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ORIGINAL RESEARCH

Hard water softening effect of a baby cleanser

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Background: Hard water is associated with atopic dermatitis (eczema). We wanted to determine if a baby cleanser and its individual components altered free ionized calcium (Ca^{2+}) in a simulated hard water baby bath. For these studies, an in vitro determination of free Ca^{2+} in a simulated hard water baby bath, and an in vivo exploratory study of free Ca^{2+} absorption into skin from hard water were performed.

Methods: Free Ca^{2+} was measured with an ion-sensitive electrode in vitro in hard water (100–500 ppm, Ca^{2+}) before and after addition of the cleanser and/or its components. In an exploratory study, absorption of Ca^{2+} into skin from hard water was determined in three female participants (aged 21–29 years).

Results: At an in-use dilution of 1%, the test cleanser reduced free Ca^{2+} from ~500 ppm to <200 ppm; a 10% in-use dilution bound virtually all free Ca^{2+}. The anionic surfactant component contributed the most to this effect. In the exploratory in vivo study, we measured a reduction of ~15% in free Ca^{2+} from simulated hard water over 10 minutes.

Conclusion: Baby cleansers can bind free Ca^{2+} and reduce the effective water hardness of bath water. Reducing the amount of free Ca^{2+} in the water will reduce the availability of the ion for binding to the skin. Altering or reducing free Ca^{2+} concentrations in bath water may be an important parameter in creating the ideal baby bath.

Keywords: bath, cleanser, hard water, infant, neonate, surfactant

Introduction

Cleansing approaches, routines, and products must be carefully considered for infants; infant skin is different from the skin of older children and adults, and continues to gradually mature in structure, composition, and function for several years after birth.[1,2] The stratum corneum (SC) corneocyte cells are smaller and the SC is much thinner.[1] Although infant skin is better hydrated than adult skin, it has lower concentrations of natural moisturizing factor.[3] Transepidermal water loss is also higher in infants, and infant skin can both absorb and lose water at a faster rate than adult skin.[3] Skin pH is more neutral at birth, but quickly becomes more acidic, with the skin's "acid mantle" providing a more protective barrier.[4] The fact that infant skin is not fully mature may place it at greater risk for the disruption of skin barrier integrity. These differences between adult and infant skin underlie the research and guidelines on factors that constitute an ideal bath for newborns and infants.[5]

Water alone is limited in its ability to gently and effectively cleanse, particularly for the removal of oily or fatty substances like feces and associated enzymes.[5–7] Cleansers can emulsify and dislodge oily materials, soils, and microorganisms more effectively than

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water, so that these materials can be more easily removed.[6,8] Appropriately formulated mild cleansers can prevent drying of the baby's skin and help support the development of the skin's natural pH.[5,9] Guidelines and expert opinion indicate that infant skin should be cleansed with mild liquid cleansers that are neutral in pH or mildly acidic (pH 5.5–7.0),[5,6,9–11] or with those that have minimal impact on the baby's skin surface pH[8,9,12] and have a record of safety.[6,9,13] A warm (~105°F) immersion bath (as opposed to a sponge bath), ideally 2 hours after birth, when the infant is stable (thermal, cardiorespiratory), with a mild cleanser that does not disrupt the skin barrier has been found to be a good first bath for newborns.[14–16]

Hard water has been defined by the US Geological Survey as water containing divalent cations, primarily ionized calcium (Ca^{2+}) and magnesium (Mg^{2+}) at concentrations >120 ppm.[17] Water hardness varies by geography and mineral content of the water supply.[17,18] Several observational studies suggest that hard water is associated with the development of atopic dermatitis (AD).[19–24] Although the relationship between water hardness and AD is not well characterized, reducing water hardness may help in reducing the potential for developing AD. In an arm washing study with different solid bars (sodium soap, triethanolamine soap, and synthetic detergent bar), harder water was found to be more irritating.[19]

Some common surfactants (soaps, sodium dodecyl sulfate, and polydisperse nonylphenol polyethoxylate [Igepal CO-660, Solvay, Brussels, Belgium]) are known to interact with Ca^{2+} and Mg^{2+} ions present in hard water, resulting in precipitation of the surfactant, alteration of micelle behavior, and potentially altering the composition of the solution.[25–30] The aim of this study was to investigate whether cleansers formulated for use in a baby bath have the potential to alter the free Ca^{2+} in the bath and reduce the effective water hardness, thereby improving bath conditions.

