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Reaction capacity characterization of shallow sedimentary deposits in geologically different regions of the Netherlands

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ABSTRACT

Quantitative insight into the reaction capacity of porous media is necessary to assess the buffering capacity of the subsurface against contaminant input via groundwater recharge. Here, reaction capacity is to be considered as a series of geochemical characteristics that control acid/base conditions, redox conditions and sorption intensity. Using existing geochemical analyses, a statistical regional assessment of the reaction capacity was performed for two geologically different areas in the Netherlands. The first area is dominated by Pleistocene aquifer sediments only, in the second area a heterogeneous Holocene confining layer is found on top of the Pleistocene aquifer sediments. Within both areas, two or more regions can be distinguished that have a distinctly different geological build-up of the shallow subsurface. The reactive compounds considered were pyrite, reactive Fe other than pyrite, sedimentary organic matter, carbonate and clay content. This characterization was complemented by the analysis of a dataset of samples newly collected, from two regions within the Pleistocene area, where the sedimentary facies of samples was additionally distinguished. The statistical assessment per area was executed at the levels of region, geological formation and lithology class. For both areas, significant differences in reaction capacities were observed between: 1. different lithology classes within a geological formation in a single region, 2. identical geological formations in different regions and 3. various geological formations within a single region. Here, the reaction capacity is not only controlled by lithostratigraphy, but also by post-depositional diagenesis and paleohydrology. Correlation coefficients among the reactive compounds were generally higher for sand than for clay, but insufficiently high to allow good estimation of reactive compounds from each other. For the sandy Pleistocene aquifer sediments, the content of reactive compounds was frequently observed to be below detection limits. From this, future characterization of sediment reaction capacity is best performed at the sublevel of lithology class, being the geochemically near-uniform unit identifiable for individual geological formations within geographic regions. Additional subdivision on facies provides particular insight in the spatial entity where relatively high reaction capacities may be encountered. To obtain quantitative insight into the reaction capacity of aquifer sediments, non-sandy minor subunits should be well characterised on their reaction capacity as well as their spatial occurrence in the geological formations. A straightforward approach is presented in which the regional statistics on geochemical reactivity become combined with a 3-dimensional geological voxel model. This results into 3-dimensional data fields on reactivity, which are suitable for, for example, groundwater transport modelling. The sedimentological architecture of the deposits becomes well maintained in the geochemical data field, which is an advantage in itself.

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1. Introduction

Sedimentary deposits form strategic groundwater resources across the world. The reactive properties of the subsurface influence the evolution of pore water quality (including the fate of contaminants and nutrients), influence the suitability of in-situ groundwater and soil remediation techniques, determine corrosion of subsurface anthropogenic constructions, and conserve or destroy archeological heritage. Insight into these properties is, therefore, necessary for environmental management. The properties should preferably refer to all potential hydrochemical processes, i.e., redox reactions, acid/base reactions, and sorption reactions should be considered for the reactive properties of the rock matrix.

Sedimentary deposits are mostly heterogeneous in their physico-chemical characteristics. Heterogeneity of aquifer sediments is frequently studied at the local scale (e.g. Allen-King et al., 1998; Barber, 1992; Davis et al., 1993; Jussel et al., 1994; Lee et al., 2007; Van Helvoort, 2003; Van Helvoort et al., 2007). Such studies have provided insight into the role of heterogeneity in natural buffering processes, but also pointed out the restrictions resulting from heterogeneity for adequate characterization. Firstly, local geochemical characterization of aquifer sediments at high spatial resolution, for the general purpose of environmental management, is practically unfeasible. Secondly, heterogeneity of sedimentary deposits appears at various scales (Dalrymple and Choi, 2007; Koltermann and Gorelick, 1996). Hence, characterization at one scale is not sufficient as such. Thirdly, contamination of groundwater not only occurs at the local scale but also at coarser scales, by diffusive processes in particular, through agricultural activities and atmospheric deposition. Bearing all this in mind, the environmental management perspective calls for the need to characterize the reactive properties of sediments at a regional scale.

