ON THE FUNDAMENTAL CAUSES OF HIGH ENVIRONMENTAL ALKALINITY (PH ≥ 9): AN ASSESSMENT OF ITS DRIVERS AND GLOBAL DISTRIBUTION

Esteban G. Jobbágy[1]* (iD), Tibor Tóth[2], Marcelo D. Nosetto[1,3], Sam Earman[4]

[1]*Grupo de Estudios Ambientales, IMASL, CONICET, Universidad Nacional de San Luis, Ejército de los Andes 950, San Luis 5700, Argentina*
[2]*Institute for Soil Sciences and Agricultural Chemistry, Centre for Agricultural Research, Hungarian Academy of Sciences, Budapest, Hungary*
[3]*Cátedra de Climatología Agrícola, Facultad de Ciencias Agropecuarias, Universidad Nacional de Entre Ríos, Concepción del Uruguay, Argentina*
[4]*Earth Sciences Department, Millersville University, Millersville, PA, USA*

ABSTRACT

Very alkaline environments exceeding calcite buffering are globally rare but conspicuous in many sedimentary plains of the World. While the deleterious effects of high alkalinity on soils are well understood, less agreement exists on its causes. We revise these causes to understand these exceptional environments and explain the pervasiveness of calcite buffering elsewhere. We argue that the injection of respired CO_2 into stagnant hydrological systems subject to evaporative discharge is the key context for high alkalinization. The evolution of evaporites in nature reaches highly alkaline stages only when excess of (bi)carbonate with respect to divalent cations occurs. In most dry landscapes, evaporating groundwater solutions lose this condition as respired inorganic carbon (recharge zone supply) equilibrates with divalent cations from rocks (whole hydro-trajectory supply). Groundwater in stagnant landscapes avoids this limitation owing to short/shallow trajectories sustaining (bi)carbonate excess until evaporative discharge zones are reached. Flat sedimentary landscapes that are (i) wet enough to develop stagnation and have shallow water tables but (ii) sufficiently dry to expose them to evaporative concentration should host very alkaline soils. This is confirmed with >9,000 soil profiles from the global WISE database, which shows that profiles with pH ≥ 9 in the top meter are 2·7% globally but 18% in areas with low slope (<0·05%, 25-km radius, SRTM digital elevation model (SRTM DEM)) and semiarid–subhumid climate (annual precipitation to potential evapotranspiration ratio = 0·2–1, CRU database). Understanding how climate and vegetation change as well as irrigation practices influence hydrological stagnation and evaporative concentration may provide the key to manage very alkaline environments. Copyright © 2017 John Wiley & Sons, Ltd.

KEY WORDS: alkalinization; groundwater; solonetz; stagnation

INTRODUCTION

Most continental environments, including soils and surface waters, rarely exceed the maximum alkalinity levels imposed by the chemical buffering of calcite (pH ~8·5) (Wright 2003). There are, however, some regions of the world in which soils and even water bodies exhibit extreme alkalinity (pH ≥ 9). Here, we explore the set of conditions and processes that yield such high pH levels to understand the genesis of these rare conditions and, more importantly, to explore to what extent they represent the "exception that proves the rule" of pervasive maximum pH limitation by calcite buffering.

Very alkaline environments are naturally abundant over large fractions of the lowest landscape positions in very flat sedimentary plains of western Asia, eastern Europe, and southern South America or have expanded with irrigation in dry valleys such as those watered by the river Ganges in India or the Nile in Egypt (Kelley 1951). The high OH⁻ concentration in the waters and soils of these areas is accompanied by the dominance of sodium among base cations both on dissolved and exchangeable forms, justifying their

designation as alkaline–sodic environments. It is important to differentiate the alkaline–sodic environments treated here with the more widespread condition of saline environments (Läuchli & Grattan, 2012). Although these two groups of environments show some geographic overlap and individual soil profiles can belong to both categories, the first are best defined by the dominance of sodium and high pH in the solution, while the second are simply defined by the total inorganic soluble load (Läuchli & Grattan, 2012). While saline environments introduce constrains to living organisms mainly through osmotic effects and next through ion toxicity, the high colloidal dispersion imposed by alkaline–sodic solutions leads to multiple soil physical constrains on plants such as reduced pore space, limited water and air storage and conduction, and high mobility and loss rates of organic matter (Nelson *et al*., 1999; Suarez *et al*., 1984). While in clay platelets saturated with Ca^{2+} and Mg^{2+}, repulsive forces from negatively charged surfaces are outweighed by attractive forces from divalent cations, in those saturated with Na^+ repulsive forces dominate, causing dispersion (Laurenson *et al*., 2011). Besides the purely physical effects of alkaline–sodic conditions on plant growth, high-pH solutions are toxic for plant roots and, more importantly, increase the toxicity of other elements such as aluminum (Ma *et al*. 2003; Naidu & Rengasamy 1993). For these reasons, natural and cultivated ecosystems on alkaline–sodic

*Correspondence to: Dr E. G. Jobbágy, IMASL, Universidad Nacional de San Luis, Ejército de los Andes 950, San Luis 5700, Argentina. Phone: +54 266 4520325 int 3031.
E-mail: jobbagy@unsl.edu.ar

soils have lower vegetation cover and primary productivity compared with those located on more pH-neutral soils under otherwise similar environmental conditions (Perelman *et al.* 2001; Rengasamy 2002). Farming possibilities are often limited in natural alkaline–sodic environments and can become severely constrained where bad irrigation practices trigger soil alkalinization, as seen in many cultivated river valleys worldwide (Rengasamy 2002). In the case of alkaline–sodic aquatic environments, unique chemical constrains and adaptations of organisms emerge in response to the effects of high pH on the bioavailability/toxicity of different chemical elements (Jones *et al.* 1998).

