphate removal was also studied and compared to the effect of sodium on phosphate removal (Comeau et al. [34]). Comeau et al. [34] reported that in biochemical models of sodium and potassium effects on phosphate, only potassium was utilized in co-transport with phosphate uptake.

The actual overall benefit or drawback of potassium and sodium in anaerobic (or aerobic) sludge digestion processes remains unclear. As previously mentioned, the current research trend has been geared toward the effect of KCl and NaCl on organisms present within various treatment schemes. The presence of potassium and sodium are both required in varying concentrations by microorganisms for metabolic activity. In an anaerobic digestion process there are two main groups of microorganisms present in the digester: acidogenic and methanogenic. The ability of acidogenic organisms to tolerate higher levels of alkali salts, such as NaCl and KCl, than methanogenic organisms has been demonstrated by Kugelman and McCarty [30]. Kugelman and McCarty concluded that methanogenic bacteria are more sensitive to slight changes in environmental conditions such as pH, ionic strength, and temperature than the acid-forming bacteria [30].

In reviewing literature for the effect of potassium and sodium on methanogenesis, the focus was directed to those organisms that are predominant in an anaerobic digester, typically *Methanosprillium, Methanotrix* and *Methanosarcina*. The ion transport mechanisms in methanogens are of special relevance to digester performance and optimization [35]. The importance of potassium is seen in the ammonia/potassium exchange [36-40]. Potassium is also required for the activation of phosphoenolpyruvate, although the specific amount of potassium that is required remains unclear. Sodium cannot be substituted for potassium [36].

According to the chemiosmotic theory, it is suggested that sodium and potassium play important roles for adenosine triphosphate synthesis and nutrient transport [37]. The chemiosmotic theory states that bacteria cells can expel protons from their cytosol using the energy derived from the hydrolysis of adenosine triphosphate, or by using light energy in the case of photosynthetic organisms and halobacteria, or oxidation of an electron donor by membrane bound respiration. This process results in energy conservation in the form of a membrane potential and an osmotic component. The proton motive force is then the summation of the membrane potential and chemical potential. Therefore, in media that have high potassium concentrations ($K^+ > 3.9$ g/L), there might be a decrease in methanogenesis. It is speculated that potassium may simply enter cells through membrane leaks or via a potassium transport carrier, thus decreasing the transmembrane electron potential [37].

Sprott et al. investigated the capability of methanogenic bacteria to maintain transmembrane gradients of various cations [38]. As in most procaryotes, potassium is accumulated in the cytoplasm of methanogens and sodium is extruded, although an accumulation of sodium, to several times that in the medium, can occur. Sodium content of the cells varies widely, from 0.3 to 4.0 percent, as does the potassium content, 0.13 to 5.4 percent. Methanogens can maintain a fairly constant internal pH in response to an imposed pH gradient once a membrane potential has been established. The presence of a high potassium concentration in the medium can interfere with membrane potential [38]. The concentration of potassium that is problematic is usually higher than that of cytoplasmic concentration. The internal potassium concentration is normally about 7.8 g/L for most methanogens [38, 39].

Methanogens and acidogens utilize similar metabolic mechanisms for the autotrophic fixation of carbon dioxide. Given that sodium is required for methanogenesis, and that the Na^+/H^+ antiporter exists in the acidogen, the potential importance of sodium in energy conservation during acidogenesis has been postulated [41]. Sodium ion requirements by methanogenic bacteria can be attributed to at least four different functions for bacteria cells [12]. First, a sodium ion-solute co-transport system can exist. Secondly, a sodium-coupled energy conservation and energy transduction mechanisms are present. Thirdly, pH homeostasis mechanisms are present. Finally, sodium ions are required for the activation of special enzymes.

2.3 Land Application

Land farming is known as the application of sludge from wastewater to agriculture land for potential use as fertilizer [42]. It is possible that harmful effects on some soil microbial groups can arise after exposure to high concentrations of potassium and sodium from land farming effluent [43]. Soil microorganisms of interest are Coryneform, *Bacillus*, Actinomycetes, *Micrococcus, Acinetobacter, Pseudomonas, Alcaligenes, Aerococcus*, Enterobacteria, and Yeasts.

