Reply

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Before commenting on the areas where we differ with Winkler and Junge, it seems appropriate to note those areas where agreement exists. It seems clear that they believe as we do that the deliquescence phenomenon is highly dependent on the chemical properties of the sea spray aerosol, and that such aerosols do not behave at all like NaCl. Their use of our suggested relationship of $b_{\text{scat}} \propto r^p$ for inferring size (or mass) dependence on humidity indicates that they accept it. There is also qualitative agreement between their data and ours that the mass of water accumulated by NaCl is greater than that collected by natural sea salt mixtures at any given humidity above $\sim 75\%$.

However, direct comparison of the data presented by Winkler and Junge with those in our paper is difficult because of the widely differing measuring techniques employed in both cases, viz., collection of aerosols by impaction prior to investigating their hygroscopicity by weight vs optical procedures to determine their light scattering coefficient *in situ* at varying environmental humidities. The impaction process itself might be expected to alter the behavior of aerosols from that observed *in situ* by several mechanisms:

- 1) The effects of particle size should be seriously altered, both by the presence of a surface and by parti-

cles contacting other particles. Deliquescence in the airborne state is influenced by size due to the increased solubility of the smaller particles.

2) The surface particle contact affords a site for capillary condensation that does not exist in the airborne state.

3) The presence of a surface with its own surface chemical properties could influence those of deposited particles.

4) The deposition process could volatilize organic materials due to the reduced pressure used in most impactors.

Needless to say, the evaporation of sea water cannot be expected to produce particles with surface chemical properties which are necessarily similar to those produced naturally by the sea surface. For one thing, organic surfactants and/or oils are concentrated in a thin (perhaps micron thick) layer at the sea surface. Aerosol or evaporated residue from this thin layer will clearly have a different composition from the bulk, or even from a layer collected "close to the sea surface."

Apparent disagreement exists in the interpretation of the results from natural and synthetic sea water. While they have a point in criticizing the composition of our "artificial sea water," it does have the main ionic constituents (Na^+ , Cl^- , Mg^{++} and $\text{SO}_4^{=}$) of real sea water. Further, these experiments were a small part of our paper and were exploratory and semi-quantitative in nature. Our main point was to show that sea salt aerosols do *not* behave like NaCl, which is apparently agreed upon.

From their discussion it is not clear whether all the data in Fig. 1 are collected on aerosols, as compared to sea water residues from evaporation, nor do they elaborate on the way the aerosols were produced from the water collected in the Atlantic Ocean and the Baltic Sea. Each of these procedures is important for correct interpretation of the results due to the influence of the process of formation of aerosols and their aging on the ratio of ions (Duce *et al.*, 1965) and the proportions of organic matter (Blanchard, 1968) attached to the sea spray aerosol.

Recent measurements (unpublished) confirm previous findings by Goetz (1965) and Blanchard (1968) that the bursting bubble mechanism at the sea surface, aside from being a major source for sea salt particles, releases organic material into the air in both the vapor phase and in particulate form, and that the proportions of the airborne organic materials differ considerably from their ratios within the ocean. Blanchard's investigations indicate that an association between sea salt particles and surface active organic matter exists. In order for an organics-salt-water mixture to form a stable droplet configuration in terms of minimum free energy, it is required that the material with the lower surface energy forms the outer layer of the droplet, thus altering the surface vapor pressure. Impaction will distort this

configuration with the possibility that a difference of the hygroscopicity between airborne and deposited aerosols results.

The assumption that the process of formation of aerosols influences their deliquescence is supported by Winkler and Junge's measurements on giant maritime particles represented by curve 4 in Fig. 1. This is apparently the only natural aerosol investigated by the authors and interestingly shows the least water uptake, i.e., minimum growth. We agree with their conclusion that "this slightly lower growth is most likely due to the influence by maritime aerosol components other than sea salt," and, in addition, support the assumption that such components can be of organic nature. That this experimental finding is in only qualitative agreement with our data is most likely due to the different geographic location of maritime aerosol production and/or the difference in experimental techniques.

While MgCl_2 would remain in solution if our aerosols were not dried below 30–40%, its effect on radius (and therefore light scattering) is indeed small. Hänel (1970) shows the radius of sea salt particles to change by perhaps 5–6% at ~35% relative humidity, based on the data of Winkler. We felt that studying the range of humidity from 30–90% was adequate to show anomalous behavior (i.e., departure from NaCl behavior) under realistic atmospheric conditions.

It is true that interpretation of light scattering data is difficult at times due to uncertainties in particle shape and refractive index. It is for this reason that the result in Fig. 1 of our paper is presented in terms of light scattering coefficient rather than particle size. The disadvantage of light scattering techniques is compensated for, however, by the possibility of investigating aerosols *in situ*. One argument of Winkler and Junge regarding interpreting our data can be answered as follows: A coating of, e.g., MgCl_2 solution surrounding a solid salt particle reduces the refractive index at its surface. This could result in an increase or decrease of the scattering cross section, depending on what size of a particle is investigated and at what wavelength. However, because of the distribution of sizes of the aerosols we investigated, and because of the spectral distribution of sizes of the xenon-filled light source of the scattering instrument employed in our investigation, a reduced refractive index most likely results in a reduced average light scattering coefficient. This is opposite to an increased scattering due to the size of hydrated sea salt if compared to non-hydrated sodium chloride, or an influence of a larger hysteresis of sea salt.

In summary the data presented by Winkler and Junge indicate that they have perfected the accuracy of weighing to a remarkable degree which deserves appreciation. Apparently, this accuracy does not permit the investigation *in situ* of the hygroscopicity of salt aerosols. This and the fact that the majority of their samples do not represent naturally produced aerosols makes a comparison of their results with ours difficult,

leaving the question about the roles which surface active organic materials play in the deliquescence of natural sea salt aerosols still unanswered.

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