Although the mechanisms that lead from high alkalinity to chemical and physical deterioration of soils are well understood and many indicators of alkaline–sodic conditions have been proposed and tested, there has been a much poorer development of conceptual models explaining the most fundamental causes that drive the genesis of very alkaline environments, with the important exception of Kelley's treatise published more than 60 years ago (Kelley 1951). Why is calcite buffering overwhelmed only in some regions of the world? Under what environmental conditions is this likely to occur? Can these conditions be affected by climate and vegetation change or human intervention?

We propose a broader explanation for the occurrence of very alkaline environments and responses to the previous questions, combining two independent conceptual models that describe the evolution of salty solutions and salt deposits in nature (Eugster & Jones 1979) and the trajectories of groundwater flow at multiple spatial scales (Tóth 1978). We suggest that hydrological stagnation and evaporative concentration offer the necessary context for the formation of very alkaline solutions and, ultimately, soils. Our conceptual model explains the rarity of very alkaline environments in most landscapes but their abundance in very flat sedimentary regions worldwide. We discuss how this distribution may shift in response to global and local environmental changes. We first examine the chemical evolution of very alkaline solutions and soils; next, we show how it depends on a specific set of hydrological conditions; and finally, we link these hydrological conditions to climate and topography to explain the current distribution of very alkaline environments as described by existing soil profile databases.

CHEMICAL EVOLUTION

Waters with stoichiometric excess of dissolved carbonate species in relation to dissolved divalent cations (equivalent-based, $(HCO_3^- + CO_3^{2-}) > (Ca^{2+} + Mg^{2+})$) are required for the development of very alkaline environments (Figure 1). Early work on the chemical evolution of natural solutions feeding surface salt deposits across dry regions has highlighted the need of carbonate excess throughout the entire concentration process in order to reach very alkaline precipitates such as trona and soda lime (Eugster & Jones 1979)(Figure 1). Independently, researchers concerned with the practical problem of soil degradation in irrigated fields

have identified the composition of these same ions as a good predictor of dispersive damage to soils by irrigation waters, often expressing it as a molar subtraction rather than the ratio (i.e., residual sodium carbonate) (Eaton 1950).In the case of alkaline soils and their challenging physical limitations, carbonate excess is also critical to increasing the dispersive power of sodium. Without carbonate excess, sodium salts in the soil solution have a limited capacity to displace, via ion exchange, calcium and magnesium sorbed to the soil surfaces, given their higher sorptive affinity (Sposito, 2008). However, if calcium and magnesium concentration in soil water decline owing to precipitation of carbonates (e.g., calcite and magnesite), sodium sorption will become more prevalent, as described in the following equation, and the increased sodium in soils will increase soil dispersion:

$$Ca - X_2 \; + \; 2Na^+ + CO_3^{2-} \leftrightarrow 2Na - X + CaCO_3\downarrow \quad (1)$$
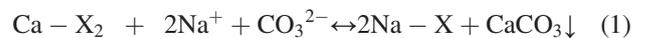
Where: *X* represents a monovalent cation exchange site.

Indicators based solely on the concentration of sodium relative to magnesium and calcium (e.g., sodium absorption ratio, SAR (Sumner 1993)) are widely used to understand how solutions may lead to increasing soil alkalinity and physical dispersion. Yet they may often fail to do so as they ignore the potent effect of carbonates engaging in calcite precipitation shown earlier. Seawater offers an extreme example of the limitation of indicators like SAR, achieving extremely high values (SAR = 58·6) with sodium representing 77% of cationic charges but having little dispersive or alkalinizing effects on soils (Schlesinger & Bernhardt, 2013). The extremely low (bi)carbonate content of these waters explains why saline but not alkaline–sodic soils are found in the coastal areas that they influence. An opposite example comes from rivers like the Ganges or the Niger that have a relatively low sodium concentration (<20% of cationic charges, SAR < 15) (Gaillardet *et al.* 1999) but a strong dominance of (bi)carbonates among anions. Soils and water tables in the areas that are irrigated with these two rivers often display sodicitiy and alkalinization (Singh *et al.* 2006; Sharma & Swarup 1988; Barbiéro *et al.* 2001). It is important to note that adjusted SAR indicators that take into account the importance of (bi)carbonates have been proposed (Lesch & Suarez 2009). In addition to the previous considerations, the deleterious effects of alkaline–sodic solutions on the physical fertility of soils have to be seen in the context of the combined and opposed effects of concentrating salts, driving flocculation, and exchangeable sodium dominance, driving dispersion. For this reason, combined indicators of total salinity and sodicity are used to predict the dispersive behavior of soils (Rengasamy *et al.* 1984), and the worst dispersive impacts should be expected under relatively diluted sodium (bi)carbonate solutions.