Methods

Materials

In order to simulate baby bath water, a solution of deionized water and calcium chloride ($CaCl_2$) was created at various concentrations to reach water hardness equivalents between 100 and 500 ppm. Calcium chloride salt was obtained from Sigma-Aldrich (St Louis, MO, USA). Molar concentrations of calcium chloride solutions were obtained from Ricca Chemical Company (Arlington, TX, USA).

Test solutions

Three test cleansers (commercial baby wash products) and four individual ingredients, components of the test cleaners, were tested for their Ca^{+2} binding. The three test cleansers were obtained from www.drugstore.com (USA): Johnson's® Head-To-Toe® Baby Wash (HTT; Johnson & Johnson Consumer Inc., Skillman, NJ, USA), Burt's Bees® (BB; Burt's Bees Baby Bee Shampoo & Wash, Durham, NC, USA), and California Baby® (CB; California Baby Super Sensitive™ Shampoo & Bodywash, Los Angeles, CA, USA). As stated on the label, HTT contained water, cocamidopropyl betaine (CAPB), polyethylene glycol (PEG)-80 sorbitan laurate, sodium laureth sulfate (SLES), PEG-150 distearate, glycerin, polyquaternium-10, tetrasodium ethylenediaminetetraacetic acid (EDTA), citric acid, sodium hydroxide, sodium benzoate, ethylhexylglycerin, phenoxyethanol, and fragrance. Four individual components as aqueous solutions, made using deionized water, were also tested: SLES, PEG-80 sorbitan laurate (PEG80SL), EDTA, and decyl glucoside (obtained from Sigma-Aldrich). Additionally, a four component aqueous solution comprising SLES, CAPB, and PEG80SL (SLES/CAPB/PEG80SL) in a 1:1:1 weight ratio was created and tested.

Calcium measurements

All measurements were performed using a Mettler-Toledo DC420 calcium-selective electrode and Mettler-Toledo S47-K SevenMulti™ with ion-selective expansion unit (Mettler-Toledo, LLC, Columbus, OH, USA). The probe was calibrated with commercially prepared calcium carbonate molar solutions (Sigma-Aldrich) from 10 to 1,000 ppm Ca^{2+} ions. Stirring and measurement were done at room temperature. For measurements, the calcium probe was lowered into the glass beaker (50 mL) containing the test solution, and the concentration was recorded continuously. A reading was obtained when the measurement had stabilized, usually after 30 seconds.

In vitro

The effect of the test cleansers on apparent Ca^{2+} ion concentrations in solution were made after adding the test cleansers at typical in-use cleanser dilutions of 1% and 10% concentration in deionized water containing 100, 200, 300, and 500 ppm Ca^{2+}. EDTA and test cleanser components were also tested at typical in-use dilutions of 1% and 10% relative to their concentration in commercially supplied test cleansers using 200 and 500 ppm Ca^{2+} ion solutions. EDTA is typically used at a concentration of 0.5% in products. In this study, EDTA was tested at a dilution of 1% and 10% of the 0.5% stock solution (0.05 wt% and 0.005 wt% of EDTA). Surfactants in typical baby cleansers are about 10 wt% active. Individual surfactant or combinations of surfactants were tested at 1% and 10% dilutions of 10% solution (0.1 wt% and 1.0 wt% of surfactant). Each solution was independently created and measured twice.