Various studies have been completed to review the potential pitfalls or advantages of land farming of municipal wastewater sludge [44-49]. These studies listed sodium as a potential harmful element in sludges that are land farmed because of the potential impacts of sodium on the soil and crops. Potassium was not listed as a harmful element to the crops, but could have potential problems associated with indigenous soil microorganisms. The effectiveness to which the soil and crops were able to remove potassium from the effluent that percolated through the soil was greater than the removal efficiency of either nitrogen or phosphorous [44, 45]. Uradnisheck and Corcoran concluded that crops (not specifically stated) and soils are effective in removing virtually all of the nitrogen, phosphorous and potassium from the wastewater [46]. The crop yields were substantially increased by plant nutrients in the effluent. Overman and Leseman concluded that the coliform index and potassium concentrations in groundwater did not increase, but the sodium concentrations did increase in groundwater [48]. This provided further evidence that sodium was not consumed by the crops or the soil flora that were present.

The potential benefit of potassium in the sewage sludge is cited in numerous literature reports [44-49]. Lui reported that the lack of coliform bacteria and other microbial consortium in anaerobically digested sewage sludge that was land farmed is due to soil permeability and the elevation of the groundwater table [47]. The possibility of potassium and sodium being utilized by microorganisms in the soil after land application was reported as unlikely [47]. Overman and Leseman [48] confirmed the findings of microbial non-utilization of potassium and sodium. They also reported that the potassium was probably removed by the crops. Overman and Leseman also suggest that sodium was neither removed by crops nor soil bacteria, but instead, sodium had accumulated in the soil [48]. These results would indicate that the removal of potassium was completed mainly through plant uptake, and sodium concentration was neither affected by surrounding crops or indigenous microorganisms. More recent publications have contested this observation [49, 58]. Paredes et al. have observed a persistent twenty-fold increase in colony forming units in high soil salinity throughout their study [49]. In a follow up study, Paredes et al. suggested that the increase in soil microflora could be a result of the nitrogen and phosphorous in the effluent, although the potassium and sodium did play a role [50]. The role of potassium and sodium was never clarified by Paredes et al. These findings are supported by the fact that both potassium and sodium play equally major roles in nutrient transport and are active components of general metabolic pathways in microorganisms.

2.4 Disinfection

There is strong evidence that the concentration of chlorine that will inactivate bacteria to acceptable levels for drinking water will typically not reduce virus concentration to the same level [51]. There is also evidence that aggregation, or clumps, of viruses survive exposures to chlorination which inactivate singular dispersed particles (Scarpino et al. [52]). Virus aggregation is substantially more resistant than a suspension of single particles [53, 54]. In viral aggregation, pH and ionic strength are critical [55, 56]. Floyd and Sharp reported that the state of aggregation of a virus suspension was strictly dependent on the ionic composition of the suspending medium [53]. Other publications have stated that the aggregation at low pH could not be prevented by suitable concentration of sodium ions [57]. Aggregation in water, at pH 7, was found to be reversible by the addition of NaCl and KCl. Monovalent ions, such as potassium and sodium, were capable of preventing aggregation [53]. Addition of mono- and divalent cations in concentration covering those typically found in natural water bodies were generally found to cause a decrease in aggregation [54].

The rate of inactivation of poliovirus in water by chlorine is strongly influenced by pH, which in turn influences the relative amount of the HOCl and OCl^- that is present and acting on the viruses [56]. The inactivation rate of the HOCl is a function of the dissociation constant. The dissociation constant of HOCl is 7.3. It is documented that OCl^- is less effective as a disinfecting agent than HOCl [51, 58].