While the chemical pathway towards high alkalinity may simply require solutions with carbonate excess that are
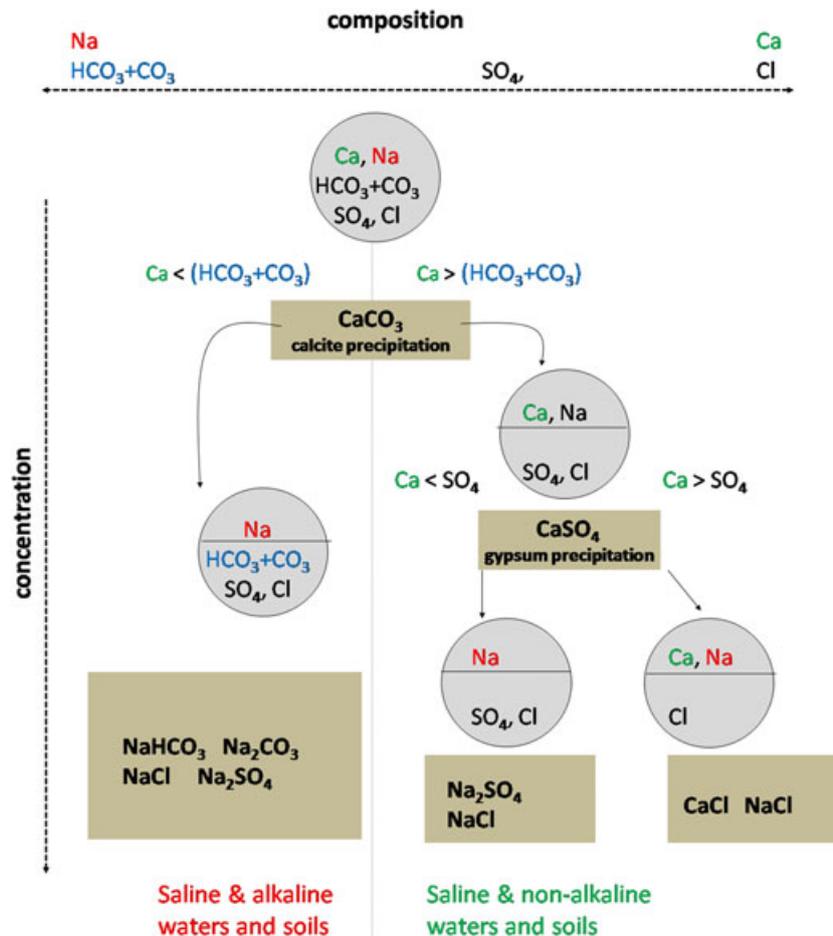
Figure 1. Precipitation pathways for evaporating solutions containing Na^+, Ca^{2+}, SO_4^{2-}, Cl^-, HCO_3^-, and CO_3^{2-}. Precipitation products are indicated in boxes and dissolved ions in circles. In this simplified analyses of possible precipitation trajectories Mg^{2+} and K^+ were not included but would behave closely to Ca^{2+} and Na^+, respectively. The ratios of Ca^{2+} to carbonate + bicarbonate and Ca^{2+} to SO_4^{2-}, considered as charge equivalents, play a key role determining precipitation products. Adapted from Eugster & Jones (1979). [Colour figure can be viewed at wileyonlinelibrary.com]

subject to evaporative concentration, the most fundamental questions is how carbonate excess originates and is maintained in groundwaters that eventually drive the alkalinization of surface environments. While previous attempts to address this question have focused mainly on the composition of rocks, we propose that this is only a secondary aspect subordinated to the dominant role of hydrological stagnation.

HYDROLOGICAL STAGNATION

Solutions with carbonate excess that become exposed to evaporative concentration are not easily found in nature. Their paucity can be explained by the partial decoupling of the sources of inorganic carbon and divalent cations along hydrological trajectories. Typically, respiration by the biota is the main source of inorganic carbon entering the soil solutions, and its injection takes place only along the biologically active portion of soil–rock continuum, close to the surface (Figure 2a). This input, which can be rapidly lost through degassing in the acidic solutions of highly weathered soils, remains as dissolved CO_2 or bicarbonate under more neutral conditions. Inorganic carbon supply beyond