In vivo

After providing verbal consent to participate, an exploratory pilot study was performed in three female participants (coauthors KC, MCM, and SA, aged 21–29 years) to determine the absorption of Ca^{2+} ions into the skin from a simulated baby bath. The authors did not obtain IRB approval for the in-vivo aspect of the study. It was very exploratory in nature and was carried out by the three authors who conceived of the specific experiments, and who are acknowledged as the participants/subjects. Simulated bath water containing 200 and 500 ppm free Ca^{2+} ions was placed on the skin of the volar forearm over a diameter of 2.5 cm (an area of 4.9 cm^2) in a volume of 25 or 50 mL in a glass vial (Fisher Scientific, Waltham, MA, USA). Separate chambers were used for each sampling time of 1, 5, or 10 minutes. The bath solution was added to the chamber and the skin of the arm was pressed against the open top of the chamber (held in place by the participant's other hand). The participant's arm was then rotated over so that the solution was against the skin. After the indicated time (1, 5, or 10 minutes), the arm and chamber were rotated back over and the entire sample, in the chamber, was removed from the skin, and then the free Ca^{2+} ion in solution was determined by placing the ion-selective probe into the chamber. An additional larger 50 mL chamber was used for a 10 minute exposure to confirm the findings from the 25 mL chamber. This volume provided a larger reservoir of Ca^{2+} to control for possible depletion of the supply of Ca^{2+} available for absorption by the skin.

Concentrations were monitored for up to 10 minutes as the recommended length of a newborn baby bath is 5–10 minutes.[9] Absolute free Ca^{2+} concentrations as well as change from baseline concentrations were determined. Each exposure was repeated three times for each participant, and the mean concentration for each exposure was recorded.

Reduction in Ca^{2+} from donor solution was assumed to be due to absorption into the skin. The differences between starting concentration and ending concentration at the different time points were reported as a positive absorption per area of skin exposed (mg/mm^2).

Results

In vitro effect of test cleansers and their components on free Ca^{2+} concentrations in a simulated baby bath

At typical in-use cleanser dilutions of 1% and 10%, the HTT test cleanser reduced measured free Ca^{2+} in solution at all tested calcium concentrations (Figure 1). The effect of HTT test cleanser components on free Ca^{2+} ion in solution are shown after an in-use dilution in simulated bath water of 1% (Figure 2A) and 10% (Figure 2B). EDTA had only a slight effect on free Ca^{2+} ion in solution. The surfactant component SLES appeared to have the greatest effect on free Ca^{2+}. At the 1% in-use dilution, the SLES/CAPB/PEG80SL solution had an effective concentration of 0.33 wt% SLES, 0.33 wt% CAPB, and 0.33 wt% PEG80SL. The 1:1:1 blend resulted in a lower SLES concentration in the final solution, and correspondingly less of an effect on free Ca^{2+} (Figure 2A). At a 10% in-use dilution, the SLES/CAPB/PEG80SL solution had an effective concentration of 3.3 wt% SLES, 3.3 wt% CAPB, and 3.3 wt% PEG80SL, and reduced free Ca^{2+} to 17 and 289 ppm from the 200 and 500 ppm $CaCl_2$ water solutions, respectively (Figure 2B).

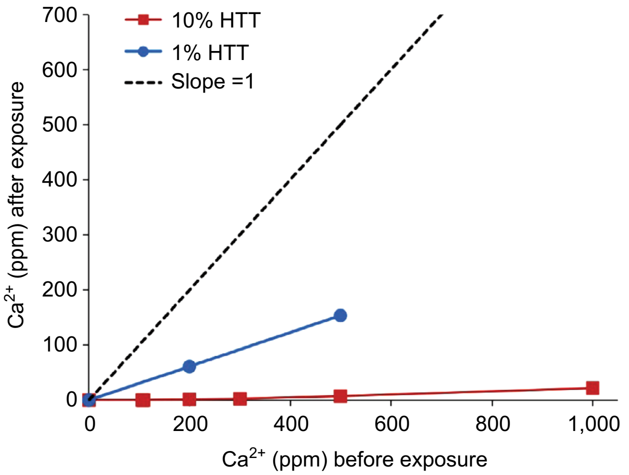

Figure 1 Effect of HTT at 1% and 10% dilution on calcium concentration in simulated baby bath.