Studies indicate that the addition of alkali cations, such as potassium and sodium, to HOCl solutions enhance the virucidal efficiency of such solutions. It is postulated that the basis for this effect is the formation of neutral alkali cation-hypochlorite ion pairs producing biocidal potency greater than hypochlorous acid [59]. The concentration of the NaCl and KCl was 2.3 g/L and 3.9 g/L, respectively, in the studies performed by Haas et al. [59]. These results might suggest that the potassium ion or sodium ion either is having some effect on the virus, or is reacting with the OCl– and forming ion pairs which may be as effective as HOCl. This is coupled with the observation that the presence of potassium chloride greatly decreased the aggregation of viruses as compared to the presence of equal molar sodium chloride [60]. Sharp et al. stated the distribution of HOCl and OCl^- is influenced to a lesser extent by the addition of sodium chloride than potassium chloride [56]. Jensen et al. [60] reported that between sodium chloride and potassium chloride, KCl was more effective in making the inactivation effect of OCl^- at pH 10 equal to that of HOCl at pH 6. Both Sharp et al. [56] and Jensen et al. [60] give no explanation for this phenomenon, but current research is still being pursued by Berg et al. [61-63].

Current research by Berg et al. [63] suggests there may be another disinfection scenario, Berg et al. [63] found that the rate of inactivation increased 15 fold with 1.2 g/L of KCl present, and virus inactivation was seven times faster with 0.526 g/L of KCl present. Berg et al. [62, 63] suggested that the alkali cations, present in greater concentration than OCl^-, neutralize negative charges on the virions. Typically, vital sites on virions are negatively charged repelling OCl^-. Neutralizing these sites will facilitate OCl^- access [62].

3. MOBILITY AND IMPACT OF SODIUM AND POTASSIUM IN THE ENVIRONMENT

Among the major cations (Na^+, K^+, Ca^{++}, or Mg^{++}), sodium appears to be the most mobile ion leading to groundwater pollution [64]. Investigating the impact of sewage farming on soils, Henry et al. observed marked movement of sodium because of its low fixation capacity [44]. Furthermore, they observed that high additions of sodium caused releases and movement of calcium and magnesium from the soil surface as a result of ion exchange. Similar effects were observed by Dance and Reardon in assessing migration of contaminants in groundwater [65]. The order of attenuation for major cations was observed to be $K^+ > Mg^{++} > Na^+$. Dance and Reardon also observed development of a calcium-halo as a result of liberation of calcium ions due to cation exchange on the soil surface [65]. Hayes et al. [66] reported similar replacement of calcium and magnesium ions as a result of sodium in irrigation waters.

Fixation and subsequent release are very important processes governing the migration of potassium ions in the environment. The mechanism of potassium fixation is due to entrapment of these ions in the interlayer space of clays [67]. Potassium is preferentially fixed as a result of low hydration energy of potassium ions and its size, similar to that of the ditrigonal holes in the tetrahedral sheets [68]. According to Conkling and Blanchar [69], potassium has diffusion coefficients of 2.13 to 4.49 x 10^{-10} m^2/s in solution and 0.55 to 1.21 x 10^{-10} m^2/s on surfaces. As mentioned earlier, potassium has been reported to exhibit pronounced attenuation as compared to other major cations. Studying the impact of sewage irrigation on Miami silt loam, Henry et al. [44] observed negligible amounts of potassium losses from the soil matrix. Fixation of potassium by the soil in unexchangeable forms was postulated because of potassium attenuation. When synthetic sewage effluent was leached through undisturbed soil cores, Hill [64] reported 75 percent loss in potassium, but only a 10 percent loss in sodium from the aqueous phase. In a case study on migration of contaminants in groundwater, Dance and Reardon observed that the bulk of injected potassium sorbed very close to the point of injection and subsequently desorbed as the background concentrations dropped [65]. The fate of potassium applied to crops in soil, runoff and drainage waters was reported by a number of investigators [66, 70-72]. Based on results from continuous monitoring of potassium concentrations from sludge and fertilizer-amended soils, Jones and Hinsley reported that compared to potassium reserves in soil profile, losses due to runoff were negligible indicating low mobility of potassium in soils [72]. This study also reported no variation in potassium mobility as a result of accumulations of organic matter.