that zone, however, is extremely scarce, as the lack of organic matter and/or the reducing environment limit additional respiration inputs. Hence, in areas of hydrological recharge (downward water flux), soil inorganic carbon supply takes place only at the beginning of the hydrological trajectory, where it may be retained if the environment is not acidic enough to degas it. Early empirical idealizations of chemical changes of groundwater proposed a gradual replacement of HCO_3^- and CO_3^{2-} by SO_4^{2-} and Cl^- along the trajectory from recharge to discharge zones (Chebotarev, 1955). In contrast to inorganic carbon, divalent cations can be supplied by the mineral matrix throughout the whole hydrological trajectory both via weathering and exchange processes. Therefore, given enough length on any water trajectory, the supply of divalent cations will eventually exceed the initial load of inorganic carbon, leading to solutions with $(HCO_3^- + CO_3^{2-}) < (Ca^{2+} + Mg^{2+})$ (Figure 2a). If the saturation level for calcite and other carbonate minerals is achieved along the hydrological trajectory, precipitation will consume both inorganic carbon and divalent cations while weathering or ion exchange will only supply the latter. Along extensive hydrological trajectories, solutions will switch from $(HCO_3^- + CO_3^{2-})$ excess to
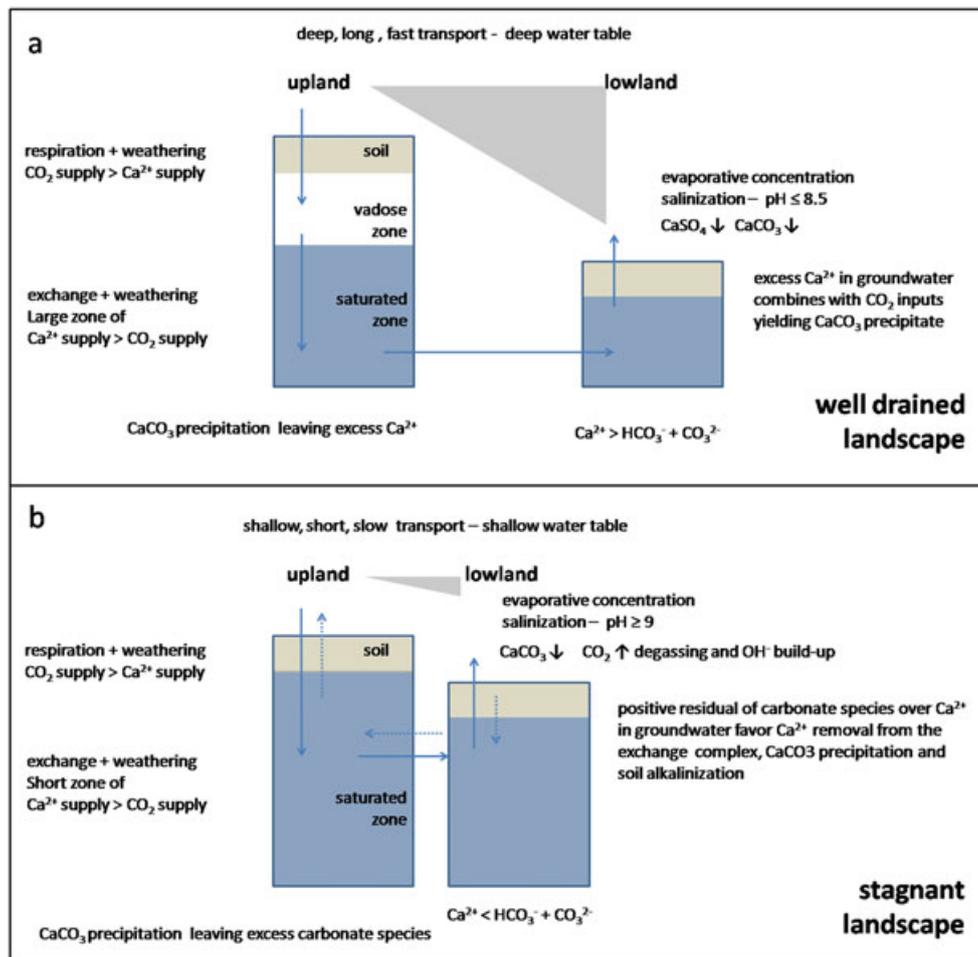
Figure 2. Conceptual model capturing the vertical and horizontal complexity of soil–sediment systems into a three-horizon two-landscape position scheme. (a) Horizons include (i) a biologically active zone that supplies respired CO_2, (ii) a vadose zone with low respiration and higher primary mineral abundance capable of sustaining the supply of cations, (iii) a saturated zone capable of transporting dissolved species. Landscape positions include topographically higher recharge zones, where water excesses are drained and topographically lower zones where water excesses are discharged as liquid (towards rivers/streams) or vapor. (b) A very flat and stagnant landscape develops shorter and shallower hydrological paths. This path can be temporarily reversed (dotted arrows) when, for example, high water-excess periods with surface runoff raise the water table at faster rates in lowlands than uplands. The soil (horizon i) and the saturated zone (horizon iii) are in contact and the zone where Ca^{2+} supply exceeds CO_2 supply becomes shorter. [Colour figure can be viewed at wileyonlinelibrary.com]

$(Ca^{2+}+Mg^{2+})$ excess (Figure 2a), while short trajectories, instead, open the possibility of solutions with $(HCO_3^-+CO_3^{2-})$ excess reaching the discharge zone (Figure 2b). It is important to highlight that the only abundant rocks whose weathering can supply inorganic carbon are the calcareous ones, and they also supply a balanced load of divalent cations, without raising the $(HCO_3^-+CO_3^{2-})$:$(Ca^{2+}+Mg^{2+})$ ratio above the unit. An additional aspect of stagnant landscapes that needs to be considered is that, when subject to dry climates, they are more prone to accumulate salts than sloped landscapes because of the larger area with capillary contact between water tables and the surface. Soluble salt accumulation in alkaline medium favors the selective concentration of Na^+ and repression of Ca^{2+} as a result of the lower solubility of Ca^{2+} salts becomes (Chebotarev, 1955).

Many researchers have focused on soil and parent material mineralogy as a central cause for high soil alkalinity (Kelley 1951; Nyamapfene 1986; Pal *et al.* 2003; Shvartsev & Wang 2006; Wang *et al.* 2009). We argue that this aspect is important but subordinate to the hydrogeological conditions described earlier. Certainly, the sodium and divalent cation content and availability upon weathering of the minerals to which groundwater is exposed along the paths described in Figure 2 influence the possibility of solutions reaching discharge zones with (bi)carbonate excess. For example, Na-rich feldspars would favor (bi)carbonate excess, whereas Ca/Mg-rich basalts will prevent it. Yet, even under Ca/Mg poor conditions, non-stagnant landscapes would host hydrological trajectories that are long enough to consume the (bi)carbonate excess pulse that is only generated at the recharge. Under stagnant conditions, Ca/Mg-rich sediments would partially restrain the development of highly alkaline soils requiring shorter and shallower hydrological paths for them to develop compared with Na-rich sediments (Nyamapfene 1986).