Environmentally relevant geochemical properties of the subsurface are related to the geological properties of the rock matrix and additionally to the diagenetic and paleohydrological evolution of the area. Anthropogenic influence is strongest in the shallow, sedimentary deposits, where environmental management issues are thus most pressing. The question, therefore, arises as to what is the most appropriate approach for a generic characterization of the reactive properties of the subsurface. The scale of subsurface management is typically in the range of tens to ten thousands of meters, being smaller than or equal to the extent of geological formations (Koltermann and Gorelick, 1996), but exceeding internal facies structures of sedimentary deposits. Several workers have followed a facies-based approach while determining chemical properties of sediments (Allen-King et al., 1998; Van Helvoort, 2003; Van Helvoort et al., 2007). The application of a facies-based approach is, however, complicated when samples are obtained by drilling. The sedimentary structure observed is not always unique in a drill core for a single facies and the 2-dimensional architecture is needed for unique recognition of the facies. A lithological approach then becomes an alternative because lithology is easily recognized. In addition to the problem of matching the management scale to that of recognisable homogeneous units, cost-effectiveness must also be considered. The internal variation of relatively unreactive sandy deposits may not only be difficult to detect (below detection limits) but thereby also of limited interest. Therefore, limited effort should be spend on the sampling and analyses for such non-reactive units.

For management purposes one needs 3-dimensional data fields on the geochemical properties of the subsurface, e.g., grid models of groundwater transport models must be parameterised for purpose of groundwater quality prognosis. When the uniform spatial unit is smaller than the sampling density one cannot rely on geostatistical techniques. An alternative approach that is suitable at least for the Netherlands is spatial interpolation using geological or sedimentological modelling techniques and geochemical parameterisation of the uniform geological or sedimentological units. For the Netherlands, reliable information at the regional scale on the spatial occurrence of the lithology classes is present from the digital availability of several hundreds of thousands of borehole descriptions (see www.dinoloket.nl). A lithological voxel model is constructed for the first tens of meters below surface, from these borehole descriptions (Van der Meulen et al., 2005; Van der Meulen et al., 2007). Such a geological model may form the basis for spatial interpolation of geochemical characteristics of the sedimentary deposits once the uniform spatial units are identified and geochemically characterised.

Van Gaans et al. (2011) recently discussed the information needs for environmental geochemical data of sedimentary deposits. They distinguished four situations with respect to the nature of the reaction and related type of statistical distribution of the reactive, solid compound. First, the presence of a compound, rather than its content, determines reactivity. For example, the exact carbonate content is of little or no relevance above a certain minimum carbonate content. Second, low contents predominantly determine the effective reactivity. Sand layers generally have low reaction capacities and a large part of the measured values may be below the detection limit. The frequency of occurrence of higher contents of the reactive compound then largely defines the average reaction capacity. Third, the relatively homogeneous content of the reactive compound determines reactivity. This typically occurs for the CEC in confining clay layers: clay content does not vary much and it is normally or linearly distributed. Last, the strongly inhomogeneous content of the reactive compound determines reactivity. This situation exists, for example, for sedimentary organic matter in heterogeneous deposits. The sorption capacity for organic contaminants is governed by the average organic matter content. Here, diffusive transport between groundwater-advection zones and stagnant zones may further limit overall equilibrium within the groundwater environment. Overall, one needs effective average reaction capacities when dealing with sorption reactions to obtain good insight into retardation. For dissolution reactions (including redox reactions), presence may be more important than content when the solid compound is practically present in unlimited amounts or insight into average contents is needed when propagating reaction fronts exists. The latter holds for nitrate infiltration where denitrification by mineralisation of sedimentary organic matter or oxidation of pyrite is controlling (Korom, 1992; Rivett et al., 2008). The time scale also plays a role here: the first situation may hold for a certain compound for time scales of tens of years and associated active groundwater