Effects of trace metals such as copper and cadmium on the adsorption kinetics of potassium were reported [73]. Addition of copper and cadmium increased exchange-site selectivity for potassium, suggesting reduction in potassium mobility due to the presence of trace metals. In a recent study by Ceazan et al. on the transport of K^+ and NH_4+ ions through a sand and gravel aquifer it was demonstrated that clay contents of less than 0.1 percent markedly affected the transport of both ions [23]. Adsorption of cations in a nonexchangeable form in the interlayer region of expanding 2:1 layer aluminosilicate clay minerals (fixation) may reduce fertilizer-use efficiency of K when added to soils in which such minerals predominate [74]. This study reported decreased potassium fixation due to preferential adsorption of ammonium (NH_4+) ion. Sadusky and Sparks showed the impact of anions on K^+ ion mobility and retention on two variable-charge Atlantic Coastal Plain soils at pH 5 and 6 [75]. It was reported that the amount of cation adsorption in the presence of a particular accompanying anion followed the order $SiO_3^{3}– > PO_4^{3}–> SO_4^{2}– > Cl^- > ClO_4–$. This may be a direct result of outer sphere complexes formed with the various anions.

3.1 Effects on Soil Properties

It is adequately documented in the literature that sodium reduces hydraulic conductivity (HC) of clay-laden soils. Swelling of expansible clays and dispersions of nonexpanding clays have been responsible for reductions in HC. HC decreases with decreasing electrolyte concentration and increasing sodium adsorption ratio (SAR) [76]. Relative decreases in hydraulic conductivity were observed as a result of clay dispersion and subsequent clogging of pores. The effect of low electrolyte concentration and exchangeable sodium percentage (ESP) have been studied by numerous investigators [76-78]. A commonly observed effect was that permeability of a soil tends to decrease with increasing ESP and decreasing electrolyte concentration. Dispersion related decreases in HC as a result of increased pH were also observed [79, 80]. Although soils with high ESP have been observed to be sensitive to changes in cation composition and electrolyte concentrations, Gal et al. have demonstrated that soils with low ESP can also be dispersive [81]. Some studies also demonstrated significant dispersion of low sodium soils under low electrolyte conditions [77, 82, 83]. These studies indicate that deterioration of soil properties is not only a function of ESP, electrolyte concentration, and pH, but also depends on clay mineralogy and clay content. The effect of SAR, electrolyte concentration, and clay mineralogy was investigated by Velasco-Molina et al., who demonstrated that montmorillonitic and micaceous soils disperse more in low salt solutions at low SAR than the kaolinitic soils [84]. The effect of mineral weathering on HC was demonstrated by Shainberg et al. [82] and Alperovitch et al. [85]. Soils containing minerals that readily release soluble electrolytes prevent soil dispersion due to high salt concentrations in the leaching solution as a result of dissolution.

The effects of adsorbed potassium on soil HC seem to vary, possibly due to differences in clay mineralogy and sample preparation procedures [86, 87]. Ahmed et al. reported the relative impact of four major cations on HC of Tropical Red Earths and Tropical Black Earths by four major cations in the order of Na $\geq$ K > Mg = Ca [88]. They indicated similar structural deterioration in soil properties by sodium and potassium. Martin and Richards also reported reduction in HC due to increasing potassium [89]. However, other studies reported increasing physical deterioration as a result of increasing exchangeable sodium, but potassium seemed to favor structural stability [90, 91]. Gardner et al., investigating the impact of electrolyte concentration and ESP on diffusivity in soils, concluded that potassium was responsible for only 25 percent of the deleterious impact caused by sodium on unsaturated water transmission [92]. Potassium saturated soils were found to have larger aggregates and greater aggregate stability than sodium saturated soils, suggesting that exchangeable potassium should have a favorable effect on soil permeability K > Ca = Mg > Na [93] and K > Ca [94]. Chen et al. compared small exchangeable potassium percentage (EPP)-effects on relative HC of three types of soils [95]. Small EPPs increased HC up to 20 percent in some soils and decreased in others. However, large EPP values produced deleterious effects in all soil types. A comparison of the effect of sodium with that of potassium indicated that a 15 percent ESP reduced HC by 80 percent whereas 60 to 70 percent of EPP were required to cause a similar reduction suggesting that the deleterious effect of potassium is less severe than in sodium in accordance with other studies. Shainberg et al. investigated the effect of exchangeable potassium on the HC of smectite-sand mixtures in relation to charge density of clays [86]. They observed an increase in the HC, with an increase in the charge density of the clay for the same