Notes: The dotted line with slope =1 illustrates the starting conditions. HTT = Johnson's® Head-To-Toe® Baby wash (Johnson & Johnson Consumer Inc., Skillman, NJ, USA).

Abbreviation: Ca^{2+}, ionized calcium.

HTT, CB, and BB were evaluated at a 10% dilution in a simulated baby bath containing 200 and 500 ppm free Ca^{2+} (Figure 2B). HTT reduced free Ca^{2+} to 29 and 4.9 ppm in 200 and 500 ppm $CaCl_2$ test solutions, respectively. CB was as effective as HTT in reducing free Ca^{2+} to 0.8 and 2.0 ppm. BB and decyl glucoside alone (a component of CB and BB) had similar efficacy and reduced free Ca^{2+} to 103 ppm in the 200 ppm $CaCl_2$ test solution and 136 ppm in the 500 ppm $CaCl_2$ test solution.

In vivo absorption of calcium into skin

Exposure of Ca^{2+}-containing simulated baby bath to skin for up to 10 minutes (600 seconds) in adult volunteers resulted in a reduction of free Ca^{2+} in solution, presumably through absorption into the skin (Figure 3A). The absorption of Ca^{2+} was similar from both 25 and 50 mL exposure chambers,

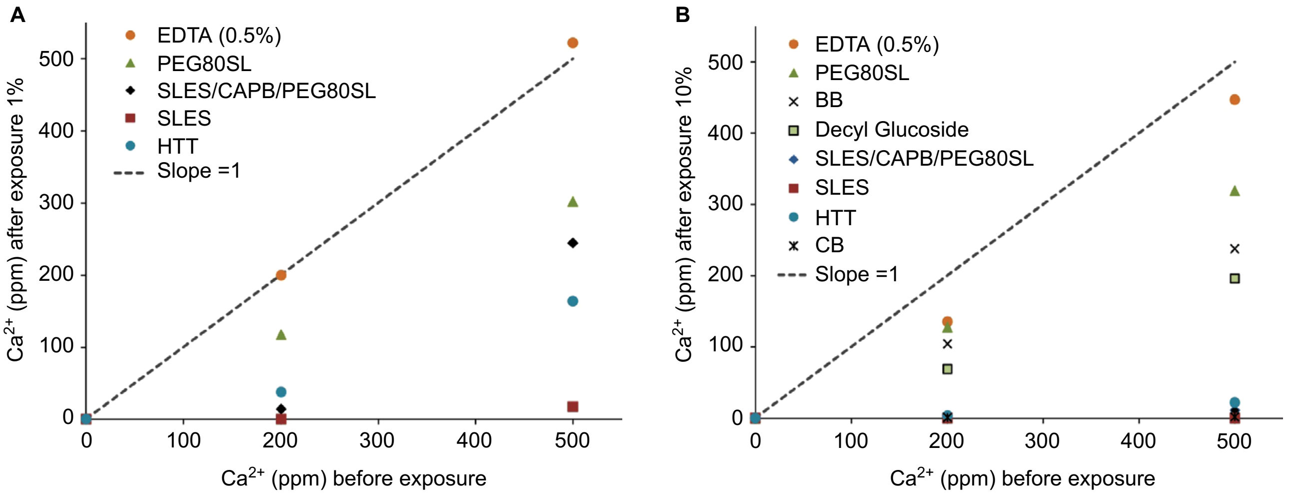

Figure 2 The effect of HTT cleanser components on free Ca^{2+} ion in solution.

Notes: (**A**) In-use dilution 1% and (**B**) 10%. The line with slope =1 illustrates the starting conditions. BB= Burt's Bees® (Burt's Bees Baby Bee Shampoo & Wash, Durham, NC, USA). HTT= Johnson's® Head-To-Toe® Baby Wash (Johnson & Johnson Consumer Inc., Skillman, NJ, USA. CB= California Baby® Super Sensitive™ Shampoo & Bodywash (Los Angeles, CA, USA).