The next requirement to achieve high alkalinity in soils or surface waters is to have solutions with $(HCO_3^-+CO_3^{2-}) > (Ca^{2+}+Mg^{2+})$ going through evaporative concentration. Upon concentration, calcite

precipitation and calcium-to-sodium replacement from the exchange complex will be favored, bicarbonate will be replaced by more alkaline carbonate, and CO_2 released. Repeated drying and wetting cycles may enhance the speed of this final stage in the development of alkaline–sodic soils, as careful chemical modeling has suggested (van der Zee *et al*. 2010). Therefore, the specific hydrological conditions described earlier involve (i) not only relatively short and shallow saturated trajectories that are able to convey solutions with (bi)carbonate excess to surface discharge zones but also (ii) a negative climatic water balance (precipitation < potential evapotranspiration) that warrants that episodes of surface evaporative concentration would not be overridden by pluvial dilution (Figure 2). In nature, these hydrological conditions are most likely to be found in very flat regions with semiarid to subhumid climate where stagnant groundwater systems occur. It is interesting to highlight that stagnation may be enhanced by the dispersive effect of alkaline–sodic solutions on sediments and soils, which could introduce a positive feedback on their development.

Flat topographies, particularly low regional slopes, favor the presence of shallow water tables as well as short and slow recharge–discharge groundwater trajectories (Tóth 1978; Tóth 1999). It is important to highlight that stagnation in flat regions can be alleviated if recharge fluxes are very low, as it can be expected under arid climates (Fan & Schaller 2009). Thus, condition (i) is more likely met in flat landscapes that have a climate that is humid enough to sustain shallow water tables. Condition (ii) requires a climate that is arid enough to allow the evaporative concentration of groundwater at the surface. As a result of these two conditions, semiarid to subhumid climates and very flat topographies provide the necessary context for the development of highly alkaline waters and soils in nature. Climates that are too dry will prevent hydrological stagnation. Climates that are too wet will block evaporative concentration and on top of that will be more likely to host acidic topsoils, preventing the retention of inorganic carbon in the recharge zone. Noticeably, in Western Siberia, where the largest span of very alkaline environments has been described, the abundance of alkaline–sodic soils increases from dry to humid belts peaking in the humid extreme of steppes where they become the main variant of salt accumulation before entering the wetter forest systems in which salty soils are no longer found (Bazilevich 1970).

Human interventions, particularly irrigation, can expose river or aquifer waters with $(HCO_3^- + CO_3^{2-}) > (Ca^{2+} + Mg^{2+})$ to intense evaporative concentration after short-cutting their path from recharge to discharge. Waters that would otherwise reach the ocean or enter long natural hydrological trajectories are applied to arid surfaces. If irrigation is accompanied by poor drainage infrastructure, as it often happens, water tables approach the topsoil, changing the hydrological context even closer to the one described for very flat plains (Figure 2). Flat arid farming land irrigated with rivers with

high $(HCO_3^- + CO_3^{2-}) > (Ca^{2+} + Mg^{2+})$ such as the Ganges, Narmada, and Godavari in India or the Nile and Niger in Africa (Gaillardet *et al*. 1999) are examples of this anthropogenic mechanism of soil alkalinization (Elewa & El Nahry 2009; Sharma & Swarup 1988; Subramanian & Ittekkot 1991; Barbiéro *et al*. 2001). Without irrigation, some large basins lead naturally to the same type of situation when rivers with $(HCO_3^- + CO_3^{2-}) > (Ca^{2+} + Mg^{2+})$ leave their humid sources to feed arid lowlands, creating highly alkaline wetland environments. One of the best documented examples is the Okavango delta, where the Jao–Boro River waters $(HCO_3^- + CO_3^{2-} : Ca^{2+} + Mg^{2+} = 1·3$, Sawula & Martins 1991) fan out over a very flat portion of the Kalahari desert, creating highly alkaline soils in slightly elevated but concave interfluvial zones that are supplied by their shallow water tables (McCarthy 2006). Another example comes from the flood plain of the lower Limpopo river in Mozambique $(HCO_3^- + CO_3^{2-} : Ca^{2+} + Mg^{2+} = 1·4)$ where naturally alkaline soils are dominant (FAO 2004).

An illustrative exception to the rules proposed earlier emerges when deep source of inorganic carbon is present along groundwater trajectories. In volcanically active regions such as the Rift Valley of Africa, deep regional groundwater systems sustain concentrations of $HCO_3^- + CO_3^{2-} : Ca^{2+} + Mg^{2+} > 1$ thanks to the injection of deep CO_2 of geological origin, explaining the presence of vast saline lakes and salt pans of sodium (bi)carbonate such the Magadi system in Kenya (Chernet *et al*. 2001; Eugster & Jones 1979). A similar hydrogeochemical setting explains the sodium (bi)carbonate deposits of Wyoming in North America (Earman *et al*. 2005). Without this exceptional deep source of dissolved inorganic carbon, these systems would develop neutral (sulfate or chloride-dominated) salt deposits as seen in the majority of discharge lakes and salt flats of arid regions (Eugster & Jones 1979).