ESP values and suggested that low hydration energy of potassium ions in association with the strong electrostatic attraction between platelets of smectities being responsible for higher HC for clays with high charge density. Recently, Levy and van der Watt reported reduction in HC with increasing exchangeable potassium, but potassium did not have as adverse an effect as exchangeable sodium on the permeability [87]. In an interesting study, Hesterberg and Page investigated the effects of pH on critical coagulation concentrations (CCCs) of cation (Na or K) saturated illite soils [96]. Their study revealed that potassium was three times more effective than sodium for coagulating illite due to greater surface complexation of potassium, suggesting less dispersive nature of potassium saturated illite soils for a given electrolyte concentration.

3.2 Effects on Algae

Algae are photosynthetic eucaryotes. In natural water bodies, algae can be detrimental to fresh water ecosystems. Various algae that may be present include chlorophyta (green algae), euglenophta, cyanophyta (blue-green algae), and chrysophyta. Green algae is the major group observed in natural aquatic environments. The other algal group of concern is blue-green algae. The prokaryotic blue-green algae are mainly responsible for large "algal blooms." Algal blooms are usually caused by increased nutrient concentrations in the water, optimum temperatures (for the particular species), and increased light, or all three. Blue-green algae can fix atmospheric nitrogen, increasing nitrogen content of the water upon their decomposition, thus increasing the chance of an algal bloom in the case where nitrogen is the limiting nutrient in the water [97].

Increases in potassium ions could increase growth rates in existing algae [98, 99]. Neither Corbitt [98] nor Kappe and Kappe [99] discuss specific mechanisms of the metabolic pathway that describes how potassium contributes to increased growth rates or the effect on nitrogen fixation. Kappe and Kappe speculate that potassium increases growth rate because it is considered the major cation of the cytoplasm with electrochemical and some catalytic functions [99]. Kappe and Kappe also stated sodium is a potential contributor to increased algal growth [99].

In the Great Lakes, an increase in cation levels may contribute to accelerating eutrophication [100]. Phosphorous uptake experiments investigated sodium concentrations in the range of 0 to 20 mg/L, and potassium concentrations in the range of 0 to 100 mg/L. Potassium concentrations in many unpolluted freshwater systems normally exist in the range of 1 to 5 mg/L, while unpolluted freshwater lakes and streams contain 5 to 10 mg/L of sodium [100]. In the absence of potassium, external concentrations of sodium increase phosphorous uptake by green algae. In the absence of sodium, external concentrations of potassium seemed to decrease the phosphorous uptake by green algae [100]. Mohleji and Verhoff hypothesized that sodium increases phosphorous absorption by converting insoluble nutrients to an available supply of soluble nutrients through the stimulation of phosphorous transport [100]. According to this hypothesis, sodium and phosphate react with a carrier to form a complex which is transported across the cell membrane, and then the phosphate is released inside the cell. The carrier returns to the outside of the membrane and reacts with more sodium and phosphate—thus continuing the cycle. The same hypothesis was reported for blue-green algae [101]. The uptake of phosphorous by blue-green algae is affected by sodium concentration and not potassium. Sodium-stimulated phosphorous uptake in algae is in contrast to the microbial uptake of phosphorous stimulated by potassium cited previously. When sodium is present in concentrations greater than 5 mg/L, the blue-green algal group exhibit higher nutrient uptakes, particularly related to phosphorous [101]. In addition, sodium has positive effects on photosynthetic nitrogen-fixation by blue-green algae, while potassium does not exhibit this relationship [102]. Sodium and potassium have effects on cellular growth and metabolism of nutrients. Sodium has been shown to inhibit reductase activity in cultures of blue-green algae [103]. Ward and Wetzel state that blue-green algae have an absolute requirement for sodium [103]. Ecologically, nitrogen-fixing blue-green algae are of particular interest because of their potential to contribute simultaneously to the carbon and nitrogen input of certain water strata.