Abbreviations: Ca^{2+}, ionized calcium; EDTA, ethylenediaminetetraacetic acid; PEG80SL, PEG-80 sorbitan laurate; SLES, sodium laureth sulfate; SLES/CAPB/PEG80SL, sodium laureth sulfate, cocamidopropyl betaine, and PEG-80 sorbitan laurate in a 1:1:1 weight ratio.

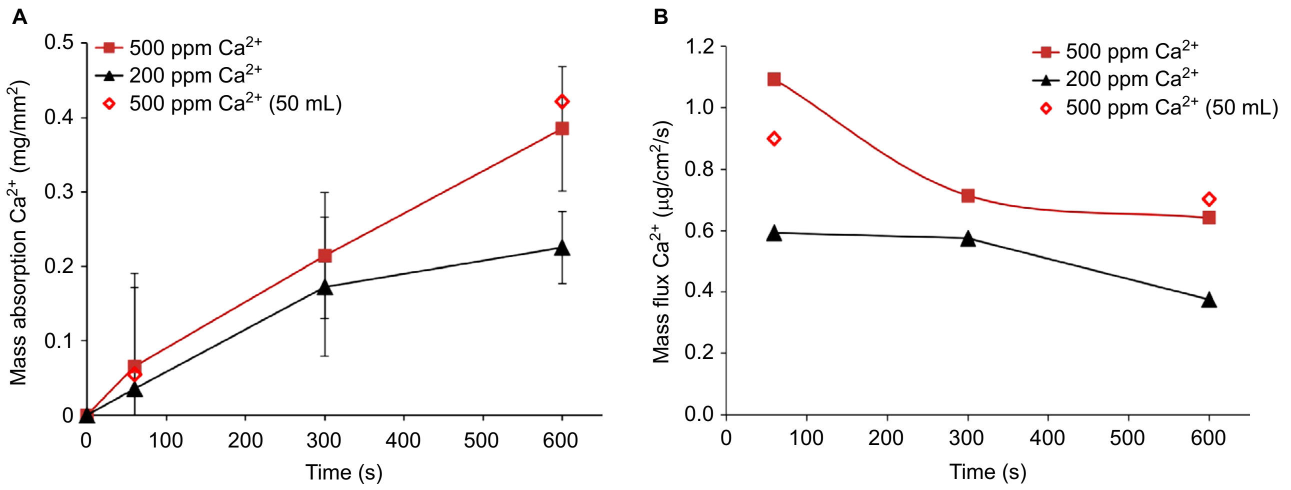

Figure 3 Absorption of Ca^{2+} from donor solutions into volar forearm skin of human volunteers.

Notes: (**A**) Mass flux (± standard deviation) into the skin per mm^2 exposed area. (**B**) Mass flux per second. Closed symbols are from 25 mL chambers. Open symbols are from 50 mL chambers.

Abbreviation: Ca^{2+}, ionized calcium.

demonstrating that the free Ca^{2+} in solution was not being depleted in the smaller chamber. For 200 and 500 ppm Ca^{2+} solutions, the amount of Ca^{2+} that absorbed into the skin increased with time across the 10 minute test period. Ca^{2+} absorption appeared to occur faster from the 500 ppm solution compared with the 200 ppm solution.

The driving force for absorption of Ca^{2+} into the skin decreased over the time course of the experiment (Figure 3B). The flux of Ca^{2+} into the skin decreased slightly over time for the 200 and 500 ppm Ca^{2+} solutions. As Ca^{2+} absorbed into the skin, the concentration in the source solution decreased over the time course of the experiment. At 10 minutes (600 seconds), the Ca^{2+} concentration was ~15% lower than the initial Ca^{2+} concentration.

Discussion

This study demonstrated that specially formulated baby cleansers can reduce free Ca^{2+} and thus reduce water hardness of bath water. HTT and CB at in-use dilutions of 1% and 10% were the most effective of the tested cleansers in reducing free Ca^{2+} in defined hard water solutions. The surfactant components of HTT, SLES, and PEG80SL appeared to be responsible for the majority of the effect of HTT on Ca^{2+}. CB provided reductions in free Ca^{2+} similar to those observed with HTT. BB reduced free Ca^{2+}, but was not as effective as HTT or CB. Unexpectedly, EDTA alone, a well-known chelator of calcium, did not have much impact on free Ca^{2+} at the concentrations used in this study.