Perhaps, the ultimate example of highly alkaline environments on Earth comes from the "Soda Ocean" hypothesis (Grotzinger & Kasting 1993), which suggests that in Archean to Proterozoic times continental water supply to the ocean with $HCO_3^- + CO_3^{2-} : Ca^{2+} + Mg^{2+} > 1$ may have occurred, explaining the puzzling lack of gypsum precipitation on those stages of our planet and suggesting that very alkaline aquatic environments may have been the norm, rather than the exception, for the early evolution of life (Grotzinger & Kasting 1993). Whether high atmospheric CO_2 or highly stagnant vegetation-free watersheds may have favored this condition remains to be explored.

GLOBAL DISTRIBUTION

Extremely flat plains or "hyperplains" can be globally mapped using a simple topographic criterion, such as regional slopes (measured on a 10-km radius) <0·05% (Jobbágy *et al*. 2008) (Figure 3a). Many of these hyperplains coincide with vast shallow groundwater areas as suggested by a recent global map that combined an ecohydrological
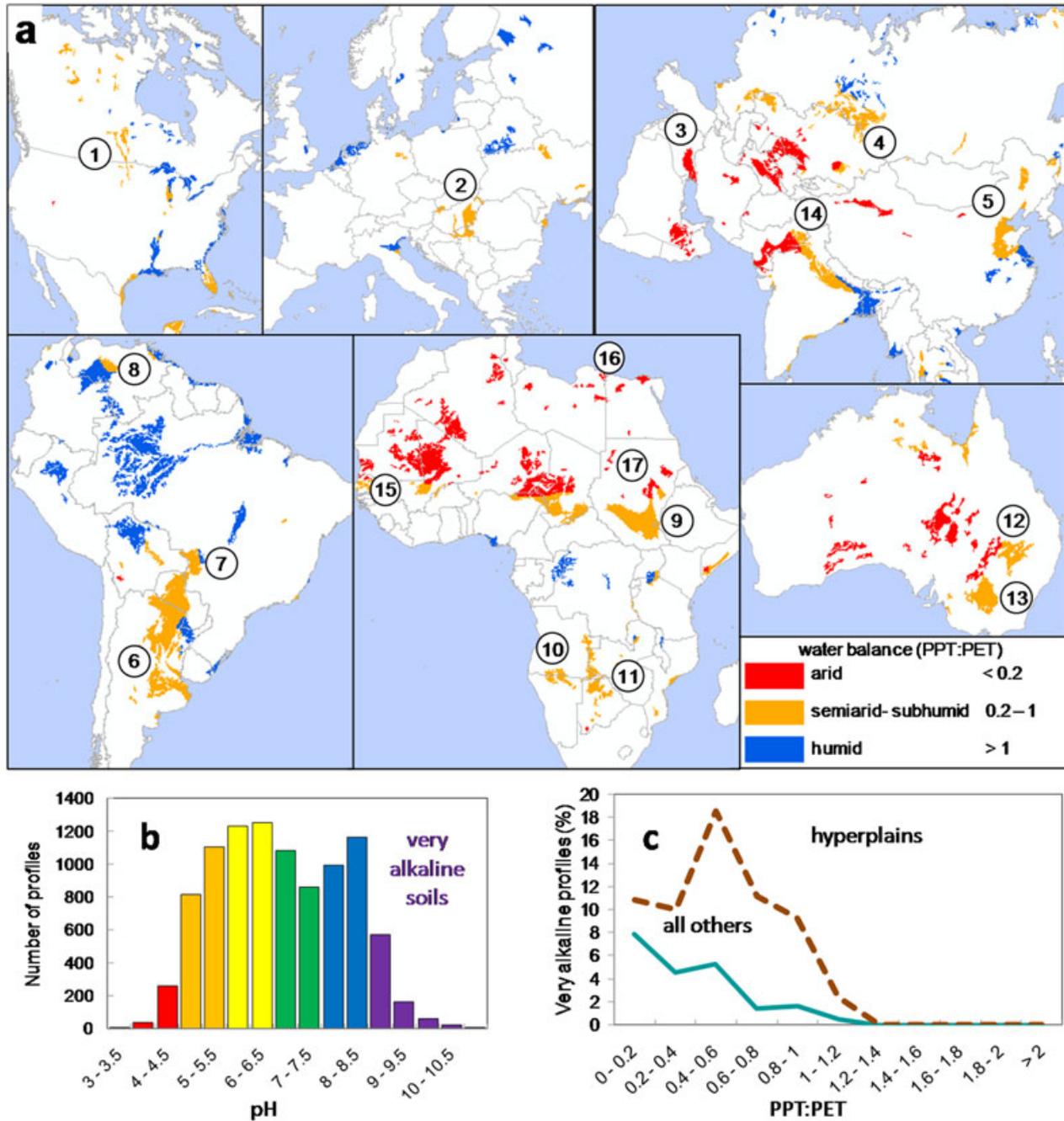
Figure 3. (a) Global distribution of very flat regions (hyperplains) according to their climatic water balance. Hyperplains were defined as those areas with slopes ≤0·05% based on SRTM digital elevation model with a spatial resolution of 10 km (Rabus *et al*. 2003). The maps show only hyperplains ≥2,000 km2 (~70% of global hyperplain area) and characterize the water balance as the ratio between annual precipitation and potential Penman-Monteith evapotranspiration based on CRU climatic database (New *et al*. 2002). Hyperplains with documented abundant alkaline-sodic soils are indicated and correspond to (1) Central Canada, (2) eastern Hungary, (3) northern Caspian basin, (4) Western Siberia, (5) Northeastern China, (6) Pampas and Chaco central Argentina, (7) Brazilian Pantanal, (8) Venezuelan Llanos, (9) Southern Sudan, (10) Etosha basin, (11) Okavango basin, (12, 13) southeastern Australia. Arid hyperplains with alkaline irrigated soils along river valleys are also indicated and correspond to the (14) Ganges in India, (15) Niger in West Africa, and (16, 17) Nile in Sudan and Egypt. (b) Frequency histogram for the maximum pH value observed in the top meter of soil profiles. Maximum pH values (measured in water) across all the soil horizons that had their upper boundary within the top meter of the profile as recorded in the WISE 3·1 database (*n* = 9661) (Batjes 2009). (c) Distribution of alkaline soils along a climatic gradient for hyperplains and for the rest of the territory. The percentages of alkaline soils (pH ≥ 9 in the top meter) across 11 ranges of climatic water balance (PPT:PET at 0·2 steps) are shown for hyperplains (slope ≤ 0·05% and area ≥ 2,000 km²) and for all other topographic situations. [Colour figure can be viewed at wileyonlinelibrary.com]