3.3 Effects on Natural Flora

A wide consortium of prokaryotic and eukaryotic microorganisms exist as natural flora. Much of the literature on microorganisms have been directed toward isolated (or pure) cultures. Literature cited in this section does not deal specifically with any of the previously mentioned processes such as land farming and biological treatment. Instead, these studies were performed in many cases for species specific cultures.

Many procaryotes can grow in the absence of sodium, but some halophilic, methanogenic, acetogenic and marine organisms require this cation [12, 15]. It has been reported in numerous studies [11-13; 41; 104-109] that low concentration (< 2.3 mg/L) of sodium chloride stimulates biological action, and a higher concentration inhibits biological action. Similar results were obtained for studies that concentrated on potassium chloride [110-119]. In general, these studies indicate similar relative potencies of the various cations.

It has been proposed by many authors [11, 13, 107, 120, 121] that all marine bacterium, but not all terrestrial forms, have an absolute requirement for sodium ion in their metabolism and for cell structure stability. In the case of marine bacteria, the sodium ion cannot be replaced by potassium ions [11, 120]. The primary reason for this is that the potassium required for growth requires sodium for transport into the cell. This type of sodium pump has the same configuration in terrestrial bacteria. In most terrestrial organisms, it is the increased intracellular potassium that drives the cation exchange pump. In marine bacteria, however, there is a Na^+/H^+ antiporter. This antiporter system extrudes cations from the cytosol to maintain intracellular pH.

Like other terrestrial organisms, soil bacteria tend to establish gradients of Na^+ and K^+ ions between their cytoplasm and surrounding medium, such that the K^+ concentration of the cytoplasm is greater than, and the Na^+ concentration is less than, that of the environment. Cytoplasmic potassium ions activate a number of enzymes and are required for ribosomal protein synthesis. Beyond that, the movement of potassium and sodium ions across the cytoplasmic membrane have been implicated in several homeostatic mechanisms, including the regulation of turgor and of the cytoplasmic pH [111]. In general, bacteria will maintain an internal osmolarity higher than that of the external media, resulting in turgor pressure that is necessary for cell growth. In hypertonic environments, ionic pumps are generally thought to extrude salts and water to regulate cell volume and maintain an almost constant intracellular pH [118, 119]. When many of these soil bacteria are presented with increased potassium ions, an increase in some metabolic enzyme activity is observed [112]. As described previously for methanogenic bacteria, increasing potassium ions in the environment can effect the proton motive force across the cytoplasmic membrane of soil bacteria [114]. The proton motive force across the cytoplasmic membrane plays a key role in biological energy transduction. The proton motive force is the sum of the transmembrane electrical potential and the transmembrane pH gradient. In increased potassium ion concentration environments, a depolarization of the transmembrane electrical potential can occur. This will interfere with the pH regulation of the bacteria [14].

All organisms require water, hence water availability is one of the most important factors affecting the growth of microorganisms in a natural environment. Water availability is generally expressed in physical terms, such as water activity. Water availability does not depend directly on the water content of the environment because various solid substances and surfaces are able to adsorb water molecules to various degrees, hence varying available water. Also, solutes such as salts that are dissolved in water have an affinity for water, and the water associated with such solutes may become unavailable to organisms. Different affinities for cations exist with a proposed order of affinity for bacteria as $K^+ > Na^+$ [122]. The presence of excess KCl and NaCl in the environment can decrease the water availability [105, 122]. Nielsen and Zeuthen stated that there is a slight difference in water availability between solutes of NaCl and KCl, and that KCl had a lower water activity [122]. This is contrary to expected water availability [123]. Vinopal stated that water availability should not depend on the type of solute, only the quantity of elements [123].