In vivo, it was observed that higher concentrations of free Ca^{2+} in water were associated with higher rates of Ca^{2+} absorption into the skin surface in adults. Thus, bathing in hard water in the absence of a cleanser might result in excess calcium absorption into the skin. The implications of this process for skin health is unclear, however, as the properties of adult and pediatric skin are different. In use (during cleansing and/or in the bath), Ca^{2+} is likely held within a complex of surfactant molecules. Synthetic detergents, such as alkyl sulfates, form stable soluble complexes with Ca^{2+}[31,32] (over certain concentration ranges of Ca^{2+})[33] and, unlike bar soaps, do not form insoluble complexes that come out of solution and produce soap scum. Furthermore, the addition of the ethylene oxide to alkyl sulfate (eg, SLES) further increases the solubility in hard water.[34] As this Ca^{2+} complex remains stable in solution, the Ca^{2+} is likely to be washed away during rinsing. Thereby, the Ca^{2+} likely does not end up on or in the skin after the cleansing, as can happen during washing with soap. Reducing the amount of free Ca^{2+} in bath water could thereby reduce exposure of the skin to the uncomplexed Ca^{2+} ion.

Increased exposure to Ca^{2+} may interfere with normal epidermal calcium distribution/calcium gradient. Normal calcium gradient has been shown to be necessary for terminal differentiation of corneocytes and SC barrier formation.[35–37] Interference with skin-barrier formation may be related to development of susceptibility for skin irritation in the presence of hard water.[19–21,24]

In the US, geological survey data indicate significant variation in water hardness, with hard water ($CaCl_2$ 121–180 mg/L) generally localized to the Midwestern states and very hard water ($CaCl_2$ 181–250 mg/L) generally localized to the Upper Plains and Rocky Mountain areas.[17] Similarly, hard water is found in many areas throughout the world.[18]

Several studies have demonstrated an association between hard water and the incidence of AD. McNally et al studied atopic eczema prevalence in primary school-aged children in the UK and found a positive association between prevalence of atopic eczema and water hardness.[23] No significant association was seen in secondary school-aged children, leading the authors to speculate that the risk was greater in younger children. Similar increased risk of this disease in areas of hard water exposure was noted in Japanese and Spanish children.[21,22] The increased susceptibility of younger children to develop AD in the presence of hard water suggested that there might be a critical window of opportunity to protect skin integrity/skin health over the long term, and that hard water softening may offer the most benefit for younger children.

There are only a few studies that attempted to directly evaluate the effect of hard water exposure on AD. In one study in which ion exchange water softeners were installed in participants' homes, no consistent evidence was presented that hard water softening could reduce the incidence of eczema in areas with naturally hard water.[38–40] In another study, ion exchange water softening systems (replacing Ca^{2+} and Mg^{2+} with sodium ions) were installed in participants' homes for 12 weeks, again with little effect on their eczema symptoms or amount of drug usage (eg, steroids, calcineurin inhibitors).[38,39] However, a more recent, 6-week, blinded crossover study in participants with less severe AD did show significant symptom improvement[40] after installation of an ion exchange water softening system compared with a placebo system, suggesting a possible benefit in participants with moderate severity of disease. The latter study suggests, but does not prove, that reducing water hardness may improve AD. Additional studies must be performed to confirm a possible effect of hard water on AD.

Conclusion

Altering or reducing free Ca^{2+} concentrations in bath water is an additional parameter in creating the ideal baby bath. Although the relationship between water hardness and development of AD is not well characterized, water softening properties of cleansers may help reduce water hardness that the skin experiences. Additional studies are needed to identify the contribution of specific ingredients, combinations of ingredients, and formulation parameters to achieve water softening in typical baby bath conditions. Also, a larger clinical study is needed to confirm a possible benefit to the skin of cleanser-induced water softening in bath water.

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