model and numerous water table depth observations (Fan *et al*. 2013). Regions with documented abundant alkaline–sodic soils and, in some cases, surface water bodies correspond to hyperplains with semiarid to subhumid climates

in the map, calculated based on precipitation to potential evapotranspiration (CRU climate database 1961–1990) (New *et al*. 2002) (Figure 3a). This includes the sedimentary plains of Western Siberia (Bazilevich 1970), the northern

Caspian basin (Khitrov 2005), eastern Hungary (Molnár & Borhidi 2003; Tóth & Rajkai 1994), the Pampas and Chaco in Central Argentina and western Paraguay (Cisneros *et al.* 1999; Lavado & Alconada 1994; Miretzky *et al.* 2000), the Brazilian Pantanal (Furquim *et al.* 2010), the driest section of the Venezuelan Llanos (Guerrero-Alves *et al.* 2004), several areas in Central Canada (Buckland *et al.* 2002; Carter & Pearen 1985), the Songnen Plains in Northeastern China (Shvartsev & Wang 2006; Yang & Li 2003; Luo *et al.* 2011), and Southern Sudan (De Vivo *et al.*, 1981) (Figure 3a, Numbers 1 to 9). In Southern Africa, the closed-basins of the Etosha (Namibia) and Okavango (Botswana) hyperplains host very alkaline soils and salt deposits (Buch & Rose 1996; McCarthy 2006) (Figure 3a, Numbers 10 and 11). In Australia, two vast semiarid to subhumid hyperplains are found in the southeastern states around the mid-basins of the Murray and Darling rivers where very alkaline soils and groundwaters have been reported (De Caritat *et al.* 2011) (Figure 3a, Numbers 12 and 13). It is important to highlight, however, that Australia hosts what is perhaps the largest fraction of very alkaline soils of all continents, many of which are outside these two hyperplains, located under more arid climates and in areas with higher slopes (De Caritat *et al.* 2011) where groundwater influence is not obvious in present times (Fan *et al.* 2013). We speculate that some of these very alkaline areas, however, may reflect a legacy of stagnant hydrological conditions from past climates that remain in the old surfaces of Australian landscapes.

Arid hyperplains along the dry valleys of the Niger (West Africa), Nile (Egypt and Sudan), Indus (India and Pakistan), Ganges (India), Euphrates (Syria, Irak), Amu Darya (Turkemenistan and Uzbequistan), and Syr Darya (Kazakstan) provide conditions for strong hydrological stagnation when subsidized by additional water inputs from irrigation (Figure 3a). Where those irrigation waters have high $HCO_3^- + CO_3^{2-} : Ca^{2+} + Mg^{2+}$ ratios, as it is the case of the Ganges, Nile, and Niger rivers (Gaillardet *et al.* 1999) (Figure 3a, Numbers 14 to 17), high alkalinization of soil profiles is often documented as in the examples from Egypt (Elewa & El Nahry 2009), India (Bajwa *et al.* 1992), and Niger (Barbiéro *et al.* 2001).

In order to evaluate quantitatively to what extent very alkaline soils tend to concentrate in hyperplains with intermediate climatic water balances, we took advantage of the largest existing global database of individual soil profiles ($n = 10253$, WISE 3·1, Batjes 2009). Using the geographic coordinates provided for most of the profiles in this database, we obtained (i) the average regional slope in a 25-km radius around each soil profile on the basis of the SRTM global digital elevation (Rabus *et al.* 2003) and (ii) the annual precipitation to potential evapotranspiration ratio (PPT:PET) using the CRU database (New *et al.* 2002). In order to identify highly alkaline soils, we first obtained the maximum pH values recorded within each profile in the top meter (pH measured in water in all soil horizons with their top boundary located above 1 m of depth). The