3.4 Effects on Aquatic Life

Since aquatic organisms, including fish, have a high bioaccumulation index for heavy metals and many organic compounds [124], elevated concentrations of potassium in treated effluent could impact the existing ecosystem. Potassium was listed by de March as a marine toxin because it can cause an additive effect with relationship to heavy metals such as copper, cadmium and zinc [125]. de March hypothesized that potassium ions increase the heavy metal binding capacity and distribution on the gills and in the liver cytosol of many aquatic species [125]. Acute forms of this phenomenon exist naturally, and no maximum potassium limit was given for this effect to become chronic [125].

One of the most important aspects of aquatic systems is dissolved oxygen, and although potassium does not directly decrease the dissolved oxygen concentration, it can contribute to the decline of dissolved oxygen indirectly. A decrease in dissolved oxygen can be realized through an increase in algal blooms [126].

Potassium does have some advantages over sodium in a relationship to aquatic plants. Several articles report that the presence of potassium in an aquatic system can be beneficial to aquatic plants [127-129]. Strauss states that the presence of sodium may not inhibit growth of some aquatic plants because they can survive in brackish waters [128]. Potassium, however, is a required growth factor, and as such, any increase in concentration will be utilized for growth. Strauss' results agreed with those of Volt and Phinney, who cited a minimum potassium concentration of 2.5 mg/L [127].

Potassium chloride, at low concentrations, was reported to be efficacious in controlling *Dreissena polymorpha* [130]. *Dreissena polymorpha*, zebra mussel, has become a major concern in the Great Lakes. Fisher et al. determined that the K^+ ion mode of action was via destruction of gill epithelium cellular integrity [130]. Although a zebra mussel potassium chloride LC_{50} of 138 mg/L was reported, KCl was reported to be benign to other non-target organisms such as *Gambusia affinis*, mosquito fish (upto tested concentrations of 186 mg/L); *Helisoma* spp., aquatic snail (upto tested concentrations of 186 mg/L); *Corbicula fluminea*, freshwater mussel (upto tested concentrations of 500 mg/L as KH_2PO_4); and *Anodonta imbecillus*, juvenile freshwater mussel (upto tested concentrations of 100 mg/L).

3.5 Effects on Plants

The impact of sodium in relation to soil surface sealing was evaluated by Painuli and Abrol [131]. They demonstrated that sodic soils are more susceptible to surface sealing because surface sealing increases with increasing ESP. Excess exchangeable sodium is responsible for poor physical conditions of soils, including restricted aeration of moisture content; adversely affected growth yield, chemical composition, and nutrient uptake by plants. Sodium toxicity can cause leaf burn and defoliation [132]. Effect of sodium in irrigation waters on crop yields has been reported in a number of studies [132-135]. Effect of soil sodicity on growth yield and chemical composition of various agricultural products is also adequately documented in the literature [136-138]. A commonly observed trend in all of these studies was a decrease in crop yield and quality with increase in sodium percentage.

Potassium is an essential element for plant growth and is taken up selectively by plants in the presence of a large excess of sodium [139]. Plants have a very high capacity to accumulate potassium in fertilized soils. Likewise, animal cells contain more potassium than sodium, in spite of intercellular fluids being sodium rich. Physiologically, potassium functions in two major ways:

1. It forms loose associations with proteins and is an activator pyruvate kinase and many other enzymes; and
2. It is an osmotic regulator in association with organic acids ions (but is not normally replaceable by sodium).