histogram of these values across 9,661 profiles reveals the important effect of calcite buffering soil pH (Figure 3b). While the mode of pH values occurs at slightly acidic values, a distribution that is skewed towards alkaline values appears "held" around pH = 8·5 boundary where a second mode occurs. Only 2·7% of the reported soil profiles have at least one horizon with pH values equal or higher to 9 on the top meter. We quantified the frequency with which this population of highly alkaline soils occurred under hyperplains (regional slope < 0·05%) or under the rest of the continental territory (regional slope > 0·05%) across 11 ranges of climatic water balance (PPT:PET at 0·2 steps). Very alkaline profiles were absent with PPT:PET ratios >1·4 and very rare with ratios >1; increasing their proportion with increasingly drier climates (Figure 3c). A clear maximum presence of very alkaline soil profiles was found in hyperplains with intermediate water balance (PPT:PET =0·4 to 0·6), representing 18% of all the reported profiles under those conditions. Under the same water balance, the rest of the territory had only 5% the reported cases with maximum profile pH ≥ 9. This population of soil profiles was still relatively abundant in the driest climatic range, where differences between hyperplains and the rest of the territory became smaller (Figure 3c). Remarkably, 91% of all the arid cases with pH ≥ 9, out of semiarid–subhumid hyperplains, corresponded to irrigated soils (Ganges, Indus, Niger, Nile, Saloum and Upper Euphrates rivers) or wetlands (predominantly not only the Okavango in Botswana but also Azraq Oasis in Jordan and Conch Lake in Kenya) as found after a detailed inspection of the soil profile location in the Google Earth system. Overall, semiarid to subhumid (PPT:ETP = 0·2 to 1) very flat plains hosted 4·2% of all sampled profiles but 16·1% of those with pH ≥ 9. These results suggest that the broad and qualitative regional topographic and climatic conditions outlined earlier contribute to explain the occurrence of very alkaline soils. The global analysis presented earlier suggests that very alkaline soils can prevail across vast areas if the right but unusual hydrological settings required are present, challenging the notion of the azonal and isolated character of these environments.

ENVIRONMENTAL CHANGE AND HIGH ALKALINITY

By focusing on hydrology (stagnation combined with negative water balance) for the formation of highly alkaline soils, we can anticipate how human-induced environmental changes could alter their distribution. Direct hydrological interventions such as the build-up of channels and drains on very flat subhumid landscapes can depress groundwater-levels decoupling recharge and discharge zones and eliminating the source of alkaline water on large areas, as seen in the eastern Hungary (Nosetto *et al.* 2007; Szabolcs 1979). Alternatively, the construction of impoundments or elevated roads that block surface water evacuation can increase stagnation, creating recharge-

discharge shortcuts, and expanding the area of alkaline-sodic soils. Finally, irrigation has already caused the same problem over very flat landscapes such as the Ganges and Niger valleys and will likely worsen in these and other irrigated regions of the world if management practices do not improve as fast as utilization expands. Other human influences on the water balance of a region can expand or shrink the area covered by alkaline-sodic soils. Climate and vegetation change can act separately or interact, influencing the water balance of flat sedimentary regions and stagnation regimes. For example, increasing rainfall and/or the replacement of native perennial vegetation with crops consuming less water can push semiarid systems to higher stagnation levels, as seen in cultivated regions of Australia and Argentina (Contreras *et al*. 2012; George *et al*. 1997; Gimenez *et al*., 2016). On the other hand, decreasing rainfall or the introduction of vegetation types with high water consumption rates (e.g., fast growing tree plantation on grasslands) in subhumid plains with stagnant hydrology can depress water table levels, create longer groundwater trajectories, and decrease the alkalinizing potential of the solutions that reach evaporative discharge areas (Jobbágy & Jackson 2007; Nosetto *et al*. 2008). Whether stagnation and alkalinization will increase or decrease in the coming decades is difficult to predict based solely on climate projections, yet the displacement of natural and cultivated perennial vegetation by annual crops and the sustained expansion of the global irrigated areas are likely to tilt the balance towards more alkaline-sodic land in the future.

CONCLUSIONS

Naturally occurring or human-induced hydrological stagnation in environments with a negative water balance create the conditions for the production and concentration of groundwater solutions with an excess of dissolved inorganic carbon with respect to dissolved divalent cations. This hydrochemical setting is the key determinant of the formation of very alkaline environments including soils and surface water bodies with pH $\geq$ 9. Being rare across the globe, these conditions can be dominant in very flat sedimentary landscapes with semiarid to subhumid climate in which shallow and short groundwater trajectories are able to maintain high inorganic carbon to divalent cation ratios all the way from recharge to discharge zones. While other pathways to produce extreme alkaline environments that rely on very specific geological features providing deep CO_2 sources, such as hydrothermal venting, can be found, the setting and mechanism that we propose here are more universal and have hydrological stagnation and respired CO_2 as the main setting and vector of alkalinization, respectively.

General conceptualized biogeochemical equilibria representing the integrated transformation of minerals for closed semiarid to subhumid basins under (i) well drained versus (ii) stagnant can be presented as follows:

(i) primary minerals + respiration = secondary minerals + calcite + neutral salts.

(ii) primary minerals + respiration = secondary minerals + calcite + alkaline salts + CO_2 degassing.

While real stagnant basins will likely fall at intermediate stages between (i) and (ii), the extreme equilibrium (ii) shows the endpoint towards which hydrological stagnation and its drivers (including climate, topography, and human interventions like irrigation) take the chemistry of soils, surface waters, and salt deposits when evaporative discharge occurs. Preserving the unique natural life and sustaining the challenging production of very alkaline environments will benefit from an integrative view that sits at the interface of the biogeochemistry and hydrology of these systems.

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