The level of total potassium in mineral soils is usually 0.4-29 mg/Kg [140]. Potassium is most available in soil water. Its diffusion to plant roots provides adequate potassium for plant uptake. The diffusion process depends on soil water content, tortuosity of the diffusion pathway, temperature, diffusion coefficients and the K^+ ion concentration gradient [140]. The uptake of potassium by plants is rapid, and the level of potassium in soil water is relatively low, therefore, continuous replenishment of soluble potassium is necessary to maintain an adequate supply to plants. Application of potassium in any form increases the level of K^+ ions in the soil water, but in the presence of clay, much of the added K^+ ion is adsorbed. In the presence of clay minerals with high fixation capacities, potassium ions may become strongly bound and converted to non-exchangeable forms. Yanishevskiy et al., studying the long term effects of application of potassium fertilizers, observed that doubling the amount of potassium reduced the amount of nitrogen compounds in the nonhydrolizable residue, and increased the amino acids content, indicating loosening and degradation of the stable components of the humic materials in the matrix [141]. Although potassium is an essential plant nutrient, excessive applications of potassium can result in unbalanced plant uptake and luxury consumption [142, 143]. Elevated concentrations of potassium in heartwood of trees as a result of groundwater contamination from a potassium rich munitions waste was reported by Vroblesky et al. [144]. Such disproportioned consumption would alter the uptake of other elements by plants and reduce the quality of forage as a feed for grazing animals [145].

4. SUMMARY

This article summarized available literature on environmental impacts of sodium and potassium. Based on the literature reviewed, replacing potassium chloride for sodium chloride as a water softener regenerant may, in certain instances, be environmentally beneficial.

There appear to be somewhat desirable consequences of replacing sodium with potassium in the areas of land application of sewage sludge, mobility in soil, effects on soil properties and viral inactivation. No significant differences would be expected in the areas of engineered physicochemical processes or aquatic life. One area reviewed in this article revealed that the impact of sodium may be detrimental to the environment, where, in fact, sodium enhanced the uptake of phosphorus by algae. Potassium, on the other hand, was reported to exhibit no correlation to enhanced uptake of phosphorous. Review highlights of these areas are summarized below.

Concerning land application, it may be advantageous to have potassium-cycle softener regeneration brine discharged to publicly-owned treatment works. Land application of sludge is used by many farmers as fertilizer, and unlike sodium, potassium is an essential nutrient for agricultural crops. The crop's fixation capacities can inhibit potassium migration and increase its availability as a nutrient. However, this can also cause excessive build up of potassium and result in nutritional imbalances for plants.

Although permeability of soils is a function of clay type, pH, and electrolyte concentration, high exchangeable sodium percentage values have been largely responsible for deterioration of soil properties. Sodium has been reported to cause dispersion, swelling and surface sealing of soils resulting in significant deterioration of soil properties. Initial studies reported that potassium and sodium had similar deleterious effects on HC. But a majority of the later studies indicate an intermediate effect of potassium on hydraulic conductivity, suggesting that adsorbed potassium is not as beneficial as calcium or magnesium, but less detrimental than sodium. Among the major cations, sodium and potassium have the highest and lowest mobilities, respectively, in the environment. As a result of its mobility, sodium may have greater pollution potential than potassium. In addition to causing reduction in hydraulic conductivity, sodium can cause leaching of calcium and magnesium from the soil matrix. Loss of calcium and magnesium can deprive soils of essential plant nutrients and seriously impact soil fertility. Although potassium is preferentially adsorbed over many cations, no study has reported liberation of calcium or magnesium due to potassium adsorption.

Although both elements may have partially detrimental effects on environmental systems, only potassium can be considered beneficial. The potassium that enters the environment through seepage fields and land application, although consumed by some indigenous soil bacterial, is primarily consumed by crops. Some questions remain about the impact of potassium and sodium on septic tank bacteria, biological processes of wastewater treatment, and effects on natural flora. Sodium is transported through the ecosystem and not largely consumed by any organism. The literature reviewed for this section was somewhat conflicting. Further efforts to assess the impact of potassium and sodium should be directed at resolving these discrepancies.

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